The utilisation of layered hydroxysalts in the separation, immobilisation and long term storage of long-lived radio-anions of nuclear power legacy waste origin.

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by

Andrew D Butterworth

Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University
November 2013

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Abstract

Long lived radioactive species such as $^{129}\text{I}^-$ and $^{99}\text{TcO}_4^-$ are formed as by-products of nuclear fission. These species have extremely long half-lives (1.5 million and 211,000 years respectively), are biologically assimilating and due to their anionic nature, can move freely within a geosphere. Historical disposal methods for active species are no longer considered acceptable to the general public and other ways in which to treat the waste are being explored. One ‘remove and concentrate’ method to remove radioactive species from the biosphere is using alkaline-resistant materials which trap active species that can be encapsulated in a high pH concrete matrix. Layered hydroxides and layered double salts which consist of positively charged layers between which exchangeable anions and water molecules lie are good candidates for these materials due to the basic conditions in which they form.

The synthesis, anion exchange properties and stability of copper, lanthanum, nickel and zinc hydroxysalts have been investigated. The structures consist of layers of edge-sharing metal hydroxide octahedra together with an interlayer space containing the anion and in some cases water molecules. Products were characterised by powder X-ray diffraction and vibrational spectroscopy to confirm the identity of structure of the material formed and the anion incorporated.

Only $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$, $\text{Cu}_2(\text{OH})_3(\text{OAc}).\text{H}_2\text{O}$, $\text{Ni}_2(\text{OH})_3(\text{NO}_3)$ and $\text{Zn}_5(\text{OH})_3(\text{NO}_3).2\text{H}_2\text{O}$ consistently exhibited exchange capabilities with iodide as the target anion. In terms of exchange rate and efficiency, copper hydroxyacetate is a more suitable precursor as equilibrium is achieved in 10 mins; whereas other LHS containing nitrate as the occupying require longer than 1 day to reach equilibrium. $\text{Cu}_2(\text{OH})_3(\text{Ac}).\text{H}_2\text{O}$ has been shown to easily exchange acetate for monovalent anions $X^-$ ($X = \text{Ha}^-, \text{NO}_3^-, \text{ClO}_4^-, \text{IO}_4^-, \text{SbO}_3^-, \text{OH}^{-}$). Exchange reactions with $\text{ReO}_4^-$ (used as a surrogate to $\text{TcO}_4^-$) and trigonal pyramidal monovalent anions (such as $\text{IO}_3^-$) were unsuccessful. Exposure to divalent anions ($\text{CO}_3^{2-}, \text{Cr}_2\text{O}_4^{2-}, \text{SeO}_3^{-}$) resulted in no interaction whereas exposure to trivalent $\text{PO}_4^{3-}$ forms $\text{Cu}_3(\text{PO}_4)_2$. Quantitative analysis has shown that, contrary to XRPD and FTIR data, full exchange of acetate for an equimolar amount of iodide within a $\text{Cu}_2(\text{OH})_3^+$ framework does not occur with 100% efficiency. Activity counting, gravimetric analysis and ion specific probe analysis suggested that only ~92-93% exchange occurs.

The stability of $\text{TcO}_4^-$ and $\Gamma$ analogues with respect to pH has been investigated. Activity counting has shown that even in pH 9.5 solution, 57-73% of $^{125}\text{I}^-$ and $^{99}\text{TcO}_4^-$ immobilised with a $\text{Cu}_2(\text{OH})_3^+$ framework is leached into solution after 16 days. Exposure of $\text{Cu}_2(\text{OH})_3\text{I}$ to high carbonate, nitrate and chloride environments shows a progressive loss of iodide into solution as the anionic radius of the incoming anion decreases and the concentration of the incoming anion increases. In the case of chloride and nitrate incoming anions, only a 2:1 chloride to iodide ratio is need for full exchange whereas a ratio of 10:1 nitrate to iodide is required. In situ ion exchange experiments at Diamond allowed the exchange of the hydroxyacetate material to be investigated in flow experiments showing similar facile exchange as demonstrated under batch conditions. Rietveld refinements on deuterated samples of halide analogues of the materials have allowed accurate structure determinations for the first time ($\text{Cu}_2(\text{OD})_3\text{Cl}$ - $a = 5.726\text{Å}$, $b = 6.125 \text{Å}$, $c = 5.634 \text{Å}$, $\beta = 93.100^\circ$, $\text{Cu}_2(\text{OD})_3\text{Br}$ - $a = 6.085 \text{Å}$, $b = 6.144 \text{Å}$, $c = 5.650 \text{Å}$, $\beta = 93.593^\circ$, $\text{Cu}_2(\text{OD})_3\text{I}$ – $a = 6.587 \text{Å}$, $b = 6.179 \text{Å}$, $c = 5.680 \text{Å}$, $\beta = 95.044^\circ$). As the size of the halide increases, the hydroxide coordination alters reflecting to changing sigma/pi donor capability of the halide.
Acknowledgements

Firstly I would like to thank Sandie Dann and Caroline Kirk for giving me this fantastic opportunity. Those long nights running samples at diamond and ISIS were “character building” to say the least but one of many examples of the support I was given throughout my PhD. I wish both Sandie and Caroline all the best for the future and success with current/future students.

I would like to thank the EPSRC for funding the project and the DIAMOND university consortium for providing incredible support and the opportunity the share ideas with fellow students and experts in the nuclear industry. Dr Kevin Knight and Prof Chiu Tang also deserve a big thank you for their expert support when collecting data at ISIS and diamond respectively. I would also like to thanks Emma Stubbs, Hayley Gillings for all their help collecting data and a special thanks to Dr Marijana Dragosavac for her work that was so vital in this thesis.

Everyone in the department has helped me at some point and they all deserve a big thank you. More specifically I would like to show my appreciation for Pauline King as without her the lab would fall apart. I would like to give a special thank you to my lab colleagues and friends. Chris, Joe, Lee, Rob, Nuria, Rachel, Angelés, Tere, Tom, Simon, Hayley, Rose, Glyn and Jenna, you all made the lab an enjoyable place to work and were always there to help if needed.

Last but by no means least I would like to thank my family. I may not say it enough but you have always been there for me. My Mum, Dad, Sister, Nan, girlfriend and my Aunties and Uncles helped me every step of the way and I am truly grateful.
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List of Abbreviations

VLLW Very low level waste
LLW Low level waste
ILW Intermediate level waste
HLW High level waste
LH Layered hydroxide
LDH Layered double hydroxide
LTH Layered triple hydroxide
LHS Layered hydroxy salt
LDS Layered hydroxy salt
XRD X-ray diffraction
XRPD X-ray powder diffraction
PD Powder diffraction
NPD Neutron powder diffraction
FTIR Fourier transform infrared
IR Infra-red
TGA Thermal gravimetric analysis
Cu$_2$HX Cu$_2$(OH)$_2$X (X = occupying anion (A = CH$_3$CO$_2^-$, N = NO$_3^-$))
Ni$_2$HX Ni$_2$(OH)$_2$X (X = occupying anion (A = CH$_3$CO$_2^-$, N = NO$_3^-$))
Zn$_3$HX Zn$_3$(OH)$_3$X$_{2,n}$H$_2$O (X = occupying anion (A = CH$_3$CO$_2^-$, N = NO$_3^-$))
Zn$_5$HX Zn$_5$(OH)$_5$X$_{2,n}$H$_2$O (X = occupying anion (A = CH$_3$CO$_2^-$, N = NO$_3^-$))
LaHX La(OH)$_3$X$_{2,n}$H$_2$O (X = occupying anion (A = CH$_3$CO$_2^-$, N = NO$_3^-$))
Ac Acetate
Bz Benzoate
Ha$^-$ Halide
ICDD-PDF International Centre for Diffraction Data – Powder Diffraction File
CIF Crystallographic Information File
CPM Activity (counts per minute)
Chapter 1

An Introduction into Nuclear Energy, Subsequent Waste and Possible Routes for Treatment
1.1 Introduction

In recent years, fossil fuel based energy has become unsustainable due to the depletion of natural non-renewable resources, such as coal, oil, and gas, which take millions of years to form and hence cannot be easily replenished. Based on current estimates related to population growth and usage, coal is expected to last 100-200 years, natural gas 40-50 years, and oil only 35-40 years \([1]\). In addition to concerns based on fossil fuel availability, there are also environmental concerns relating to carbon-based fuel use, with strong evidence to suggest burning fossil fuels has the potential to increase the onset of global warming \([2, 3]\). These factors have forced governments to seriously consider the development and utilisation of renewable energy sources (such as wind, solar, wave, and hydrothermal) and non-renewable resources that contain a more sustainable stock (such as nuclear fission and hydrogen fuel) \([4, 5]\). The use of these alternative sources of power has the additional attraction that future energy requirements can be satisfied, but at the same time carbon emissions will be reduced.

1.2 Nuclear Energy

The first nuclear reactor to reach sustained fission was built in 1942 by E. Fermi and L. Slizard in a venture that would later become part of the Manhattan project during World War II \([6]\). However, nuclear fission was not seriously considered as a source of energy on a scale to supply the general population until much later \([7]\). In 1954, the United Kingdom Atomic Energy Authority was created to pioneer and monitor the development of nuclear energy in the UK \([8]\). The first Magnox nuclear power plant began to operate commercially at Calder Hall in 1959, with a further 10 Magnox plants connected to the power grid by 1968 \([9]\). Magnox reactors are pressurised, graphite moderated utilities with carbon dioxide based cooling and use un-enriched natural uranium as a fuel with magnox alloy as fuel cladding. A magnesium, non-oxidising alloy (consisting of mainly magnesium with a small amount of aluminium) has the advantage of low neutron capture, however it has a low operating temperature that reduces thermal efficiency. Although the design has been constantly modified, all Magnox reactors still have a stainless steel pressure vessel contained within a concrete radiation shield which is cooled by an external heat exchanger (Figure 1.1) \([10]\).

In 1962, a prototype of a new advanced gas-cooled (AGR) reactor was commissioned and in 1976, two reactors at Hunterston and Hinckley Point began to operate commercially. Similar to Magnox reactors, these AGR reactors use graphite as a moderator and pressurised carbon dioxide as a coolant. Magnox fuel cladding was replaced by stainless steel, allowing for higher operating temperatures and so improving the thermal efficiency. Since stainless steel has a larger electron capture cross-section than Magnox, it was possible to use enriched \(^{235}\text{U}\) fuel as the uranium source, since the operating temperature was now elevated and \(^{238}\text{U}\) was not needed to provide additional function. Un-enriched uranium contains up to 99% of the \(^{238}\text{U}\) isotope that is proton rich and undergoes electron capture, whereas enriched uranium contains up to 5% \(^{235}\text{U}\) which does not perform this function. Both the reactor and heat exchanger are encased in a combined concrete pressure vessel and radiation shield (Figure 1.2) \([11]\).
There is also one Pressurised Water Reactor (PWR) currently in operation in the UK, using water as both a coolant and a moderator. PWRs are now favoured in the nuclear power industry due to their cheaper operating costs and safety [14]. There are currently 16 operational nuclear reactors at
9 plants in the UK and a nuclear re-processing plant at Sellafield. Of the 16 reactors, 14 are AGRs, 1 Magnox and 1 PWR that currently contribute around a sixth of the United Kingdom’s electricity. There are however currently 10 retired Magnox reactors in the UK that urgently require de-commissioning to ensure the safe treatment and storage of the associated nuclear waste.

In 2005, the ownership of retired Magnox reactors along with a re-processing site were transferred from British Nuclear Fuels Limited (BNFL) to the Nuclear Decommissioning Agency (NDA) under the Energy Act 2004. The sole purpose of the NDA is to oversee site license companies in the decommissioning and clean-up of the UK’s civil nuclear waste legacy\(^{15}\).

### 1.2.1 Nuclear waste

Radioactive waste is generated via a variety of sources including research, medicine, nuclear energy and other atomic technologies such as weapons. In terms of quantity, radioactive waste originating from nuclear energy accounts for a substantial amount of the total radioactive waste. Nuclear energy waste includes large amount of untreated legacy waste from 50 years of energy production. Waste that is yet to undergo the fission process is usually α emitting originating from the extraction of nuclear fuel from metal ores. Nuclear fuel often contains uranium, radium and their decay products. At the back end of the nuclear cycle (after fission), there are many short- \((t^{1/2} = < 1 \text{ day})\) to long- \((t^{1/2} = > 200,000 \text{ years})\) lived active waste products. Of these, there are several long-lived fission products that are causing ever-increasing concern. This concern is not necessarily due to a high toxicity, but more the long half life, meaning that potential waste problems may affect many generations to come. In general, nuclear waste is difficult to manage due to the presence of high levels of radiotoxic nuclides emitting high energy α radiation \((^{239}\text{Pu}, ^{241}\text{Am}, ^{237}\text{Np})\), radio-nuclides with long half lives \((^{14}\text{C} 5730 \text{ years}, ^{239}\text{Pu} 24110 \text{ years}, ^{129}\text{I} 15.7 \text{ million years})\), highly soluble and volatile (mobile) species \((^{226}\text{Ra}, ^{3}\text{H}, ^{137}\text{Cs}, ^{129}\text{I})\) and biologically assimilating elements \((^{129}\text{I} \text{ thyroid,} ^{90}\text{Sr} \text{ bones})\) \(^{16}\).

### 1.2.2 Long-lived fission products

There are several long-lived fission products (LLFPs) with half lives of over 200,000 years that require long term treatment and storage that will separate such waste from the geosphere and biosphere indefinitely (Table 1.1).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half life (Ma)</th>
<th>Decay mode</th>
<th>Fission Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{79}\text{Se})</td>
<td>0.327</td>
<td>β</td>
<td>0.0447</td>
</tr>
<tr>
<td>(^{93}\text{Zr})</td>
<td>1.530</td>
<td>β, γ</td>
<td>6.3575</td>
</tr>
<tr>
<td>(^{98}\text{Tc})</td>
<td>0.211</td>
<td>β</td>
<td>6.1185</td>
</tr>
<tr>
<td>(^{107}\text{Pd})</td>
<td>1.500</td>
<td>β</td>
<td>1.2499</td>
</tr>
<tr>
<td>(^{126}\text{Sb})</td>
<td>0.230</td>
<td>β, γ</td>
<td>0.0561</td>
</tr>
<tr>
<td>(^{129}\text{I})</td>
<td>15.70</td>
<td>β, γ</td>
<td>0.7061</td>
</tr>
<tr>
<td>(^{135}\text{Cs})</td>
<td>2.30</td>
<td>β</td>
<td>6.5400*</td>
</tr>
</tbody>
</table>

*Table 1.1* Long-lived fission isotopes produced on the thermal neutron fission of U-135 \(^{171}\) (* see next page).
Of the LLFPs, $^{93}\text{Zr}$, $^{107}\text{Pd}$ and $^{126}\text{Sn}$ are relatively inert and so are easily managed and pose little threat to the environment. $^{135}\text{Cs}$ (as the singularly charged cation) is a decay product of $^{135}\text{Xe}$ ($t_{1/2} = 9.2$ hours), which in turn is produced either as a fission product or from the beta decay of $^{135}\text{Te}$. $^{135}\text{Xe}$ has a fission yield of approximately 6.33\% (for $^{235}\text{U}$) and also has the highest known thermal neutron capture of any nuclide. When produced in current thermal reactors, as much as 90\% of $^{135}\text{Xe}$ is converted into stable $^{136}\text{Xe}$ before it can decay into $^{135}\text{Cs}$ \[18\]. $^{135}\text{Cs}^+$ is extremely mobile in the environment and along with $^{93}\text{Zr}^{4+}$, $^{107}\text{Pd}^{2+}$ and $^{126}\text{Sn}^{4+}$ are removed by cation-exchange materials (such as SuperLig® Resin) \[19, 20\]. Selenium-79, iodine-129 and technetium-99 (as $^{79}\text{SeO}_3^-$, $^{79}\text{SeO}_4^{2-}$, $^{129}\text{I}^-$, $^{129}\text{IO}_3^-$, $^{129}\text{IO}_4^-$ and $^{99}\text{TcO}_4^-$) are anionic in nature, therefore are able to pass through any cation exchange materials. The fission yield of $^{78}\text{Se}$ is extremely low (0.0447\%) and therefore not considered a serious risk, whereas $^{129}\text{I}$ (0.7061\%) and especially $^{99}\text{Tc}$ (6.1185\%) have considerable fission yields. Currently $^{129}\text{I}$ (as $^{129}\text{I}^-$, $^{129}\text{IO}_3^-$ and $^{129}\text{IO}_4^-$) is discharged via pipeline into aquatic environments and $^{99}\text{Tc}$ and (as $^{99}\text{TcO}_4^-$) is captured via the addition of tetraphenylphosphonium bromide (TPPB) \[21\].

### 1.2.3 Nuclear waste classification

As a result of past leakages, the taboo of nuclear waste, public pressure and environmental concerns, nuclear waste must be immobilised in order to become manageable. This involves converting the waste into a durable and stable form, for example liquids and gases into solids. The waste is then immobilised and incorporated into the structure of a suitable matrix so it can be encapsulated, retained and unable to escape \[22\]. In the UK, products of the nuclear process are defined in four categories; very low-level waste (VLLW), low-level waste (LLW), intermediate level waste (ILW) and high level waste (HLW) depending on the nature, radioactivity and half-life of the waste \[23\].

VLLW is classed as nuclear waste simply due to its origin, however it actually contains very little radioactivity and is disposed of with normal domestic waste. LLW has the highest volume in terms of total waste (90\%) and is defined as having an activity of $< 4$ GBq/t $\alpha$ and $< 12$ GBq/t $\beta/\gamma$, however LLW contains less 0.1\% of the total activity. Much of the LLW has less radioactivity than some granite rock formations in Cornwall, generally has short half lives (10’s yrs) and comprises of copious amounts of cellulose and other organics. ILW is lesser in volume than that of LLW waste and is defined as having an activity of $> 4$ GBq/t $\alpha$ and $> 12$ GBq/t $\beta/\gamma$, with both long and short life radio nuclides present, created mainly as a by-product of the fission process along with cellulose and other organic materials such as EDTA \[24\]. HLW is very low in volume, however it contains a high concentration of heat generating, long-lived and transuranic (elements with an atomic number greater than 92) radio nuclides that solely originate from reprocessed and spent fuel \[25\].

### 1.3 Current waste solutions

Compared to non-radioactive waste, the quantity of radioactive waste is relatively small (Table 1.2) however, the toxicity of the active waste means it must be dealt with carefully. There are two approaches to radioactive waste disposal known as “concentrate and contain” and “dilute and disperse”. The latter involves discharging low level liquid waste originating from water used in cooling, gaseous waste from ventilation and soluble by-products from nuclear fission into a marine
environment. The waste is low in activity and when coupled with the large volume of discharged water, is viable as a solution for some non-solid LLW’s. According to the Radioactive Substances Act guidelines set out by the Environmental Agency in England and Wales (EA) and by the Scottish Environmental Protection Agency (SEPA), all discharges are limited according to type of waste and disposal route.

<table>
<thead>
<tr>
<th>Non-Radioactive Waste</th>
<th>Waste Amount m³/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Waste</td>
<td>40,000,000</td>
</tr>
<tr>
<td>Domestic Waste</td>
<td>40,000,000</td>
</tr>
<tr>
<td>Solid Toxic Waste</td>
<td>3,100,000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solid Radioactive Waste</th>
<th>Amount m³/year (current)</th>
<th>Amount m³/year (Predicted 2120)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-level (LLW)</td>
<td>10,000 – 13,000</td>
<td>1,500,000</td>
</tr>
<tr>
<td>Intermediate-level (ILW)</td>
<td>3,600</td>
<td>350,000</td>
</tr>
<tr>
<td>High-level (HLW)</td>
<td>65</td>
<td>1,300</td>
</tr>
</tbody>
</table>

Table 1.2 The amount of radioactive waste compared to domestic and industrial waste[^26].

In order to put the amount of radioactive waste produced into context, it is important to consider the amount of natural radioactivity that the population encounters and recognise that natural radioactivity is the primary source of radiation exposure to the population, including those living close to nuclear establishments. Individual doses from natural radioactivity in the UK range broadly from 1000 µSv to 100,000 with an average annual dose per person in the UK of 2230 µSv[^27]. Typically, natural sources contribute approximately 84% of the total dose with sources including cosmic rays (12%), rocks and soils producing radon gas (50%), foodstuffs giving internal exposure (9.5%) and gamma radiation (13%). Artificial sources account for approximately 16% of the total dose with sources including medical (15%), disposal of radioactive waste (<0.1%), occupational (0.2%), products (<0.1%) and the widespread radioactive fallout from the testing of nuclear weapons and from the Chernobyl disaster (0.2%)[^28]. In areas of higher natural background radiation (e.g. Cornwall), the average dose may exceed 7000 µSv per year (Figure 1.3)[^29, 30].
1.3.1 Concentrate and contain

The “concentrate and contain” method is applicable to both liquid and solid waste and ensures that radioactivity is confined to either an interim storage facility or a long term disposal facility. Ion exchange materials have been used to treat ILW and LLW sludge for many years in order to convert the waste into an insoluble form and concentrate the radioactivity into a small volume. The treated radioactive sludge is often discharged into the sea due to the bulk of the radioactivity being taken up by the ion exchange material. A type of Synroc can also be used to immobilise cationic long-lived fission products and actinides [20, 31].

Once the solid waste has been treated and the activity concentrated, it must be suitably contained and immobilised in order to prevent the waste from entering the geosphere. This is achieved by incorporating the waste form into either a glass (vitrification (Figure 1.4) or a ceramic matrix which is then encapsulated in a cement lined repository underground or an interim storage facility. Both glass and ceramic matrices provide a long term storage solution for the radioactive waste and adequately stabilise the waste into a form which is sustainable.

Vitrification is currently undertaken at several locations where treated radioactive waste is mixed with sucrose and then calcined. Calcination involves passing the waste through a heated, rotating tube. The purpose of calcination is to evaporate water from the waste and to remove nitrates.
from the fission products in order to assist the stability of the glass produced in the next step. The 'calcine' generated is fed continuously into an induction heated furnace with fragmented glass, resulting in a 'glassy' material that contains the calcined waste products trapped within a glass matrix as it solidifies. The molten fluid is then poured into stainless steel or copper cylindrical containers in a batch process, and when cooled, the fluid solidifies into a glass. The cylinder is then sealed by a weld, washed and transported to an interim storage facility or an underground repository.

![Image of a continuous vitrification process]

Figure 1.4 A continuous vitrification process.

The glass formed is highly resistant to water, and in this form, the waste products are expected to be immobilised for a very long period of time (many thousands of years). In the United Kingdom, Europe and United States, a borosilicate glass similar to Pyrex is used to produce a black glassy substance, whilst in the former Soviet Union it is normal to use a phosphate glass. Sucrose is added to control ruthenium chemistry and to stop the formation of volatile RuO$_4$ species. Radioactive ruthenium species have a half life of less than 1 year so treatment with sugar and storage is sufficient to contain radioactivity derived from ruthenium. The amount of fission products in the glass must be limited because some species (palladium, other platinum group metals, and tellurium) tend to form metallic phases which can separate from the glass matrix over time.

Ceramic based materials can also be used to incorporate treated waste into a matrix, for example, it is possible to use a ferric hydroxide (Fe(OH)$_3$) floc to remove radioactive metals from aqueous mixtures. After the radioisotopes are absorbed onto ferric hydroxide, the resulting sludge
can be placed in a metal drum before being mixed with cement to form a solid waste form (Figure 1.5). In order to improve long-term performance (mechanical stability) of such waste forms, a mixture of fly ash, or blast furnace slag, and Portland cement may be added, instead of normal concrete (made with Portland cement, gravel and sand) [32].

Figure 1.5 Concrete mixed with a nuclear waste surrogate contained within a stainless steel drum [33].

The preferred method for the disposal of ILW and LLW in the UK is encapsulation in cement. The low permeability matrix formed in cements aids immobilization of waste by incorporation into hydrated phases and by precipitation.

1.3.2 Radioactive discharges, disposals and long term management of nuclear waste

In the United Kingdom, disposals are regulated by the Environmental Permit for Radioactive Substances (EPR 2010) and are categorised into liquid, aerial or solid discharges. Radioactive liquid waste often arises from fuel reprocessing and storage operations, on-site decommissioning operations and laboratories. Liquids that are highly active from reprocessing plants are not discharged from site but put into storage pending incorporation into solid glass form. Medium active waste streams from reprocessing are usually routed via an evaporator to an interim decay storage facility pending treatment in an Actinide Removal Plant (ARP) prior to discharge. Remaining low-level liquid effluents are, after monitoring, discharged into an aquatic environment (rivers and sea), usually via pipeline. The main sources of such low activity liquid waste includes storage pond, ARP discharges, off-gas scrubber liquors following treatment to remove $^{14}$C as solid waste and minor waste streams, such as surface drainage water and laundry effluent.

The timeframe in question when dealing with radioactive waste ranges from 10,000 to 1,000,000 years however, practical studies can only consider up to 100 years as far as effective planning and cost evaluations are concerned. The process of selecting an appropriate long term
Chapter 1 - An introduction into Nuclear Energy, Subsequent Waste and Possible Routes for Treatment  A.D. Butterworth

waste solution has led to five general hypotheses – some realised others speculative; land based disposal, sea based disposal, transmutation into less harmful radio nuclides, re-use of the waste and space disposal.

Underground repositories for ILW and HLW are generally considered the most cost effective and safest way of storing waste long term. The concept is to locate a large, geologically stable underground location and to excavate a tunnel 500–1,000 metres below the surface where rooms or vaults can be used for waste disposal and long term storage. Using this method it may be possible to permanently isolate the waste from the geosphere and biosphere. Although this method is very popular among scientists, many of the general public remains uncomfortable with the close proximity of land based disposal. The main concern with this method is the presence of radioactive species possessing half-lives of over 1 million years. Species such as $^{129}$I, raise concerns due to long half-lives and therefore even an extremely small container leakage causes a problem as more than one half-life may be required until some nuclear waste lose enough radioactivity to be considered no longer biologically active. Storing both medium and short lived nuclear waste above ground for two or more centuries is considered a sensible approach by many scientists as this allows the material to be more easily observed and any problems detected and managed. A new approach to the problem, Remix & Return, has been conceived and involves blending high-level waste with uranium mine tailings to the level of the original radioactivity of the uranium ore. This material can then be returned to fill the space left by the excavated uranium ore. Although this method can be used for high level waste, the majority of high level waste comes from spent fuel and due to the presence of highly toxic radioactive species such as plutonium which is not naturally present in uranium ore, this method may be inappropriate [34].

Sea based options for disposal of radioactive waste include dilution and dispersion, burial in a tectonic plate boundary known as a subduction zone and burial beneath a remote natural or human-made island. These methods are feasible ways of disposing of nuclear waste, however due to the legal barrier of International Ocean dumping agreements (the Law of the Sea) and the public fear that such a repository could leak, they are not currently being seriously considered. Sea based approaches may come under consideration in the future by individual countries or groups of countries that cannot find other acceptable solutions. Sea-land based subductive zone disposal involves disposing the nuclear waste in a subduction zone accessed from land. This method is not prohibited by any international agreement and so has been described as one of the most viable means of disposing radioactive waste. However, inevitably this method can only be implemented by nations that lie on a subduction zone meaning major powers such as the UK, France, Russia and Germany cannot access this disposal technology [35]. Although there is a possibility of transporting the waste into an area that lies within a subduction zone, the political implications of moving one country's radioactive waste to another’s for disposal is likely to be met with significant opposition.

Recently, reactors that consume nuclear waste and transmute it to other, less-harmful nuclear waste have been investigated. The integral fast nuclear reactor has been proposed with a nuclear fuel cycle that produces no transuranic waste and in fact consumes such waste. Another similar approach
is to dedicate subcritical reactors to the transmutation of transuranic elements, however both transmutation approaches are mainly theoretical and there have been no large scale tests \[36\].

Another option is to find applications of the isotopes in nuclear waste and therefore re-use them. Already, $^{137}$Cs and $^{90}$Sr and a few other isotopes are extracted for certain industrial applications such as food irradiation and radioisotope thermoelectric generators. The reuse of certain isotopes is considered a sensible approach for recycling nuclear waste however it would account for only a relatively small fraction of the total volume of nuclear waste and the selective extraction of specific isotopes is difficult \[37\].

Space disposal is another option that permanently removes all nuclear waste from the geosphere and biosphere. The idea currently has no real application due to practical, economic and political reasons. The high number of launches that would be required to transport a relatively large amount of material and the risk of vehicle failure in the atmosphere makes the proposal impractical. To further complicate matters, international agreements on the regulation of such a program would need to be established. The technology needed to implement such a complex plan simply does not exist and it would take 10’s to 100’s years of research and development to make the idea feasible \[38\].

1.4 The DIAMOND university consortium

The DIAMOND (Decommissioning, Immobilization and Management of Nuclear waste for Disposal) University research consortium is a UK based collaboration formed to deal with nuclear waste management and decommissioning in response to a call for proposals issued in August 2007 by the Engineering and Physical Sciences Research Council

1.4.1 Research aims

The consortium is led by the University of Leeds, with other members including Imperial College London, Loughborough University, University of Manchester, University of Sheffield and University College London. The consortium hopes to tackle many aspects of nuclear waste including environmental migration, risk assessment, decommissioning legacy, site termination and materials design (Figure 1.6)

Many of the technological challenges that lie ahead in decommissioning and provision of long term storage for nuclear waste are highly complex and will require new, multidisciplinary approaches to achieve innovative solutions. DIAMOND aims to deliver a high quality research and training programme, through development of new collaborations with stakeholders across the nuclear industry and expand academic nuclear waste research capacity in the UK. In this study, anion exchange materials will be explored for the treatment of anionic mobile species that derive from the fission process. In particular, long-lived fission products such as $^{129}$I and $^{99}$Tc will be the main target when investigating potential ion exchange materials.
1.4.2 Radioactive iodine

$^{129}\text{I}$ and $^{131}\text{I}$ are β and γ ($^{129}\text{I}$ weak γ, $^{131}\text{I}$ strong γ) emitters that are released as fission products of radioactive uranium and plutonium in nuclear reactors. Although $^{129}\text{I}$ has a relatively low activity and fission yield (0.7061% per fission of $^{235}\text{U}$)\[40\], it is very volatile, has corrosive salts, is biologically assimilating, mobile in the geosphere and has an extremely long half life of 15.7 million years. $^{131}\text{I}$ has a higher fission yield (2.8336% per fission from $^{235}\text{U}$) and similar properties to that of $^{129}\text{I}$. $^{131}\text{I}$ is sometimes used in nuclear medicine imaging techniques; however other less harmful isotopes are tending to be preferred.

The low energy beta emissions from $^{129}\text{I}$ do not present a significant external exposure hazard because they barely penetrate the outer dead layer of skin; however beta emission from $^{131}\text{I}$ can present an external exposure hazard to skin and eyes. Gamma and x-ray emissions from both species can present a penetrating external exposure hazard. An individual’s iodine metabolism can vary considerably, however it may be assumed that approximately 30% of iodine is concentrated to the thyroid and 70% directly excreted in urine, faeces and sweat. Iodine in the body, as organic iodine, is assumed to be uniformly distributed in all organs and tissues of the body except the thyroid, and retained with a biological half-life in the thyroid for 120 days, bone for 14 days, and kidney, spleen, and reproductive organs for 7 days. The uptake of $^{129}\text{I}$ to the thyroid is in practice limited by the physical mass of $^{129}\text{I}$ due to its very low specific activity and the committed dose is significantly
reduced due to the short physical half-life of $^{131}\text{I}$. $^{129}\text{I}$ and $^{131}\text{I}$ both undergo beta decay and form a xenon species that are stable (Equation 1.1) \cite{41}.

$^{129}\text{I}$ and $^{131}\text{I}$ are initially gaseous products that form within uranium fuel rods as they fission. The rate at which these gases are produced must be carefully monitored as they can build up too fast and increase pressure. This increased pressure causes degradation of the fuel rods and ultimately may cause a breach releasing radioactive iodine into the water that is used to cool the fuel rods. Spent fuel rods are dissolved in strong acids to recover plutonium and other valuable materials, however during this process, $^{129}\text{I}$ and $^{131}\text{I}$ are also released into the airborne, liquid, and solid waste processing systems \cite{42}.

\[ ^{129}\text{I} \rightarrow \frac{t_{1/2}}{= 1.57 \times 10^7 \text{y}} \beta (100\%) \]
\[ \beta (100\%) = 0.152 \text{ MeV} \]
\[ ^{131}\text{Xe} \rightarrow \text{Stable} \]

\[ ^{131}\text{I} \rightarrow ^{131}\text{Xe} \rightarrow \frac{t_{1/2}}{= 8.04 \text{d}} \beta (7.27\%) \]
\[ \beta (7.27\%) = 0.334 \text{ MeV} \]
\[ \beta (89.3\%) = 0.606 \text{ MeV} \]
\[ ^{131}\text{Xe} \rightarrow \text{Stable} \]

Equation 1.1 The beta decay scheme of $^{129}\text{I}$ and $^{131}\text{I}$ \cite{43, 44}.

1.4.3 Radioactive technetium

$^{99}\text{Tc}$ is a weak $\beta$ emitter with a very large fission yield of 6.1185\% (per fission of $^{235}\text{U}$) and half life of 212,000 years. $^{99}\text{Tc}$, like $^{129}\text{I}$, is also produced as a by-product from the operation of nuclear reactors. $^{99}\text{Tc}$ also exists as a metastable nuclear isomer that is used nuclear medicine. $^{99m}\text{Tc}$ has a relatively short half life of 6 hours and undergoes isomeric transition decay to form $^{99}\text{Tc}$ that, when present in small amounts, is more than tolerable in the body. $^{99}\text{Tc}$ decays to form $^{99}\text{Ru}$, which is stable, by emitting primarily beta particles (Equation 1.2).
Equation 1.2  The beta decay scheme of $^{99}$Tc $^{[45]}$. 

Technetium is one of two synthetic transition metals. It dissolves in nitric acid, warm sulphuric acid and aqua regia, but is insoluble in hydrochloric acid. The $\beta$ radiation of $^{99}$Tc is stopped by laboratory glassware and although it is relatively safe in its elemental form, it is easily oxidised into the pertechnetate anion, $^{99}$TcO$_4^-$ . The pertechnetate anion is extremely mobile in the environment and the primary route into the body is ingestion in food and water. Once in the human body, $^{99}$Tc concentrates primarily in the gastrointestinal tract and thyroid gland. $^{99}$Tc has a biological half life of approximately 60 h and so after 120 h, only one quarter of any ingested $^{99}$Tc remains in the body. Nearly all ingested technetium will be excreted from the body within a month, however, as with any radioactive material, there is an increased chance that cancer or other adverse health effects can result from exposure to radioactivity $^{[46]}$.

1.4.4 Interactions with the geo- and bio-sphere

The current disposal route of ocean discharge has become less acceptable as the profile of nuclear waste has become more prevalent. Currently discharge via this method is limited to 2000 TBq (around 140 kg) per year. Radioactive iodine can be inhaled as a gas or ingested in food or water as iodide or iodate species. Dissolved iodide in water moves easily from the atmosphere into humans and other living organisms. $^{129}$I and $^{131}$I can settle on grass where farm animal graze resulting in ingestion of the radioactive species. Radioactivity can then be passed to humans in meat and milk products. Iodine, if passed into water systems, may also concentrate in marine and freshwater animal, which may come into contact with humans in food products.

Currently, TcO$_4^-$ is separated from a spent fuel reprocessing waste stream by the addition of tetraphenylphosphonium bromide, TPPB, with an efficiency of 95%. A study by Aldridge et al has shown that exposure of TPPB to an alkaline environment, such as that found in the pores of cement, can result in the degradation of TPPB and subsequent release of TcO$_4^-$ into the environment $^{[47]}$.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Waste stream</th>
<th>Annual discharge (GBq)</th>
<th>Authorised limit (TBq)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2007</td>
<td>2008</td>
<td>2009</td>
</tr>
<tr>
<td>Iodine-129</td>
<td>Liquid</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Iodine-129</td>
<td>Aerial</td>
<td>4.8</td>
<td>5.7</td>
</tr>
<tr>
<td>Iodine-131</td>
<td>Aerial</td>
<td>0.56</td>
<td>0.63</td>
</tr>
<tr>
<td>Iodine-129</td>
<td>Solid</td>
<td>0.17</td>
<td>0.08</td>
</tr>
<tr>
<td>Technetium-99</td>
<td>Liquid</td>
<td>4.9</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Table 1.3  Annual discharges of active iodine and technetium from Sellafield $^{[48]}$. 

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1.4.5 Other radioactive species

Graphite is a material that has been used in the nuclear industry for a very long time. In the UK, graphite is principally used as a moderator in Magnox and advanced gas cooled reactors. Prior to use, boron impurities are removed from the graphite via exposure to chlorine gas and/or chlorine containing compounds at high temperature (>2500K). Whilst this was an effective way to remove boron impurities, residues of stable $^{35}\text{Cl}$ remain in the graphite post treatment, that upon irradiation during service, forms radioactive $^{36}\text{Cl}$. $^{36}\text{Cl}$ has a half-life of 301,000 years and decays via weak beta emission (98%) and electron capture (2%) to form $^{36}\text{S}$ and $^{36}\text{Ar}$ (Equation 1.3) [49].

$$^{36}\text{Cl} \xrightarrow{\text{EC}} \text{Stable} \quad \beta (98.2 \%) = 0.709 \text{ MeV} \quad t_{1/2} = 1.57 \times 10^7 \text{y}$$

Stable $^{0.511 \text{MeV} \gamma}$$^{36}\text{S}$ $^{36}\text{Ar}$ Stable

Equation 1.3 The beta and electron capture decay schemes of $^{36}\text{Cl}$ [50].

1.4.6 Suggested possible treatment routes for anion waste

It has been suggested by Hyatt et al that there are two ways in which to immobilise $^{129}\text{I}$ using zeolite-like materials; dissolution, where the iodide is chemically trapped in an insoluble compound and diffusion, where the iodide is physically retained within a compatible solid matrix. Research has shown that iodide as a silver salt is able to occlude within a porous aluminosilicate framework, such as sodalite, however this approach is likely to be costly to use on an industrial scale [51].

Another option is transmutation of $^{129}\text{I}$ and $^{99}\text{Tc}$ to the more stable elements by bombarding the nucleus with neutrons. When bombarded, $^{99}\text{Tc}$ forms $^{100}\text{Tc}$, which has a half-life of 16 seconds, decays into $^{100}\text{Ru}$ by beta decay. Although transmutation has been applied mainly to $^{99}\text{Tc}$, it can also be used with the conversion of $^{129}\text{I}$ to $^{130}\text{I}$, which has a half-life of less than 12 hours. This technique has been shown to work on a small scale however the sheer volume of nuclear waste means this method is likely to be too expensive [52].

A vast number of selective cation exchange materials exist and encompass a huge variety of different materials which are both natural and synthetic in origin. For example, zeolites are used in many different industrial and domestic applications as water softeners in detergents to extract calcium and magnesium from hard water. The use of zeolites also extends into radioactive waste treatment where natural clinoptilolite is used in extraction columns to remove both caesium and strontium from effluent. In contrast to cation exchange materials, anion exchange materials are significantly less numerous and well-studied. Anion exchange materials (similar to cationic exchange materials used in the treatment of other LLFP) have received interest from radiochemistry community in the past few years due to the need for removal of radioactive anions. Selective anion exchange materials are relatively challenging to produce as the mechanism of exchanging large anions is structurally
demanding compared to the smaller cations. Various framework and layered species have been shown to exchange with many different sized and shaped anions ranging from large organic molecules to small halogens to tetrahedral perchlorate, but not generally in a selective way. Metal organic framework (MOFs) materials have been shown to exchange readily with a whole host of anions, however due to their organic nature, the harsh nature of radioactive sludges could cause breakdown of the framework and hence mobility of species; breakdown of organic bridges such as those used in cement superplasticisers are known to allow hazardous leaching of radioactive species into groundwater. One way it is envisaged that selective anion exchangers could be realised is by using materials with a well-defined interlayer spacing which restricts the species that can enter the layer. For this reason, layered anion exchange materials have been attracting increasing attention over the last few years with layered double hydroxides (LDH) and layered hydroxysalts (LHS) showing potential in the targeted separation of $^{129}\text{I}^-$ and $^{99}\text{TcO}_4^-$, due to their stability in basic environments [53]. LDHs such as hydrotalcite (Mg$_6$Al$_2$(CO$_3$)(OH)$_{16}$·4(H$_2$O)) and LHSs such as copper hydroxynitrate (Cu$_2$(NO$_3$)(OH)$_3$) have been shown to readily exchange with anions, however the factors affecting a sustainable exchange (such as temperature, concentration, competition from other anions and atmospheric CO$_2$ interference and stability to radiolytic decay) have not been fully explored.

1.5 Scope of this project

This project is concerned with evaluating layered hydroxide materials of various types to investigate their suitability for capture and long term storage of radioactive anions. There are many factors that must be considered when selecting potential ion exchange materials for use in the separation, immobilisation, and long term storage of radio anions such TcO$_4^-$, I$^-$ and Cl$^-$. The presence of target long-lived radio anions in high nitrate and carbonate aqueous solution means the exchange material must be insoluble in water, selective towards such anions and able to remain stable in a chemically diverse environment. The exchange process with the target anion also needs to take place rapidly under flow conditions. Once separated, the exchange material is likely to be mixed with a cement matrix before being placed in an underground repository for long term storage. Therefore the exchange material must be stable in a high pH environment, pH 9-11 depending on the cement used. Once placed in an underground repository for long term storage, the material must be stable for thousands of years and have a high radiolytic stability.
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Chapter 2

Solid State Synthesis Techniques and Experimental Procedures
2.1 Polycrystalline solids

Solids state materials can broadly be classified into four types: single crystal, polycrystalline solids, amorphous solids and thin films (Figure 2.1). Single crystals, or monocrystalline solids, exhibit ‘unbroken’ long range order over distances much greater than the distance between the atoms with limited internal grain boundaries. Conversely, amorphous materials contain no translational long range order and have limited or no short range order within the particles. A polycrystalline material contains many small crystallites of varying or regular size meeting at grain boundaries which may be randomly oriented or directed, and within which there is persistent order. In a thin film, crystal growth is controlled so the growth in one direction is restricted leading to continuous layers which vary in thickness ranging from a monolayer to micrometres.

![Single crystal, Polycrystalline solid, Amorphous solid](image)

Figure 2.1 The arrangement of atoms in a single crystal (diamond), polycrystalline (lines = grain boundary) solid (metal surface) and an amorphous solid (glass).

Single crystals are generally grown deliberately for determining crystal structures, especially of (macro) molecular materials. Although relatively limited, industrial applications of single crystals do exist in the use of silicon semiconductors, sapphire optical lens’ for use in lasers and nickel alloys used in the production of turbine blades. Much research has concentrated on finding new applications for single crystals and a recent discovery has been the use of single crystal copper to increase electrical conductivity.

Amorphous materials, such as glasses, have wide ranging industrial applications varying from sodium borosilicate glass used in window panes to sucrose used in candy floss. Characterisation of
these materials is however challenging since standard techniques used to investigate solid state materials such as X-ray diffraction are unsuitable due to the short range order. Generally amorphous materials are investigated with the aid of spectroscopic techniques which focus on local arrangements such as nuclear magnetic resonance, infrared and Raman vibrational spectroscopy.

Thin films may be classified as single crystal, epitaxial, polycrystalline or amorphous. The main advantages of using thin films include a high surface to volume ratio, easy geometric control and compactness. Thin films have specialized applications in microelectronics, telecommunications, optical applications, coatings, catalysts and sensors.

Polycrystalline solids are also often referred to as powders and are sometimes engineered to have high crystallinity or large surface areas. Highly crystalline powders are desirable for characterisation and are often preferred to single crystals for the measurement of physical properties since they are more representative of the bulk sample. Large surface area powders have particular applications when an increased reactivity is needed, such as catalysts and electrode materials. In this project, all the materials synthesized are polycrystalline powders due to the potential industrial applications of the products and the need to mimic bulk behaviour. Several solid state synthetic methods were used in this project depending on the materials synthesized and an overview is presented in section 2.2 [1, 2].

2.2 Solid state synthesis methods

Conventional solid state methods involve the mixing of one or more solid reagents followed by heating to form a solid product. In the case of gas and liquid phase reactions, there are many factors that may drive the rate of a reaction. However in solid state reactions, the limiting factor is usually diffusion and can be predicted using Fick’s law (Equation 2.1).

\[ J = -D \frac{dc}{dx} \]

Equation 2.1 Fick’s law.

Where \( J \) = flux of diffusing species (cm\(^2\)/s), \( D \) = the diffusion coefficient (cm\(^2\)/s) and \( \frac{dc}{dx} \) = concentration gradient (cm\(^4\)). As temperature is increased, the diffusion coefficient also increases, rapidly as the melting point of a material is approached. The rate of a solid state reaction is controlled by three factors; area of contact between reacting solids, rate of diffusion and rate of nucleation of the product phase.

To maximise the contact between reactants, starting reagents with large surface areas are necessary. With a reactant volume of 1 cm\(^3\), the number of crystallites present with edge length of 10 μm will be 10\(^6\) with a surface area of 6 x10\(^3\) cm\(^2\). If the edge length is reduced to 100 nm, the number of crystallites will increase to 10\(^18\) and the surface area increased to 6 x10\(^5\) cm\(^2\). The second factor, rate of diffusion, can be accelerated with an increased temperature and by the introduction of defects. One method which deliberately introduces defects is by using reagents such as nitrates or carbonates which decompose during the reaction process, where the generation and loss of the gaseous species generates the defects. The final factor, the rate of nucleation of the product phase, can be maximised
by using reactants with crystal structures similar to that of the products. In order to increase the rate of diffusion, conventional solid state synthetic procedures are usually carried out at high temperature, however this can present several disadvantages such as difficulties incorporating ions that readily form volatile species (such as Ag\(^{+}\)) and difficulty accessing low temperature meta-stable products\(^{3}\).

2.2.1 Conventional ceramic method

Conventional solid state methods utilise high temperatures to drive a reaction by increasing the formation of defects and improving the mobility of the ions. Other steps can also be taken to increase the rate of reaction and yield. After being weighed out, starting reagents are ground together into a fine powder using a pestle and mortar (with the aid of an organic solvent in some cases) to maximise surface area. A ball mill may also be used for maximum homogeneous mixing. Pelletisation is a technique that is often used to enhance the intimate contact of reactants and minimise contact with the crucible. The material of choice for a crucible depends on the temperature needed, reactivity, cost, strength and ductility. For low-cost reactions, Al\(_2\)O\(_3\) or ZrO\(_2\) based crucibles are often used. A furnace is used to heat the sample as required with factors influencing choice of temperature including decomposition temperature, melting points and potential for volatilisation. An initial heating cycle at a lower temperature can help to prevent spillage during volatilisation by controlling the loss of gaseous products. The choice of atmosphere is also critical. Reactions that require an oxidising atmosphere can be carried out in air, however stronger oxidising conditions (such as the use of pure oxygen gas) maybe required while reducing conditions can be achieved using nitrogen or hydrogen gas. Non-standard atmospheres can be provided by using a tube furnace that allows a constant flow of gas to be passed over reagents in a closed system (e.g. quartz reaction tube). After a heating cycle, the product is ground and analysed to determine what phases are present using a suitable technique (such as X-ray powder diffraction (XRPD)). If the reaction is incomplete, the process of grinding and firing can be repeated\(^{4,5}\).

2.2.2 High pressure synthesis

An increase in pressure during synthesis allows regions of a phase diagram not accessible at atmospheric pressure to be explored. In addition, the presence of high non-metal partial pressures (i.e. high O\(_2\) partial pressure) can be used to stabilise cations in unusually high oxidation states. High pressure synthesis equipment tends to be large and expensive, producing low product/sample volumes that make characterisation difficult. High pressure techniques vary primarily in design of the pressure transmitting device, which in turn leads to variations in the accessible pressure and temperature range, as well as the sample volume. If a stable phase is synthesized using high pressure apparatus, it may transform back to its ambient pressure phase upon release of the pressure. In order to prevent this process, it can be possible to “quench” the sample, whereby lowering the temperature back to room temperature before releasing the pressure back to ambient pressure\(^{6}\).

2.2.3 Sol-gel and combustion

As previously described, conventional ball milling and grinding techniques can be effective at reducing diffusion distances and homogenising a powder. However, other techniques that involve mixing the starting reagents in solution can also be implemented. Intimate mixing using a solute to
mix reagents on a molecular scale acts to decrease diffusion distances once the solvent has been removed. As the solution gradually evaporates, a biphasic gel-like material containing both liquid and solid phase is formed. This formation of a sol-gel is an amorphous or nano-crystalline mixture of salts containing the relevant cations and anions (usually acetate, citrate, hydroxide, oxalate, etc.). The sol-gel is then treated in the same way as if traditional grinding techniques were used and heated in a furnace to completely remove any solvent and form a powder. An organic acid such as citric or oxalic may also be introduced to promote the formation of the desired product. During heating, the organic acid combusts providing a similar intimate mixture to those previously described for the sol-gel method \cite{7,8}.

2.2.4 Solvation, transport and rapid reaction routes

The following techniques are designed to use lower reaction temperatures and/or shorten reaction times. Consequently, they have many of the same advantages as precursor routes, such as stabilisation of meta-stable phases and high cation oxidation states.

Synthesis from the melt is an approach whereby reagents are mixed and then heated to the highest melting point. The cooling rate can be adjusted to control the size of the crystals formed and so has a similar effect to the sol-gel technique, reducing diffusion distances and homogenising the resulting solid. This approach is especially useful for insoluble compounds, however many compounds melt incongruently therefore synthesis from the melt is not always possible. A molten salt flux can also be used as a good solvent for many insoluble ionic or covalent solids. Slow cooling of the melt can be used to grow crystals, however if the flux is water soluble and the product is not, then powders can also be obtained from the excess flux by washing with water. Synthesis needs to be carried out at a temperature where the flux is a liquid. The main disadvantage of using a molten salt flux is the purity of the product. This is due to incorporation of the molten salt ions in product combined with possible reactions with the reaction vessel \cite{9}.

Hydrothermal synthesis is a reaction that takes place in superheated water, in a closed reaction vessel called an autoclave. A solution containing the starting reagents is placed into a Teflon® reaction vessel that is then sealed within a steel autoclave (Figure 2.2). In this study, a Parr Instruments autoclave with a 17 ml fluorinated ethylene propylene (FEP) Teflon® reactions vessel with an effective temperature range of 100 - 250°C was used.
Reagents which are typically used in autoclave reactions are salts that dissolve in water, however insoluble reagents may also be used. The hydrothermal methodology has two distinct advantages over reactions in the solid state. Firstly, reactions that would normally require a high temperature maybe carried out at a lower temperature and, as with high pressure synthesis, parts of the phase diagram may become accessible at lower temperature in the presence of high pressure. The second advantage relates to materials that would normally be unstable at relatively low temperatures. In the presence of high pressure and a closed system, synthesis of materials that may decompose at the same temperature at atmospheric pressure, can be carried out. Although very large hydrothermal vessels are available, production on an industrial scale would be prohibitively costly and so this technique is limited to laboratory scale synthesis\(^{10,11}\).

### 2.2.5 Precipitation synthesis

Although many ceramic materials require high temperatures for synthesis, many mineral based materials are easily made at relatively low or even ambient temperatures. A simple precipitation technique involves dissolving reagents in water and then heating the solution until a solid product precipitates out. The temperature needed for synthesis depends heavily on the cations and anions present. The technique is especially useful in the synthesis of hydroxide based materials. The main advantage of this technique is relative low cost and high production yield. This method is also unsuitable for salts containing components that are unstable at temperatures greater than 100°C, such as organic anions. Another similar precipitation technique involves titration of one reagent against another to obtain the desired product. The rates of titration and stirring of the target solution is vital to ensure thorough mixing and reduce the presence of impurities. The titrated mixture may be heated either during mixing or after to improve yield and purity\(^{12}\).
2.3 Methods of data collection

The characterisation of the solid state materials prepared in this thesis was performed using a variety of diffraction, microscopic and spectroscopic techniques. Characterisation is essential to determine not only the chemical and physical properties of a material, but also its structure. This is because the structure of a material often dictates the observed physical properties. A brief summary of the theory behind each characterisation technique is discussed in the remainder of this chapter, along with standard experimental design. Standard parameters that are used throughout are also presented, with any deviations noted in the relevant experimental sections.

2.3.1 X-ray diffraction

X-ray diffraction (XRD) is a non-destructive analytical technique that relies on the interaction of X-rays with materials in the solid state. Organic materials are usually only analysed using spectroscopic techniques and this will often provide all the necessary information for characterisation. Spectroscopic information on its own does not suffice in the case of inorganic materials due to the greater structural diversity in terms of coordination numbers, geometries, presence of functional groups and the need to identify packing and connectivity of polyhedra.

2.3.1.1 Interaction of X-rays with solids and Bragg’s law

When a crystalline sample is irradiated with monochromatic X-rays, the X-rays are scattered either elastically or inelastically. Elastic scattering is scattering without loss of energy and it is the basis of diffraction whereas inelastic scattering occurs with loss of energy, subsequently the wavelength of the scattered X-rays is longer and undiagnostic. Inelastic scattering is reduced using several techniques in XRD as it only adds to background noise; however this type of scattering can be useful in determining elements present in a material. For example X-ray fluorescence (XRF) uses inelastic scattering to identify elements by characteristic energy losses. For diffraction to occur, Bragg’s law must be obeyed with the scattering of X-rays from a parallel sets of planes labelled with the Miller indices hkl(Figure 2.3). Useable data are produced from an X-ray experiment when the scattered X-ray beams from points X and Z are in phase which generates intensity in the diffraction pattern (constructive interference). If incident X-rays are out of phase, cancellation of the diffraction data occurs. The path difference is dependent on both the lattice spacing \( d_{hkl} \) and the angle of incidence of the X-ray beam, \( \theta \).
Bragg’s law (Equation 2.2) describes the long range order present in a crystalline sample and is used to geometrically associate the angle of diffraction to a particular set of Miller planes.  

\[ n\lambda = 2d_{hkl} \sin \Theta \]  

Equation 2.2  

Bragg’s law.

Where \( n \) = order number (usually 1), \( \lambda \) = wavelength of X-ray beam (Å), \( d_{hkl} \) = d-spacing (for a specific hkl plane)(Å) and \( \theta \) = the Bragg angle of incidence and reflection (degrees). The wavelength of the X-ray beam (\( \lambda \)) must be comparable to that of the periodic spacings within a crystal structure in order for scattering to occur so typically wavelengths of between 0.6 and 1.9 Å are used in diffraction experiments. There are two ways of using Bragg’s law in X-ray experiments; the first is used in laboratory X-ray diffraction and involves keeping a constant fixed wavelength radiation and the angle of incidence, \( 2\theta \), is altered whereas the second method is to have a fixed angle of incidence and to alter the wavelength of the X-rays. During an XRD experiment the Bragg angle, \( \theta \), is measured and so gives the position of the Bragg reflection, \( 2\theta \), or peak. Using the known wavelength, \( \lambda \), of the X-rays, the d-spacings can be calculated. Every crystalline material has a unique set of observed reflections which form the powder diffraction pattern, therefore theoretically Powder X-ray diffraction may be used as a fingerprint technique. It is important to note that diffraction is a three-dimensional phenomenon and the X-rays are actually diffracted in cones, called Debye cones, or Debye rings when viewed end-on. Therefore in an XRD experiment the detector scans through these cones to create a diffraction pattern that consists of a series of peaks that are more properly named Bragg reflections. On a diffraction pattern the horizontal axis is \( 2\theta \), twice the Bragg angle, and the vertical axis is the intensity,( e.g. X-ray counts/ count rate), this is a function of the crystal structure and the orientation of the crystallites in a powdered sample \(^{13, 14}\).
2.3.1.2 The generation of X-rays

X-rays are produced when electrons are fired at high speed at a metal target (e.g. copper or cobalt, commonly used in X-ray diffraction experiments). Core electrons are then ejected leaving their valency vacant by a quantised amount. These vacancies are then filled with electrons from higher energy orbitals with the difference in energy between the vacancy and higher energy orbitals being emitted as an X-ray of precise energy. The type of X-ray can be determined according to the spin state and vacancy filled. Four X-ray types are emitted from an X-ray source; $K_{\alpha 1}$, $K_{\alpha 2}$, $K_{\beta 1}$ and $K_{\beta 2}$. The α/β notation refer to transitions, i.e. $\alpha = 2p$ to $1s$ and $\beta = 3p$ to $1s$, and the 1 or 2 notation refers to the spin state of that electron. $K_{\alpha 1}$ X-ray emissions have the highest intensity and so this line is primarily selected for use in a single wavelength (monochromatic) powder diffraction experiment (Figure 2.4) [15].

![Figure 2.4](image)

**Figure 2.4** The Output from an X-ray Source.

X-rays are generated from an X-ray tube, inside this tube a tungsten filament is heated and this in turn produces electrons by thermionic emission. These electrons are accelerated in a vacuum tube towards a metal target (Cu, Co, Fe or Mo) which in turn produces X-rays. The X-rays then escape through a beryllium window (Figure 2.5).

The generated X-rays then pass through a monochromator that is aligned to allow $K_{\alpha 1}$ X-rays through and to block the $K_{\alpha 2}$, $K_{\beta 1}$ and $K_{\beta 2}$ radiation (Bremstrahlung radiation). These $K_{\alpha 1}$ X-rays are then passed through a collimator and a series of slits to define the beam into a single direction and destination. The X-ray tube can incorporate a differing metal target depending elements present in a sample.
2.3.1.3 X-ray powder diffraction experiment and parameters

The most common technique in solid state materials chemistry is powder X-ray diffraction (XRPD), as powders are normally easier to synthesize than singles crystals and they are representative of the bulk sample. However, single crystal diffraction studies can be useful for definitive characterisation of physical properties such as magnetic ordering or electron transport as the directional properties of materials are often lost in polycrystalline samples.

In a single crystal experiment, the crystal, source and detector are aligned to observe scattering from one particular plane at a time. However in XRPD, the sample contains a huge number of small crystallites, typically $10^{-7} - 10^{-4}$ m in size, which randomly orientate and so when an X-ray beam interacts with a powder, X-rays are diffracted in all possible directions. The lattice spacings in a crystal create a Debye cone of diffraction (Figure 2.6).

![Figure 2.5 A Schematic of an X-ray Tube.](image)

![Figure 2.6 A continuous Debye cone of diffraction.](image)

Each Debye cone represents a set of closely spaced dots, with each dot representing diffraction from a single crystallite within a powder and a continuous cone is formed as a result of many crystallites joining together.

In a XRPD experiment, X-rays produced by the X-ray tube are aligned and focused onto a sample through a slit, and the X-rays scattered in all directions. A detector is scanned around the
sample along the circumference of a circle in order to cut through the diffraction cones at various diffraction maxima (Figure 2.7).

![Diagram of a powder X-ray diffractometer](image)

**Figure 2.7** A schematic diagram of a powder X-ray diffractometer.

The sample behaves as a mirror, focusing the beam onto the detector. A slit close to the detector acts to remove noise in order to give well-resolved data. The output from a XRPD experiment is called an X-ray diffraction pattern and this displays peaks (reflections) with intensity as a function of the detector angle, $2\theta$. The pattern obtained is similar to that of a single crystal experiment as the data generated is from the arrangement of atoms within the unit cell. There are many factors that influence the number of reflections and intensity. These include the crystal class, lattice type, symmetry, unit cell parameters, the distribution and type of atoms in the unit cell, as a result almost all crystalline solids have a unique powder X-ray diffraction pattern \[16, 17\].

XRPD has many practical applications including identification of an unknown material, phase purity, determination and refinement of lattice parameters, type and systematic absences, crystallite size and structural refinement. In this research, data were collected using a Bruker D8 Advance diffractometer with monochromatic CuK$_\alpha$1 radiation at $\lambda = 1.5406$ Å, a germanium monochromatic window and position sensitive detector (PSD). Data were analysed using WinPlotr and Bruker EVA.

### 2.3.1.4 X-ray Diffraction using Synchrotron sources

Synchrotron light sources are designed to produce very intense beams of X-rays, infrared and ultraviolet light. Synchrotron sources can generate light from infrared through the visible range and ultraviolet up to X-rays. Synchrotron light can be as much as 100 billion times brighter than the sun and this allows samples to be studied in incredible detail, to a level that is only possible at a synchrotron. The intense light allows for better resolution, flux, deeper penetration of samples and greatly reduced data collection times. These factors are useful in the analytical techniques of single crystal diffraction, powder diffraction, microfocus X-ray spectroscopy and small angle X-ray scattering.
2.3.1.5 Synchrotron diffraction experiment and parameters

Electrons that originate from an electron gun are accelerated to very high speeds using a series of three particle accelerators. These are called the linear accelerator (LINAC), booster synchrotron and large storage ring. The storage ring is a polygon, made of straight sections angled together with dipole (bending) magnets that reflect the electrons around the ring. As the electrons pass through each magnet they lose energy in the form of an intense light beam that can then be tunneled out of the storage ring and into the experimental stations (Figure 2.8) [17, 18].

Figure 2.8 A schematic diagram of the Diamond synchrotron light source.

Light generated by electrons in the storage ring passes into beam lines, where the experiments are carried out. Each beam line is optimised for a different kind of experiment, but they have some key components in common. Synchrotron Radiation PXRD data were collected at room temperature on the ettringite and thaumasite type phases at The Diamond Light Source (Didcot, UK), I11 beamline, High Resolution Powder Diffractometer [23]. The samples were mounted in 0.5 mm Lindemann capillaries and measured in Debye-Scherrer (transmission) geometry. The data were collected over the 2θ range 5°-150° 2θ for 30 minutes. The X-ray wavelength (0.826262 Å) and 2θ zero offset were calibrated by refinement of the diffraction pattern of a silicon standard (NIST SRM640c). Data were then analysed using WinPlotr. The intensity of the synchrotron allows rapid measurements to be carried out allowing in situ reactions to be followed in real time. Typically data
collection times are the order of seconds and minutes rather than the analogous minutes and hours on a conventional laboratory X-ray source.

2.3.1.6 Neutron diffraction

Neutron diffraction is based on the interaction of neutrons with the nucleus. X-ray diffraction depends on the interaction of X-rays with the electron cloud of an element and an increase in scattering is observed as the number of electrons increases. When neutrons interact with an atom, it is the properties of the nucleus that affects the scattering of the neutrons. Generally speaking, the scattering amplitude of a neutron does increase slightly as a function of atomic number as a result of an increased nucleus size (roughly proportional to the atomic number to the power of a third). In addition to the scattering effect due to nuclear size, there is also a secondary process that affects the scattering known as ‘resonance scattering’. When the incident neutron and nucleus combine, a compound nucleus can be formed. Depending on the energy levels in this compound nucleus, further scattering may occur for thermal neutrons that are superimposed on the scattering observed due to nuclear size. As a result, the scattering amplitude as a function of atomic number is random. The variation of scattering amplitudes of atoms by neutrons is small compared to the scattering amplitudes of X-rays.

The main limitation of X-ray diffraction is loss of information on light atoms in the presence of heavier atoms. This problem is solved in the case of neutron diffraction as neighbouring atoms can have very different neutron scattering lengths. The main limitation of neutron diffraction is cost and availability. As neutron and X-ray diffraction are complimentary providing different sets of information, XRD and ND datasets are often co-refined \[ 17, 19 \].

2.3.1.7 Neutron diffraction experiment and parameters

Neutrons for use in diffraction experiments are obtained via two sources; nuclear reactor sources and spallation sources. In the former, a slow moving neutron collides with a radioactive heavy metal (for example $^{235}\text{U}$) atom and is absorbed to produce $^{236}\text{U}$. The resulting uranium isotope is unstable and splits to form lighter $^{92}\text{Kr}$ and $^{141}\text{Ba}$ atoms along with neutrons (Fig 2.9). These neutrons can be collected and fired at a sample to collect data. An example of a scientific facility that utilises nuclear fission as a source of neutrons is the Institut Laue-Langevin (ILL) that is currently the most intense continuous neutron flux source in the world with an output of $1.5 \times 10^{15} \text{s}^{-1} \text{cm}^{2}$.

\[ n^0 \rightarrow ^{235}\text{U} \rightarrow ^{236}\text{U} \rightarrow ^{141}\text{Ba} + ^{92}\text{Kr} + n^0 \]

Figure 2.9 The decay process of $^{235}\text{U}$ and the eventual formation of neutrons.

ISIS uses a process called spallation as a source of neutrons. An ion source produces $\text{H}^-$ from hydrogen gas in the presence hot caesium vapour and the formation of discharge plasma. The $\text{H}^-$ ions are injected into a LINear ACcelerator (LINAC) that accelerates the beam to 70 MeV. $\text{Al}_2\text{O}_3$ foil (0.3µm thick) then strips $\text{H}^-$ ions of their electrons and the subsequent $\text{H}^+$ ions are then injected into a
synchrotron ring for ~10000 revolutions. The protons are then extracted from the synchrotron and fired at a heavy tungsten target, clad with tantalum to reduce corrosion, which induces intra-nuclear cascading. The W nuclei are promoted into an excited state with energy released by the “evaporation” of neutrons with each proton producing ~ 15 neutrons.

Figure 2.10 A schematic diagram of the ISIS neutron and muon source.

Neutrons are the slowed down using a moderator (such as H₂O or CH₄) and subsequently fired towards a variety of experiments located in two target stations. A moderator is needed to reduce the speed of the incoming neutrons to an energy that can be used for diffraction [20].

Powder neutron diffraction (ND) data were collected on the high resolution powder diffractometer HRPD, at the UK spallation source ISIS, (Rutherford Appleton Laboratory), from the highest resolution back-scattering detectors, over the time-of-flight range 30-130 ms (Figure 2.10). The HRPD is the highest resolution neutron powder diffractometer of its type in the world with a Δd/d resolution of ~4x10⁻⁴ which is effective over a wide –spacing range. Structural analyses of the powder ND data were carried out using the program GSAS.

2.3.1.8 Rietveld refinements

Reflections observed in a powder diffraction pattern occur along the same axis and so frequently overlap. This overlapping of reflections makes extracting intensities of individual reflections extremely difficult. To solve this, the Rietveld method refines a pattern as a whole [16]. A method of least squares is used to find a best fit between experimental diffraction data and a calculated model.
Using the least squares method, the problem of overlapping reflections can be avoided as only the points along the experimentally observed pattern and the calculated pattern, and not the individual peaks, are compared. The technique is similar to that used in single crystal refinements, however experimental parameters such as background, peak broadening and lattice constants must also be fit \(^{21}\).

Using the Rietveld method, an approximate model of a structure is used to generate a list of expected reflections that are based on the structure facture \(F_{hkl}\) multiplied by the multiplicity of the hkl values. The expected reflections are then convoluted using experimental and crystal factors, and a background added in order to produce a pattern that more closely represents a real life diffraction pattern. A Rietveld refinement can be thought of as a very complex curve fitting problem whereby a model function is parameterised by both the crystal structure (atomic coordinates, thermal displacement and site occupancies) and diffraction experiment (unit cell, peak profile broadening, etc). The principle of the Rietveld Method is to minimise a function \(M\) which analyzes the difference between a calculated profile \(y^{\text{calc}}\) and the observed data \(y^{\text{obs}}\) where \(W_i\) is the statistical weight and \(c\) is an overall scale factor such that \(y^{\text{calc}} = c y^{\text{obs}}\) (Equation 2.4) \(^{22}\).

\[
M = \sum_i W_i \left\{ y_{i}^{\text{obs}} - \frac{1}{c} y_{i}^{\text{calc}} \right\}^2
\]

Equation 2.4 Refinement equation.

Samples for a Rietveld analysis must be well prepared and the data collected on a well aligned diffractometer to reduce instrumental factors. Data collected using high energy light (such as that at diamond light source) or a neutron source (such as that at ISIS) offer increased resolution and, in the case of neutron data, the ability to calculate occupancy. Rietveld refinements of powder data have many applications in crystallographic structure determination, quantitative analysis, engineering properties and lattice constant determination.

2.3.2 Vibrational spectroscopy

Infrared (IR) and Raman spectroscopy are techniques used to study the vibrational and rotational modes present in a molecule. Both IR and Raman techniques provide similar and complementary information, however a clear difference between the two techniques is discussed in this section.

2.3.2.1 IR spectroscopy

IR spectroscopy is an analytical technique used to study the absorption of electromagnetic radiation by a molecule over a number of wavelengths. The technique operates in the infrared region of the electromagnetic spectrum and is split into three regions between ranges 14000-10 cm\(^{-1}\); near- (1400-4000 cm\(^{-1}\)), mid- (4000-400 cm\(^{-1}\)) and far- (400-10 cm\(^{-1}\)) infrared.

When a molecule adsorbs energy it becomes excited. Depending on the nature of the bonds and functional groups present in a sample, energy is absorbed at certain quanta of energy. In order
for a vibration to become IR active, a change in dipole must occur during a vibration. This is known as the selection rule. A molecule composed of n-atoms has 3n degrees of freedom, six of which are translations and rotations of the molecule itself. This leaves 3n-6 degrees of vibrational freedom (3n-5 if the molecule is linear), giving six fundamental vibrations (12 minus 6). Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting (Figure 2.11) [23, 24].

![Figure 2.11](image)

Vibrational modes in a simple tetrahedral molecule.

The vibrations are due to a change in bond angle and bond lengths and using Hooke’s law it is possible to estimate the vibrational frequencies based on the size of the atoms surrounding a bond (Equation 2.5).

\[ v = \frac{1}{(2\pi c)} \sqrt{\frac{F}{m}} \]

Equation 2.5 Hooke’s law.

Where \( v \) = frequency, \( c \) = the speed of light (constant), \( F \) = the strength of a bond and \( m \) = mass of an atom. Using this formula it can be shown that the heavier the atoms surrounding a bond, the lower the frequency and the more bonds between atoms, the higher the frequency [25].

Hooke’s law treats a bond like a “spring” and when a mass (atom) is added to the end of this spring, the bond oscillates harmonically. This in turn can be used to analyse which vibrations in a spectrum are due to which bond or functional group [26].

### 2.3.2.2 FT-IR experiment

In an FT-IR experiment, light from a laser source travels through a monochromatic prism, an interferometer containing several mirrors and a beam splitter and then the sample. A second beam
with a longer wavelength then combines with the first to form a complex interference pattern at the
detector (Figure 2.12).

![A schematic diagram of an FT-IR experiment.](image)

Computer software then analyses the complex interference patterns to produce an IR
spectrum of a sample. The whole process from start to the appearance of an IR spectrum on a
computer screen takes less than a minute and this method gives greater sensitivity and better
resolution than more traditional direct plot IR systems. Data were collected between ranges 400-4000
cm$^{-1}$ using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an ATR accessory fitted. Data were
analysed using Perkin Elmer Spectrum, Microsoft Excel and Essential FTIR.

### 2.3.2.3 Raman spectroscopy

Raman is an optical technique that is similar to FT-IR spectroscopy in that it detects vibrations
produced by bending/stretching frequencies of bonds within a molecule, however it relies on inelastic
(Raman) scattering of monochromatic light. When photons are passed through a molecule, they are
scattered in two distinct ways; elastically and inelastically. Elastic (Rayleigh) scattering occurs when
the incident photon reflects towards the direction of origin with the same frequency and wavelength,
and accounts for most of the scattered photons. A small number of photons (approximately 1 in 10
million) are scattered inelastically (Raman) with a frequency greater than or less than the incident
photon (Figure 2.13) \(^{[27]}\).
If an electron in the ground state (v=0) is excited, it will move to a virtual energy state, and upon relaxation, will move to an elevated vibrational energy state (v=1). This results in the loss of net energy of the incident photon and is known as Stokes Raman scattering. If an electron already in an elevated vibrational state is excited, it will move to a virtual energy state and upon relaxation, move back to the ground state. A net gain in energy of the incident photo is observed and this is called anti-Stokes scattering. It is the vibration of the molecule that determines the Raman scattering and so a spectrum similar to that of IR spectroscopy is obtained. In order for a bond to be Raman active, the selection rules state that it must be anisotropically polarisable and the stretching or vibration mode generates a change in polarisation.

In rotational Raman spectroscopy, both Stokes and anti-Stokes scattering are observed, however in vibrational Raman spectroscopy, the anti-Stokes scattering is so small it can be discounted. Inelastic scattering is so small, the strength of the dipole moment is directly proportional to the electric field (Equation 2.6)

$$\mu_{\text{ind}} = \alpha E$$

Equation 2.6 The relationship between a dipole moment and an electric field.

Where $\mu_{\text{ind}}$ = the dipole moment, $\alpha$ = the proportionality constant, $E$ = the energy of the electric field and $W$ = the interaction energy is related to the square of the electric field. It is the proportionality constant of a molecule that is vital in Raman spectroscopy and is related to the interaction energy (Equation 2.7)\(^{28}\).

$$W = -1/2\alpha E^2$$

Equation 2.7 The relationship between a proportionality constant of a molecule and the interaction energy.
2.3.2.4 Raman experimental and parameters

An intense laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range passes through various optic lenses and mirrors to polarise and direct the beam, before it reaches the sample. From here, the scattered light is passed via mirrors to a spectrograph. A Rayleigh scatter light filter removes the more prevalent inelastic scattered light to leave just the Raman scattered light. The inelastic light then passes through a diffraction grating to remove any stray instrument light into a CCD camera where the data is analysed using a CPU to produce a spectrum (Figure 2.14).

![Figure 2.14 A schematic diagram of a Raman spectroscopy experiment.](image)

Data were collected on a Horiba John Yvon LabRAM HR800 spectrometer using a 632.6nm HeNe laser with 600 grating, 50x objective, 1000µm hole size and a 150µm slit aperture. Data were collected across a 200 - 1500cm⁻¹ range in collection sets of 200cm⁻¹ with 20 accumulations of 20s exposures. The data were analysed using LabSpec software v5.25 and Microsoft Excel.

2.3.2.5 Selection rules

As previously described, infrared spectroscopy is used to observe transitions between vibrational energy levels of a molecule induced by the absorption of infrared (IR) radiation, whereas Raman spectroscopy is used to observe vibrational transitions that occur during the scattering of light by molecules. At ambient temperature almost all molecules are in their lowest vibrational energy level, with quantum number n = 0. For each normal mode, the most probable vibrational transition is from this level to the next highest level (n = 1). The strong IR or Raman bands resulting from these transitions are called fundamental bands. Other transitions to higher excited states (n = 2) result in overtone bands, and these bands are much weaker than fundamental bands.

Not all vibrational transitions can be studied by both IR and Raman spectroscopy because they have different selection rules. Selection rules are used to determine whether a transition is allowed or forbidden. An allowed transition has a high probability of occurring and will result in a strong band. However a forbidden transition’s probability is so low that the transition will not be observed. If the point group of a molecule and the symmetry labels for the normal modes are known,
then group theory makes it easy to predict which normal modes will be IR and/or Raman active. If the symmetry label of a normal mode corresponds to \( x, y, \) or \( z \), then the fundamental transition for this normal mode will be IR active. If the symmetry label of a normal mode corresponds to products of \( x, y, \) or \( z \) (such as \( x^2 \) or \( yz \)) then the fundamental transition for this normal mode will be Raman active.

Consider the character table for the \( C_{2v} \) group shown below (Table 2.1). A normal mode with \( A_1, B_1, \) or \( B_2 \) symmetry, will be both IR and Raman active. If a normal mode has \( A_2 \) symmetry then it will be only Raman active.

<table>
<thead>
<tr>
<th>( C_{2v} )</th>
<th>E</th>
<th>( C_2 )</th>
<th>( \sigma_v(xz) )</th>
<th>( \sigma_v'(yz) )</th>
<th>IR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( z )</td>
<td>✔</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>( R_z )</td>
<td>( X_y )</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>( X, R_y )</td>
<td>( Xz )</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>( y, R_x )</td>
<td>( Yz )</td>
</tr>
</tbody>
</table>

Table 2.1 A character table for the \( C_{2v} \) point group.

Water is an example of a molecule with a \( C_{2v} \) point group with three normal modes: two of \( A_1 \) symmetry and one of \( B_2 \) symmetry. All of these modes are IR and Raman active and so it would be expected that water will have three peaks corresponding to fundamental vibrations in the IR spectrum. There also would be three peaks in its Raman spectrum at the same frequencies as in the IR spectrum.

### 2.3.3 Additional techniques

The techniques mentioned already will hold an integral part in the characterisation of all materials produced in the study. Additional techniques outlined below were used to analyse a selection of materials when required.

#### 2.3.3.1 Gamma detection and liquid cocktail scintillation counting

Due to the radiochemical nature of this project, a suitable technique was needed for the qualitative and quantitative analysis of radioactive samples. Liquid scintillation counting is a technique which incorporates a radio-labelled analyte within a liquid chemical medium, capable of converting the kinetic energy of \( \alpha \) or \( \beta \) emission into a photon. The liquid chemical medium, or liquid scintillation cocktail, is a dense liquid that acts as a solvent for the sample material. Kinetic energy of an \( \alpha \) or \( \beta \) radio emission is absorbed by solvent molecules making them excited with UV light emitted as the solvent molecule returns to ground state. The excited solvent molecules can transfer energy to each other and to a fluorophore solute. An excited solvent molecule which passes its energy to a solute molecule disturbs the orbital electron cloud of the solute raising it to a state of excitation. As the excited orbital electrons of the solute molecule return to the ground state, a photon of UV light is emitted. The light is absorbed by fluor molecules which emit blue light flashes upon return to ground state and it is the total number of photons from the excited fluor molecules constitutes the scintillation. The intensity of the light is proportional to the particle's initial energy. Blue light flashes hit the photo cathode of a photo multiplier tube (PMT). Electrons (proportional in number the blue light pulses) are ejected producing an electrical pulse that can be produced digitally.
Gamma counting is a technique that is used to quantify the activity of a gamma-emitting sample. The principle behind gamma counting is similar to that implemented by a scintillation detector. Gamma radiation emitted interacts with a crystal surrounding the sample and light produced. As with a scintillation detector, if the energy of the interacting photons is too low, the photons of light that are produced may be absorbed in the scintillation crystal and never be detected. If the energy is too high, the incoming photons may just pass through the crystal without interaction. Therefore, the thickness of the crystal is critical, and the efficiency of an instrument for detecting certain gamma-ray energies is dependent upon the thickness of the crystal. The energy of gamma radiation emitted is specific to the radioactive source. Depending on the isotope, this allows gamma radiation from a single isotope to be counted even in the presence of other gamma-emitting isotopes \[^{32, 33}\].

2.3.3.2 Thermal analysis

Thermal Analysis is a destructive technique that measures the changes in a property of a sample as a function of temperature. These include, measurement of physical and chemical properties, specific properties e.g. Enthalpy, heat capacity, coefficient of expansion and measurement of weight changes as materials decompose (e.g. hydrates, oxalates, carbonates). Two of the most common thermal techniques used are thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TGA measures the change in mass of a sample as a function of temperature to give a thermogravimetric curve. TGA has many uses including the measurement of moisture content, phase identity, decomposition modes and interactions with gases. A DTA experiment comprises of the sample of interest and an inert standard (e.g. Alumina) both heated simultaneously, whilst recording any differences in temperature between the sample and standard. Endothermic or exothermic changes in the sample in relation to the standard are measured and data presented with a thermogram. TGA and DTA experiments can be carried out simultaneously \[^{34, 35}\]. Only a small amount of sample is needed (ca. 10 mg) for analysis, however, calibration of the instrument is vital for an accurate result, therefore a standard of indium or zinc is used for calibration. Data were collected in air at a heating rate of 1.5°C/min in air up a stated temperature using a TA SDT Q600.

2.3.3.3 CHN elemental analysis

CHN Elemental analysis is a destructive analytical technique used mainly in organic chemistry that can be used to quantitatively determine the amount of carbon, hydrogen and nitrogen present in a sample. The % compositions in CHN analysis are accomplished by combustion analysis. In this technique, a small sample (ca. 5 mg) is burned in an excess of oxygen, with traps collecting the combustion products as carbon dioxide, water, and nitric oxide. The weights of these combustion products can be used to calculate the composition of a sample in terms of % weights of carbon (C), nitrogen (N) and oxygen (O) present \[^{36}\]. Data were collected using an Exeter analytical ink (EAI) CE-440 elemental analysis machine is used. The standard error of data collected using this technique is approximately 0.2% for C and N content, and 0.5% for hydrogen content.

2.3.3.4 Gravimetric analysis

Gravimetric analysis is a technique that allows the quantity of an element or functional group to be quantified based on its precipitation out of solution with an appropriate reagent. The solid containing the element to be quantified must first be oven dried for a period of time and weighed using...
an analytical balance. This is also performed with a sintered glass crucible which is used later. This process is repeated until 3 measurements agree to with a tolerance. The solid is then fully dissolved in an inert atmosphere using an appropriate solvent or acid/base with its pH adjusted to discourage the formation of any unwanted solids. An appropriate reagent that forms an insoluble product with only the target element or group is added and stirred for up to 1 day to ensure complete precipitation. The precipitate is finally filtered using a sintered glass crucible, washed and then oven dried to remove any residual solvent. The process of measuring the mass of the sintered glass crucible + the recovered solid is then repeated. The mass of element within the original compound can be determined as a % compared to the ideal mass based on its predicted formula (Equation 2.8).

\[
\text{Cu}_2(\text{OH})_3\text{I(s)} + \text{AgNO}_3(\text{aq}) + 3 \text{HNO}_3(\text{aq}) \rightarrow 2 \text{Cu(NO}_3)_2(\text{aq}) + \text{AgI(s)} + 3 \text{H}_2\text{O(l)}
\]

Equation 2.8 A typical gravimetric analysis reaction.

In this study, basic hydroxides containing a halide or carbonate group may be dissolved in nitric acid containing excess soluble silver nitrate, resulting in the precipitation of insoluble silver halide or carbonate salts. All reactions will be performed in a nitrogen atmosphere to reduce the effects of carbonate inference from the atmosphere where applicable.

The standard error was calculated by addition of silver nitrate to a known quantity of sodium iodide (99.5%, Aldrich) in solution, and the mass of a resulting AgI precipitate measured. Carbonate dissolved from the atmosphere also precipitates out of solution as a silver salt, therefore reactions were carried out in a N₂ atmosphere. The solubility of AgI in solution is negligible and in the order of 10^{-6} g/l, therefore no adjustment to the final value will be done to take this into account (Table 2.1).

<table>
<thead>
<tr>
<th>NaI in 50ml (g)</th>
<th>Expected AgI (g)</th>
<th>Observed AgI (g)</th>
<th>Yield (%)</th>
<th>Average (%)</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6425</td>
<td>1.0063</td>
<td>0.9997</td>
<td>99.34</td>
<td>99.33%</td>
<td>0.2462</td>
</tr>
<tr>
<td>0.6332</td>
<td>0.9918</td>
<td>0.9871</td>
<td>99.53</td>
<td>99.12</td>
<td>0.17</td>
</tr>
<tr>
<td>0.6501</td>
<td>1.0182</td>
<td>1.0092</td>
<td>99.12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8.2 Assessing the error in using gravimetric analysis.

2.3.3.5 Ion specific probing

Ion specific electrodes are sensors that are able to translate the activity (based on the selectivity constant (SC)) of a specific ion in solution into an electronic potential. This electronic potential can be used to quantify the amount of a certain ion in solution and the probe usually contains the anion specific electrode along with a reference electrode \([37]\). In this study, an iodide specific solid state crystalline probe will be used. As all poly-crystalline membranes contain silver sulphide, solutions containing Ag or S ions are not suitable. Cyanide ions have a SC of 1 (iodide = 1) and so will cause a significant positive error with other anions such as Br (SC = 0.0004) and Cl (SC = 0.000001) also contributing a small amount of positive error \([38]\). In this study all work using an ion
specific probe was carried out by Marijana Dragosavac in the Department of Chemical Engineering at Loughborough University.
2.4 References

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Chapter 3

Synthesis and Characterisation of Anion Exchange Materials
The main aim of this chapter is to investigate and optimise the preparative techniques used in previous studies for the synthesis of Layer Hydroxysalts (LHSs) and to propose new methods of synthesis. This investigation is carried out with a view to select the most appropriate methods for synthesis considering that the products will later be used for exchange reactions and must be stable in highly alkaline environment. The three main factors that will determine whether an exchange material will be selected are: ease of synthesis, phase purity and easy of characterisation. It is important that any material that may be used in the immobilisation of active waste must be inexpensive in both synthesis and raw materials used. Phase purity is important as the presence of additional phases, such as hydroxides and oxides, may reduce exchange capacity and/or interact with the target anion in a way that is unfavourable. Ease of characterisation allows waste to be easily separated into different streams.

### 3.1 Introduction

Ion exchange reactions date back to 3000 years B.C. and are even documented in the Old Testament when Moses produced drinking water from a saline oasis in Marah by throwing in a dead log containing decomposed organic matter \(^1\). Subsequent experiments by scientist thousands of years later discovered that this acted to remove the salts by adsorption and ion-exchange reactions \(^2\). The first scientific evidence for cation exchange was discovered to take place in soils (Equation 3.1) by an agricultural chemist named H.S. Thompson in 1850 \(^3\). The ion exchange materials were identified as clays, glauconites, zeolites, and humic acids by J. Lemberg in 1870 \(^4\).

\[
\text{Ca – Soil } + \ 2(NH_4)^+ \leftrightarrow \text{Ca}^{2+} + (NH_4)_2 – \text{Soil}
\]

Equation 3.1 A typical cation exchange reaction that occurs in soils.

Applications of ion exchange materials were not developed into a useful product until 1903. F. Harm and A. Rumpler applied ion exchange for use in water softeners with the first commercially available ion exchangers being amorphous aluminosilicate gels known as permutites. However, these materials were found to be unstable in an acidic environment and unreliable \(^5\).

The unsustainable nature of permutites led to the development of organic ion exchange resins in 1935 by B. A. Adams and E. L. Holmes. These resins were noted for their purity, stability, and the relative ease of manipulation of the materials properties by simple synthetic procedures \(^6\). After the Second World War and the rise in use of nuclear technology, ion exchange materials were required to remain stable above 150 °C and in high radiation environments. Early attention focused on hydrous oxides such as brucite, Mg(OH)\(_2\), that were previously known to absorb or co-precipitate ions. It was discovered that hydrous oxides combined with anions such as phosphates, vanadates, molybdates, and antimonates to produce extremely efficient ion exchangers such as zirconium phosphate, however these materials were amorphous in nature and prone to hydrolysis, so were never extensively used \(^7,8\). In 1964 it was demonstrated that zirconium phosphate could be crystallised, this allowed the structure of a polymorph of zirconium phosphate to be determined and the ion exchange behaviour to be explained in terms of its structure \(^9\).
Research has continued over the last 50 years not only into the ion exchange capabilities of materials, but also their use as sorbents and catalysts used for petroleum cracking. Families of mineral-related materials known as zeolites and cationic clays have attracted the most attention and have continued to expand. The tonnage of cation exchange materials consumed industrially is now larger than that of all the organic resins combined\(^{[10]}\). Cation exchange layered compounds are well known with examples such as clay minerals with silicate and/or metal oxysalt anionic centres with exchangeable cations located between the negatively charged inorganic layers. These materials are able to exchange with both organic and inorganic cationic species of different size and geometry by expansion of the layers. Polar solvent molecules are often also intercalated within the interlayer spacing. Although a variety of cation-exchange layered structures are known, anion exchangeable layered structures are comparatively rare and their properties are not fully understood\(^{[11]}\).

### 3.1.1 Types of mineral-based anion exchange materials

There are several classes of mineral based materials that have been shown to undergo anion exchange and the mechanism by which this occurs is defined by structure. Figure 3.1 shows two general structure types that are able to incorporate an interchangeable anion; tunnel structures and layered structures.

![Figure 3.1](image)

<table>
<thead>
<tr>
<th><strong>(a)</strong></th>
<th><strong>(b)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Layered copper hydroxide" /></td>
<td><img src="image" alt="Tunnel akaganeite" /></td>
</tr>
</tbody>
</table>

The structures of (a) a layered copper hydroxide based \((\text{Cu}_2(\text{OH})_3\text{Cl})\) and (b) a tunnel akaganeite based \((\text{FeO(OH,Cl})\) anion exchange material, each with Cl intercalated within the structure.

### 3.1.2 Tunnel structures

Akaganeite, the tetragonal \(\beta\) phase of \(\text{FeOOH}\), consists of double chains of edge-sharing octahedra running parallel to the \(c\) axis, forming a tunnel-like structure\(^{[12]}\). The unit cell formula can be written as \((\text{X, } \text{H}_2\text{O})_2\text{Fe}_8(\text{OOH})_{16}\), where \(\text{X}\) is \(\text{Cl}\) or \(\text{F}\). A certain number of extra framework anions (usually halides) are necessary to balance the extra protonation of oxides in the iron octahedra since synthesis is performed in acidic solution. Akaganeite has an anion capacity of up to 70g kg\(^{-1}\) or 7%
with an average 1.23 chloride per unit cell and 2/3 of tunnels occupied, with respect to chloride. Gallagher\(^{13}\) first predicted the potentially interesting ion-exchange properties of akaganeite in 1970 and this behaviour was further examined by Ellis et al, whereby fluoride was found to replace chloride. Paterson et al. showed that akaganeite had a variable pH-dependent anion-exchange capacity and larger anions, such as perchlorate, could not exchange freely with chloride in the tunnels of akaganeite because of an ion sieve effect\(^{14}\). The anion exchange capabilities of akaganeite is restricted to anions no larger in size than bromide whereby the sequence of exchange capacities is in the order hydroxide > fluoride > chloride > bromide.

3.1.3 Layered hydroxides

Layered hydroxides (LHs) (including layered hydroxysalts (LHS) and layered double hydroxides (LDH)) are a family of layered materials that are related to mineral species that have been attracting increasing amounts of attention over the last 40 years. This is due to their unique structural and physiochemical properties with applications reported in complex hybrid materials, anion exchange reactions and more recently drug delivery agents\(^{15}\). The structure of LHs can be described as deriving from the layered lattice of brucite, Mg(OH)_2, containing positively charge metal hydroxide layers, with charge balancing anions located in the interlayer spacing. Figure 3.3 shows the structure of brucite.

The charge on the layers in LDHs is as a result of partial substitution of trivalent for divalent cations, creating a net positive charge that requires charge balancing anions to be located in the interlayer spacing. In the case of LHSs, the metal cations are restricted to those of the same valency (usually divalent) and so the charge on the layers may be created by two mechanisms. The first mechanism has \(\frac{1}{4} - \frac{1}{2}\) of the hydroxide octahedral sites replaced with an anion held within the interlayer spacing, or water co-ordinated through one of the oxygen atoms to the metals centre and an anion held electro-statically within the interlayer spacing\(^{16}\). Louër et al described structures that create a positive charge in this manner as type I. In the second mechanism, octahedral vacancies are capped above and below by two tetrahedrally coordinated divalent cations, creating a surplus positive charge. Louër et al described these strictures as type II, being further subdivided into either type IIa or type IIb. In the case of type IIb, water molecules are bonded directly to the layers and an anion is electro-statically held in the interlayer spacing whereas in type IIa, water is lost and the anion is directly bonded to the metal cation. LHs have been shown to incorporate anions ranging in size from...
small monovalent anions such as chloride to large monovalent anions such as acetate, divalent anion such as carbonate and even large organic molecules such as a DNA helix. The anion capacity of LHS far exceeds those of tunnel structures with an anion capacity of up to 430 g kg\(^{-1}\) or 43% by mass with respect to chloride \(^{[17]}\).

### 3.1.4 Layered double hydroxides

Layered double hydroxides (LDH) are a class of anion exchangers based on hydrotalcite minerals and their synthetic analogues. Hydrotalcite is a magnesium based LDH that was first discovered in Sweden in 1842 but the exact formula, \([\text{Mg}_6\text{Al}_2(\text{OH})_{16}]\text{(CO}_3\text{)}\text{.4H}_2\text{O}\) was not published until 1915 by Manasse \(^{[16]}\), and further refined in 1942 by Feitknecht \(^{[19]}\). Magnesium cations are located in the centre of an octahedron, surrounded by six hydroxide groups located on the apices. Hydrocalumite is a calcium based LDH of composition \([\text{Ca}_2\text{Al}(\text{OH})_3]\text{(Cl)}\text{.3H}_2\text{O}\) that was first reported in 1934 by Tilley et al \(^{[20]}\). The increased ionic radius of calcium allows extra bonding to one of the intercalated water molecules or anions, resulting in a seven coordinate centre. LDH compounds have the general formulas \([\text{M}_3\text{M}^{3+}(\text{OH})_6]^{z}\text{[X}_1\text{z}\text{]}^{-}\) or \([\text{M}_2\text{M}^{2+}(\text{OH})_6]^{z}\text{[X}_1\text{z}\text{]}^{-}\), whereby \(z\) normally equals 1 and anions reside between the layers and the \(\text{M}^{2+}:\text{M}^{3+}\) ratio can vary. Divalent cations which form similar structures to hydrotalcite and hydrocalumite include \(\text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}\) or \(\text{Zn}^{2+}\), replacing calcium or magnesium, and \(\text{Fe}^{3+}, \text{Ga}^{3+}, \text{Co}^{3+}, \text{Ni}^{3+}, \text{Mn}^{3+}\) or \(\text{Cr}^{3+}\) may replace aluminum. Monovalent cations can also been incorporated in LDHs as shown by Biloen et al \(^{[21]}\), whereby lithium can form similar layered species of composition \([\text{Li}^{+}\text{M}^{3+}(\text{OH})_3]\text{+}\). A great variety of anions have been incorporated into the interlayer spacing from monovalent halides to divalent carbonate or sulphate to large organic anions., however carbonate intercalation is strongly preferred in alkaline solution.

The difference in ionic radius of the two cations maybe up to 0.50 Å and the interlayer spacing large enough that they are able to intercalate large inorganic molecule such as DNA and using this capability, LDHs are able to intercalate drugs such as ibuprofen that are released slowly and so reduce dose frequencies. Table 3.1 summarises these data.

<table>
<thead>
<tr>
<th>Cations</th>
<th>Radii (Å)</th>
<th>Diff (Å)</th>
<th>Cations</th>
<th>Radii (Å)</th>
<th>Diff (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>Al(^{3+}) 0.68</td>
<td>0.51</td>
<td>Zn(^{2+})</td>
<td>Cr(^{3+}) 0.74</td>
<td>0.63</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>Cr(^{2+}) 0.68</td>
<td>0.63</td>
<td>Cu(^{2+})</td>
<td>Cr(^{3+}) 0.72</td>
<td>0.63</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>Al(^{3+}) 1.02</td>
<td>0.51</td>
<td>Zn(^{2+})</td>
<td>Al(^{3+}) 0.74</td>
<td>0.51</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>Cr(^{2+}) 1.02</td>
<td>0.63</td>
<td>Cu(^{2+})</td>
<td>Al(^{3+}) 0.72</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Table 3.1 Examples of double LHSs with cationic radii shown.

Due to the nature of the positive charge on the layers, the incorporation and exchange of anions of varying valency is highly facile whereby carbonate and sulphates have been shown to exchange with nitrates very effectively. LDHs are also extremely stable in high pH solutions up to 13.5. Heating of LDHs above 600 °C converts them to an active mixed oxides, of structures \(\text{M}_2\text{M}^{3+}\text{O}_5\) and \(\text{M}^{2+}\text{O}\) which, upon addition to a solution containing anions, may reform a LDH structure in what is being termed a “memory effect” reaction \(^{[22]}\). LDHs have been shown to be effective anion exchangers, however their inherit susceptibility to carbonate in high pH solutions is a
concern. Since storage ponds are open to the atmosphere they tend to absorb significant quantities of carbon dioxide from the air due to the high alkalinity. There is some concern that if these materials were to be used for the immobilisation of radio anions from water held in a storage pond, contact with carbon dioxide in the air could result in their release into the geosphere.

### 3.1.5 Layered hydroxysalts

Research has shown that several cations including Ca$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Ln$^{3+}$ (Ln = Nd, La, Y, Zn and Gd) can be used as the metal centres in LHS materials. Divalent cation containing layered hydroxysalts (LHSs) can be defined as having either a Cu$_2$(OH)$_3$(NO$_3$)$_2$ type I $M_2$(OH)$_{n}$(X)$_{4-n,y}$H$_2$O ($n = 2$ or $3$, $y = 0$ or $1$), $M_3$(OH)$_{n}$X$_{6-m}$H$_2$O ($n = 4$ or $5$, $m = 0$, $1$ or $2$) or a Zn$_5$(OH)$_8$(NO$_4$)$_2$ type II $M_5$(OH)$_{8}$X$_2$.mH$_2$O structure. Trivalent cation containing LHSs having either a $M$(OH)$_3$X$_{1,m}$H$_2$O ($m = 0$ or $1$) or $M_3$(OH)$_3$(X)$_{3}$H$_2$O structure (Figure 3.4). Although a large number of monovalent anions (F$^-$, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, ClO$_3^-$, BrO$_3^-$, IO$_3^-$, MnO$_4^-$), divalent anions (CO$_3^{2-}$, SO$_4^{2-}$) and large organic anions (acetate, benzoate, dodecasulphate), to name a few, have been reported to intercalate into the interlayer spacing of LHSs, the vast majority have been synthesised using nitrate, acetate or benzoate as the occupying anion. Whilst the brucite like layers remain structurally the same, the interlayer spacing between the layers changes depending on the size and geometry of the occupying anion and the presence of a neutral co-species such as water or ammonia.

![Figure 3.3](image-url) The structures of (a) type I Cu$_2$(OH)$_3$(NO$_3$)$_2$, (b) type IIb Zn$_5$(OH)$_8$(NO$_4$)$_2$.H$_2$O, and (c) type $M$$_{3+}$ La(OH)$_3$(NO$_3$)$_2$.H$_2$O LHS.
3.1.5.1 Type I \((\text{M}_2\text{(OH)}_{n}\text{(X)}_{4-2n}y\text{H}_2\text{O} \text{ and } \text{M}_3\text{(OH)}_{n}\text{(X)}_{6-3n}m\text{H}_2\text{O})\)  structures

The structures of copper, nickel, cobalt and magnesium hydroxysalts, \(\text{M}_2\text{(OH)}_{n}\text{(X)}_{4-2n}y\text{H}_2\text{O}\), are generally considered to be the same, however it is the copper hydroxynitrate modification that has received the most attention and its structure researched in detail \[23\]. \(\text{Cu}_2\text{(OH)}_{3}\text{(NO}_3\text{)}\) was first prepared by the American chemist Charles Frederic Gerhardt via the reaction of copper metal with a nitrate solution in 1845 \[24\]. It wasn’t until 1885 that \(\text{Cu}_2\text{(OH)}_{3}\text{(NO}_3\text{)}\) was discovered to occur naturally as a rare secondary mineral in oxidised portions of copper deposits in the Kabali copper mines in Congo. The natural mineral was named Gerhardtite in honour of Charles F. Gerhardt by Wells et al in 1885 \[25\]. Its structure was then subsequently refined by Nowacki et al in 1952 \[26\] and Oswald et al in 1961 \[27\]. Gerhardtite is a green layered material crystallising with an orthorhombic unit cell in space group \(P\text{2}_1\text{2}_1\text{2}_1\), with lattice parameters \(a = 6.087 \text{ Å}, b = 13.813 \text{ Å}, c = 5.597 \text{ Å}\) \[28\]. Gerhardtite occurs as blue/green masses on cuprite surrounded by a malachite \((\text{Cu}_2\text{(OH)}_{2}\text{(CO}_3\text{)})\) crust and forms when copper oxide is able to react over long periods of time with nitrates from an organic source in the presence of water. Copper hydroxynitrate is also occasionally observed as a product of atmospheric corrosion of copper \[29\], in one example, the patina on copper conductors for railways in the Japanese Alps, Aoyama \[30\] noted that the \(\text{Cu}_2\text{(OH)}_{3}\text{(NO}_3\text{)}\) forms near areas where electrical discharges occur on the conductor.

A second \(\text{Cu}_2\text{(OH)}_{3}\text{(NO}_3\text{)}\) modification was first reported by Effenberger in 1983, as a blue layered structure crystallising with a monoclinic unit cell in space group \(P\text{2}_1\), with lattice parameters \(a = 5.605 \text{ Å}, b = 6.087 \text{ Å}, c = 6.929 \text{ Å}, \beta = 94.29\text{°}\). Effenberger re-examined a sample of synthetic copper hydroxynitrate, thought to be the same orthorhombic phase was that found in Congo, however it was found to be monoclinic with traces of the orthorhombic phase. The monoclinic modification was discovered in 1999 using a sample from the old copper mines in Roua, Aplies-Maritimes, France, and subtly named Roauite. The only difference between the two dimorphs is a shift in every second layer of the orthorhombic phase that causes the \(b\)-axis to double in length due to a slight shift in orientation of the \(\text{NO}_3\) anions \[31\]. The monoclinic and orthorhombic phases are often confused and have very similar XRPD patterns apart from the presence of 2 prominent reflections at \(d\)-spacings 2.74Å and 2.69Å in the orthorhombic form. As well as the synthetic monoclinic copper hydroxynitrate being reported, a new high temperature phase similar in structure to that of the monoclinic form has been reported with a phase transition occurring at 158 °C with a small endothermic energy change of 0.5 KJ mol\(^{-1}\). The high temperature phase has cell dimensions of \(a = 6.0986 \text{ Å}, b = 6.9560 \text{ Å}, c = 5.6132 \text{ Å}, \beta = 92.35 \text{°}\), showing a slight expansion of the overall unit cell due to a slight re-orientation of the \(\text{NO}_3\) anions and a change in hydrogen bonding. Experiments have shown that a pure synthetic monoclinic sample is hard to obtain, therefore it can be assumed that the monoclinic phase is meta-stable. This statement is further justified by the predominance of the orthorhombic phase in the majority of natural copper hydroxynitrate samples. Nitrate groups in the monoclinic form have a constrained orientation due to the presence of symmetry in two O atoms, whereas the orthorhombic form has no symmetry elements. This lack of symmetry means that the O atoms are free from constriction and is the reason for the slight increase in stability; however the energy difference between the two dimorphs is likely to be very small.
Magnesium, cobalt and nickel hydroxynitrates, $\text{M}_2(\text{OH})_3(\text{NO}_3)_n$, are generally considered to have a similar structure to that of copper hydroxynitrate. They have only been prepared synthetically, all crystallising with a hexagonal unit cell, with lattice parameters $a = 3.13 \ \text{Å}$, $c = 6.94 \ \text{Å}$, $a = 3.17 \ \text{Å}$, $c = 6.95 \ \text{Å}$ and $a = 3.13 \ \text{Å}$, $c = 6.94 \ \text{Å}$ respectively. The formation of a hexagonal unit cell is mainly due to a lesser distortion of its octahedral coordination \[32, 33\]. Magnesium, calcium and cobalt hydroxynitrates of structure $\text{M}_2^+\text{(OH)}\text{(NO}_3)\text{.mH}_2\text{O}$ have also been reported. The resulting inter-layer spacing of copper, magnesium and nickel hydroxyl salts are very similar (ca. 6.9Å with respect to nitrate).

$\text{M}_2(\text{OH})_n(\text{X})_{4-n.y}\text{H}_2\text{O}$ exhibits two coordination patterns, both of which show a distorted octahedron with four ligands coordinated via square planar and the other two much further away, namely the coordination is $4 + 2$ (four $\text{OH} + \text{two ONO}$) or $4 + 1 + 1$ (four $\text{OH} + \text{1 ONO} + \text{1 OH}$), with the latter reflecting that shown in the monoclinic phase \[34\]. In both cases, the four planar $\text{OH}$ anions have a bond length of approx 2.2 $\text{Å}$ with the two subsequent bonds that fill the octahedron being longer and unlike normal $\text{M-O}$ bonds.

There has also been considerable interest in the use of layered $\text{Cu}_2(\text{OH})_3(\text{OAc}).\text{H}_2\text{O}$, $a = 5.546 \ \text{Å}$, $b = 6.029 \ \text{Å}$, $c = 9.296 \ \text{Å}$, $\beta = 94.5^\circ$, as an exchange material with structural similarities to that of its nitrate analogue however a water molecule is co-ordinated in the interlayer spacing. Figure 3.5 shows an interlayer spacing of 9.3 $\text{Å}$ is as a result of the larger acetate exchangeable ion and an increase in hydration.

![Figure 3.4](image)

**Figure 3.4** The crystal structure of hydrated copper hydroxyacetate ($\text{Cu}_2(\text{OH})_3(\text{OAc}).\text{H}_2\text{O}$).

Likasite is another copper hydroxynitrate mineral named after the type locality at the Likasi mine, Congo. Its structure, $\text{Cu}_3(\text{OH})_5(\text{NO}_3)_2.2\text{H}_2\text{O}$, was first refined by Effenberger in 1986 \[35\] and found to crystallise with an orthorhombic unit cell in space group Pmmm, with lattice parameters $a = 5.83 \ \text{Å}$, $b = 6.78 \ \text{Å}$, $c = 21.71 \ \text{Å}$. The structures of $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$, $\text{Cd}_3(\text{OH})_5(\text{NO}_3)_2$ and $\text{Ni}_3(\text{OH})_4(\text{NO}_3)_2.2\text{H}_2\text{O}$ also have a layered structure similar to that found in likasite. These structures are derived from the brucite-type structure of $\text{Mg}(\text{OH})_2$ in which the cation occupy octahedral positions and are surrounded by 4 $\text{OH}^-$ and 2 $\text{NO}_3^-$ anions or 5 $\text{OH}^-$ and 1 $\text{NO}_3^-$. In $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$, the $\text{NO}_3^-$
anions are coordinated directly to the M$^{2+}$ cation and linked via hydrogen bonds to OH$^-$ anions of the adjacent layer [36] that crystallises into a monoclinic unit cell, with lattice parameters $a = 7.04$, $b = 6.93$, $c = 11.22$ Å, $\beta = 100.75^\circ$. In Ni$_3$(OH)$_4$(NO$_3$)$_2$, the NO$_3^-$ anions are coordinated directly to the M$^{2+}$ cation and linked via hydrogen bonds to OH$^-$ anions of the adjacent layer [37, 38] that crystallises in a monoclinic unit cell with lattice parameters $a = 7.04$, $b = 6.93$, $c = 11.22$ Å, $\beta = 100.75^\circ$.

### 3.1.5.2 Type II $M_6$(OH)$_8$(X)$_2$.mH$_2$O structures

Zn$_5$(OH)$_8$(NO$_3$)$_2$.2H$_2$O is a type IIb LHS that consists of brucite like layers that crystallises in a monoclinic unit cell, space group C2/m, with lattice parameters $a = 19.48$, $b = 6.23$ c = 5.51Å, $\beta = 93.28^\circ$ [39]. The structure consists of zinc atoms located in both tetrahedral and octahedral coordination, in the ratio 2:3. Layers of octahedral zinc atoms are surrounded by 6 hydroxide groups. One quarter of the octahedral sites are vacant with Zn atoms tetrahedrally co-ordinated by hydroxide groups above and below the vacant doctoral site, forming the base of a tetrahedron with a water molecule occupying the apex and unbound nitrate groups located between the layers, giving an interlayer spacing of 9.72 Å. The average tetrahedral Zn-O distance of 1.95Å is significantly shorter than that of the octahedral Zn-O bond length of 2.13Å.

The anhydrous type IIa Zn$_6$(OH)$_8$(NO$_3$)$_2$ is obtained via heating the hydrated form to 80°C and has a structure similar to that of the hydrous form, however the water molecules are replaced by nitrate anions that now directly co-ordinate to the metal centre [40, 41] and the interlayer spacing is reduced.

### 3.1.5.3 Type $M^+$ M(OH)$_3$(X)$_n$.mH$_2$O (m = 0 or 1) and $M^3+$(OH)$_5$(X)$_m$.mH$_2$O structures

Lanthanides have primarily been used in the synthesis of LHSs containing trivalent cations using both nitrate and acetate as the anion. The structures of Ln$^{3+}$(OH)$_2$NO$_3$.H$_2$O (Ln = Nd, La, Y, Zn and Gd) crystallises into a monoclinic unit cell, space group C2/m, with lattice parameters $a = 21.19$, $b = 3.98$ c = 6.39Å, $\beta = 114.14$. and the anhydrous form Ln(OH)$_2$NO$_3$ are have been shown to consist of layers of nine Ln atoms arranged into a polyhedron of tri-capped trigonal prisms, with the nitrate anions attached directly to the cation in an approximately perpendicular orientation with respect to the layers [42]. In the hydrated phase, the nitrate group acts as a unidentate ligand and a water molecule is linked to one Ln. Removal of a water molecule leaves an empty site for coordination to the Ln atoms. A new tricapped trigonal prism can then be formed by a change in the coordination of the nitrate groups; i.e., one of the non-bonded nitrate oxygen atoms fills the active empty site of the coordination sphere of La and the nitrate group acts as a bidentate ligand. A second family of lanthanide hydroxynitrates of composition $M^3+$$_2$(OH)$_5$(X)$_m$.mH$_2$O have been prepared that crystallise into an orthorhombic unit cell with lattice parameters of approximately $a = 6.0$ Å, $b = 3.8$ Å and $c = 8.5$ Å.

### 3.1.5.4 Layered double salts

Layered double salts (LDS) are LHSs with two divalent or two trivalent cations incorporated into the same crystal structure. The incorporation of two difference cations into the same structure can only be achieved if the difference in ionic radius of the two cations is no greater than 0.05Å [43] (Table 3.2). It is also noted that Ni, Cu and Co maybe freely incorporated into a type I structure at varying stoichiometries, however the incorporation of Zn into a type I structure may only be achieve up
¼ substitution. With substitution greater than one quarter, a type II Zn LHS forms. Furthermore, no incorporation of Cu, Cu, Co or Mg in a type II Zn LHS has been reported.

<table>
<thead>
<tr>
<th>Cations</th>
<th>Radii (Å)</th>
<th>Diff (Å)</th>
<th>Cations</th>
<th>Radii (Å)</th>
<th>Diff (Å)</th>
</tr>
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<td>0.72</td>
<td>Zn(^{2+})</td>
<td>0.74</td>
<td>0.66</td>
</tr>
<tr>
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<td>0.69</td>
<td>Cu(^{2+})</td>
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<td>0.99</td>
</tr>
<tr>
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<td>0.72</td>
<td>Ni(^{2+})</td>
<td>0.69</td>
<td>0.99</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
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<td>0.72</td>
<td>Ca(^{2+})</td>
<td>0.69</td>
<td>0.99</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
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<td>0.72</td>
<td>Mg(^{2+})</td>
<td>0.72</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Table 3.2 Known layered double salts (left) with an ionic radius difference of < 0.05 Å and unknown layered double salts (right) with an ionic radius of > 0.05 Å.

An example of a mixed phase LDS is Cu/Zn hydroxynitrate that has been synthesised. It has a monoclinic structure similar to that of copper hydroxynitrate, with a unit cell parameters, a = 5.536 Å, b = 6.141 Å, c = 9.447 Å, β = 94.46°. The exact stoichiometry, determined by wet chemical analysis, showed a formula of Cu\(_{1.6}\)Zn\(_{0.4}\)(NO\(_3\))(OH)\(_3\).

### 3.1.6 Diffraction and spectroscopic studies of LHSs

Figure 3.5 shows that in a typical diffraction pattern, the basal spacing reflection may be used to determine the interlayer spacing of a given LHS. The observed interlayer spacing in type II Zn\(_5\)(OH)\(_6\)(NO\(_3\))\(_2\)•2H\(_2\)O and type M\(^{3+}\) Ln(OH)\(_2\)(NO\(_3\))•H\(_2\)O structures are 9.72 Å and 9.66Å respectively, which is approximately 1 Å larger than the interlayer spacing observed for a LDHs containing occupying nitrate anions. In the case of zinc, the difference is primarily due to the increased thickness of the hydroxide layers in the zinc hydroxide salt and that the nitrate anions are not directly bonded to the layers and adopt an approximately perpendicular orientation with respect to the hydroxide layers. An increased interlayer spacing observed in the lanthanide LHS is due to thicker La(OH)\(^{2+}\) layers than those observed in brucite-like layers of LDHs. The observed interlayer spacing of 6.91 Å for type I copper, magnesium, cadmium, cobalt and nickel based LHSs is approximately 1.5 Å smaller than the interlayer spacing generally observed for a LDH containing interlayer nitrate anions. This reduction is primarily due to the fact that in these hydroxide salts the nitrate anions directly coordinate to the cations within the brucite-like layers.
Figure 3.5 The XRPD pattern of Cu$_2$(OH)$_3$Br whereby the position of the basal spacing (*1) reflection at 14.1° 2θ for monochromatic copper radiation equates to an interlayer spacing of 6.32 Å (*2).

All LHSs show a strong and broad IR absorption at approximately 3500 cm$^{-1}$ due to OH stretching vibration. Dehydrated phases display two distinct OH stretching vibrations attributed to the terminal and bridging OH groups present in the brucite like layers, whereas hydrated phases tend to show a broader OH stretching vibration region due to the presence of hydrogen bonded water in the inter-layer spacing. Layered hydroxynitrates where the nitrate is uncoordinated, such as Zn$_5$(OH)$_6$(NO$_3$)$_2$.2H$_2$O, show a single absorption band at approximately 1380 cm$^{-1}$ which is characteristic of an ionic nitrate group, NO$_3^-$, of symmetry D$_{3h}$. For layered hydroxynitrates in which the nitrate group is coordinated to the metal cation via a M-O bond, the symmetry is lowered to C$_{2v}$ and extra absorption bands are observed in the region between 900 to 1600 cm$^{-1}$. Asymmetric and symmetric NO$_2$ stretching bands are observed in the region from approximately 1425 to 1500 cm$^{-1}$ and 1315 to 1350 cm$^{-1}$.
Table 3.3 Expected IR absorption bands of several LHSs.

The general trend observed is that as the splitting of the asymmetric and symmetric bands increase, the strength of the nitrate bond to the corresponding metal cation also increases. This general trend is also confirmed by the lowering of an absorption band attributed to the N-O stretching vibration. It has been shown that N-O stretching vibrations ranged from 1050 cm\(^{-1}\) for ionic bonded (uncoordinated) nitrate to 850 cm\(^{-1}\) for covalently bonded (coordinated) nitrate containing compounds. Therefore an increased asymmetric – symmetric splitting of the NO\(_2\) stretching band is concomitant with a decreased N-O stretch, indicating the nitrate group is more strongly bound to the metal cation\(^{44}\).

Layered hydroxyl carboxylate compounds show two carboxylate bands absorption bands in the region between 1400 cm\(^{-1}\) to 1610 cm\(^{-1}\) with a splitting difference of approximately 150 cm\(^{-1}\). The observed difference is often too small for monodentate coordination, however structure determination showed that the carboxylate ions coordinate to copper by only one oxygen atom \(^{[22]}\) and, in the same study, the authors suggested the presence of a hydrogen bond between the free oxygen in the grafted carboxylate and a neighbouring hydroxyl group.

3.1.7 Synthesis and stability of LHSs

There have been several routes reported for the synthesis of LHSs that can be categorised into either hydrolysis, precipitate from a base or digestion.

A “toluene” hydrolysis method involves evaporation of a water/toluene azeotropic mixture containing the relevant metal salt using a distillation setup followed by evaporation using a dean-stark setup. This method has only been reported successful in the synthesis of copper hydroxynitrate. A “oven” hydrolysis method involves dissolving a relevant metal salt in the minimal amount of water and then placing the solution into an oven at predetermined temperature for up to 2 days. This method has been reported successful using a variety of cations (including LDSs) with nitrate as the occupying anion, however only copper based LHSs have been reported with acetate as the occupying anion \(^{[45, 46, 47]}\).

A “titration” precipitation from base method involves precipitation of the desired insoluble layered material via the titration of a base against a solution of the parent salt. This method is
generally favoured in the synthesis of acetate analogues; however this procedure has also be reported successful in the synthesis of nitrate analogues. The OH/M$^{2+}$ ratio must not exceed 1 as it is noted that an excess of base results in the formation of M$^{2+}$O or M$^{2+}$(OH)$_2$ that, like the desired product, are also insoluble and therefore unwanted as an impurity. This method has been reported successful for a range of divalent LHSs and double layered salts, however in the synthesis of nickel and magnesium based materials, a temperature of 100$^\circ$C is needed during titration with Ni analogues requiring further hydrothermal treatment at 220$^\circ$C for 18h in order to improve the crystallinity. Lanthanide containing hydroxy salts have also been reported successfully using the precipitation method however due to the La$^{3+}$ cation, the synthesis requires a OH:La ratio of 2 and a reaction temperature of 65$^\circ$C is needed [48].

“Digestion” of a metal oxide (M$^{x+}$O$^{x/2}$) in a parent salt (M$^{x+}$(NO$_3$/OAc)$_{x,y}$H$_2$O) solution at room temperature mimics the conditions necessary for the formation of LHSs in nature. Although results using a “digestion” method have been reported successful for a wide variety of layered hydroxynitrates, all reactions except those involving copper and zinc, take longer than 20 days to go to completion [49, 50]. An “autoclave” method involves the digestion of either metal dust or its oxide by a parent nitrate solution contained within a Teflon lined autoclave. Due to the closed system afforded by the autoclave, the reaction temperature can be increased above the normal decomposition of the target layered hydroxynitrate.

A general trend is observed in that as the charge density of a metal increases, the decomposition temperature of its corresponding LHS also increases [51]. The strength of the NO$_2$-O-M (in nitrate) or Ac-O-M (in acetate) bond is directly responsible for the thermal stability of the LHS. This may occur as a result of two main factors, the first through polarisation of the electron cloud of the anion by the charge density on the metal cation and secondly via back-donation of the anion electron cloud to a vacant d-orbitals of the metal ion. Zinc(II) has the highest charge density of the metals under investigation followed by copper(II). However, copper(II) has a partially filled d-orbital and therefore can accept electron density from an anion, which in turn will act to weaken the M–O bond [52]. For this reason, the decomposition temperatures of the copper and zinc hydroxy salts are not very different despite the large differences in charge density. This influence of the partially vacant d-orbitals is also shown in magnesium and nickel LH nitrates. Nickel and magnesium have similar charge densities however nickel hydroxynitrate decomposes at a much lower temperature than magnesium hydroxynitrate because nickel has available low-energy d-orbitals [53]. This in turn defines the maximum temperature at which synthesis of the LHSs occurs and can also help in determining the optimum temperature of synthesis for new layered materials. Temperature dependent reactions are generally used to synthesise layered hydroxynitrate and double layered nitrate salts, however due to the instability of the corresponding acetates analogues past 100$^\circ$C, hydroxyacetates and double layered acetate salts tend to be synthesised using room temperature methods [54].
Table 3.4 Relationship between charge density of a metal cation and decomposition temperature of its corresponding LHS \[43\].

The thermal decomposition of LHSs in oxygen differs depending on the Louër structure type, hydration and occupying anion. In type I and type \(M^{3+}\) structures, dehydration of intercalated water, if applicable, occurs from 80°C to 120°C. Single step decomposition of an anhydrous LHS is initiated via de-hydroxylation followed by cleavage of the X-O bond in X-O-M (typical in nitrates, organics and oxyhalides), in the presence of oxygen. In halide containing LHSs, two distinct weight losses are observed. De-hydroxylation occurs first forming MO and MO.MHa2. Due to an increased strength of the M-Ha bond, cleavage of this bond occurs at a higher temperature (Equation 3.2) \[55\]. LHSs containing a trivalent cation decompose in a similar fashion to type 1 LHSs.

\[
\text{Type I} \\
X - O - M \quad 2M_2(OH)_3(X-O)H_2O(a) \rightarrow 2M_2(OH)_3(X-O)(s) + H_2O(g) \\
\quad 2M_2(OH)_3(X-O)(s) + \frac{1}{2}O_2(g) \rightarrow 4MO(s) + X(g) + 3H_2O(g) \\
\text{Ha - M} \quad 2M_2(OH)_3Ha(s) \rightarrow 2MO(s) + MO.MHa_2(s) + 3H_2O(g) \\
\quad 2MO(s) + MO.MHa_2(s) + \frac{1}{2}O_2(g) \rightarrow 4MO(s) + Ha_2(g)
\]

\[
\text{Type } M^{3+} \\
X - O - M \quad 2M(X-O)(OH)_2H_2O(s) \rightarrow 2M(X)(OH)_2(s) + 2H_2O(l) \\
\quad 2M(X-O)(OH)_2(s) + \frac{1}{2}O_2(g) \rightarrow M_2O_3(s) + X(g) + H_2O(g) \\
\text{Ha – M} \quad 2M(OH)_2Ha(s) \rightarrow MO(s) + MHa_2(s) + 2H_2O(l) \\
\quad 2MO(s) + MO.MHa_2(s) + \frac{1}{2}O_2(g) \rightarrow 4MO(s) + Ha_2(g)
\]

Equation 3.2 Thermal decomposition of type I and type \(M^{3+}\) LHSs.

Decomposition in Type II structures is initiated by loss of an intercalated water molecule. LHSs containing a X-O bond decompose in two clear steps. The first step involves removal of the \([M^{3+}(H_2O)]^2\) layers located above and below the \([M_3^{oct}(OH)_3]^2\) layer, followed by de-hydroxylation to \(M_3(OH)_4(XO)_2\). The second step occurs in a similar fashion to the single step decomposition observed in type I LHSs. Halide containing type II LHSs decompose in 3 defined steps. The first steps occurs
in the same way as type X-O containing type LHSs, this is then followed by de-hydroxylation and loss of the halide in the same way as type I LHSs (equation 3.3.)

**Type II**

\[
\begin{align*}
X - O - M & \rightarrow M_5(OH)_8(M-O)_{2s} + 2H_2O_{(g)} \\
M_5(OH)_8(X-O)_{2s} & \rightarrow M_3(OH)_4(M-O)_{2s} + 2MO_{(s)} + 2H_2O_{(g)} \\
M_3(OH)_4(X-O)_{2s} + 2MO_{(s)} + \frac{1}{2}O_2_{(g)} & \rightarrow 5MO_{(s)} + 2X_{(g)} + 2H_2O_{(g)} \\
Ha - M & \rightarrow M_3(OH)_4(Ha)_{2s} + 2MO_{(s)} + 2H_2O_{(g)} \\
M_3(OH)_4(Ha)_{2s} & \rightarrow MO_{(s)} + MO.MHa_{2s} + 2H_2O_{(g)} \\
MO_{(s)} + MO.MHa_{2s} + \frac{1}{2}O_2_{(g)} & \rightarrow 3 MO_{(s)} + Ha_{2g}
\end{align*}
\]

Equation 3.3 Thermal decomposition of type II LHSs.

### 3.2 Synthesis of LHSs

The reproducibility of exchange reactions involving LHSs has not been consistent. This may be due to phase impurities that hinder the exchange abilities of the target materials. In this section, attempts at a pure phase synthesis of LHSs will be investigated and the pure products used in later anion exchange reaction in order to determine the effect of phase impurities. This is especially true of copper hydroxynitrate that exists in two forms, monoclinic and orthorhombic. It is thought that orthorhombic impurities of the synthetic monoclinic phase may hinder its exchange capacity. There will also be an interest in the synthesis of other LHSs such as zinc, magnesium, cobalt and manganese hydroxynitrate, however previous reports have shown these products hard to obtain, either due to a high reaction temperature (over 300ºC) or a prolonged reaction time (over 20 days) [56].

LHSs containing copper, zinc, nickel, lanthanum, manganese, cobalt and manganese hydroxide positive layers with both nitrate and acetate are investigated. Several modifications to the structure of all metals mentioned have been reported, so this chapter aims to investigate several techniques and determine which structures are synthesised, and to see if any clear patterns exist.

#### 3.2.1 Experimental

5 techniques have been used to synthesise nitrate analogues of copper, zinc, lanthanum, manganese and cobalt modifications, whereas 1 technique was used to synthesise the acetate analogues. In all cases, a powder product was filtered under suction, washed twice with deionised water (50ml) and once with acetone (10 ml) to remove any impurities, and oven dried at 50ºC

##### 3.2.1.1 “Toluene” method

A solution of $M^{2+}(X)_2$ or $M^{3+}(X)_3$ ($X = NO_3$ or OAc) (0.1M, 250ml) contained within a round bottom flask (RBF) was attached to a distillation apparatus and heated using an oil bath and hotplate. Nitrates were heated at 120ºC and acetates at 50ºC. The solution was heated until all the water had evaporated off leaving a powder. Toluene (100ml) was added to the RBF, the resulting solution refluxed for 3 hours and then the toluene/water azeotrope fully evaporated off. A further portion of toluene (100ml) was added and the resulting solution taken to complete dryness using a dean-stark
apparatus. This method was used in the synthesis of Cu, Zn, Ni, Co, Mn and La based LHSs including both nitrate and acetate analogues (Table 3.5).

<table>
<thead>
<tr>
<th>Parent salt</th>
<th>Colour of product</th>
<th>Parent salt</th>
<th>Colour of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NO)(_2)(_3H_2O)</td>
<td>Green</td>
<td>Cu(OAc)(_2)(_2H_2O)</td>
<td>Black</td>
</tr>
<tr>
<td>Zn(NO)(_2)(_6H_2O)</td>
<td>White</td>
<td>Zn(OAc)(_2)(_2H_2O)</td>
<td>White</td>
</tr>
<tr>
<td>Ni(NO)(_2)(_6H_2O)</td>
<td>None</td>
<td>Ni(OAc)(_2)(_4H_2O)</td>
<td>No product</td>
</tr>
<tr>
<td>Co(NO)(_2)(_6H_2O)</td>
<td>None</td>
<td>Co(OAc)(_2)(_4H_2O)</td>
<td>Dark blue</td>
</tr>
<tr>
<td>Mn(NO)(_2)(_4H_2O)</td>
<td>Pink</td>
<td>Mn(OAc)(_2)(_4H_2O)</td>
<td>Dark green</td>
</tr>
<tr>
<td>La(NO)(_3)(_3)(_6H_2O)</td>
<td>None</td>
<td>La(OAc)(_3)(_2H_2O)</td>
<td>White</td>
</tr>
</tbody>
</table>

Table 3.5 A summary of the parent salts used and products recovered using the toluene method.

3.2.1.2 “Oven” method

M\(^{2+}\)(X)\(_2\).\(_nH_2O\) or M\(^{3+}\)(X)\(_3\).\(_mH_2O\) (X = NO\(_3\) or OAc) (1g) was added to a 50ml crucible and dissolved in the minimum amount of de-ionised water. The crucible was then placed into an oven at the appropriate temperature for 2 days until the water had completely evaporated. A further portion of de-ionised water (25m) was added to the crucible and the resulting suspension heated for a further 2 days until the water had completely evaporated. This method was used in the synthesis of Cu, Zn, Ni, Co, Mn and La based LHSs including both nitrate and acetate analogues (Table 3.6).

<table>
<thead>
<tr>
<th>Parent salt</th>
<th>Colour of product</th>
<th>Temp (°C)</th>
<th>Parent salt</th>
<th>Colour of product</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NO)(_2)(_3H_2O)</td>
<td>Blue</td>
<td>170</td>
<td>Cu(OAc)(_2)(_2H_2O)</td>
<td>No product</td>
<td>170</td>
</tr>
<tr>
<td>Zn(NO)(_2)(_6H_2O)</td>
<td>White</td>
<td>180</td>
<td>Zn(OAc)(_2)(_2H_2O)</td>
<td>No product</td>
<td>170</td>
</tr>
<tr>
<td>Ni(NO)(_2)(_6H_2O)</td>
<td>Green</td>
<td>220</td>
<td>Ni(OAc)(_2)(_4H_2O)</td>
<td>No product</td>
<td>200</td>
</tr>
<tr>
<td>Co(NO)(_2)(_6H_2O)</td>
<td>Blue</td>
<td>220</td>
<td>Co(OAc)(_2)(_4H_2O)</td>
<td>No product</td>
<td>200</td>
</tr>
<tr>
<td>Mn(NO)(_2)(_4H_2O)</td>
<td>Pink</td>
<td>170</td>
<td>Mn(OAc)(_2)(_4H_2O)</td>
<td>No product</td>
<td>200</td>
</tr>
<tr>
<td>La(NO)(_3)(_3)(_6H_2O)</td>
<td>White</td>
<td>190</td>
<td>La(OAc)(_3)(_2H_2O)</td>
<td>No product</td>
<td>190</td>
</tr>
</tbody>
</table>

Table 3.6 A summary of the parent salts used, temperatures used and products recovered using the crude method.

3.2.1.3 “Titration” method

A solution of NaOH (0.1M) was added drop wise and under stirring to a solution of M\(^{2+}\)(X)\(_2\) or M\(^{3+}\)(NO\(_3\))\(_3\) (0.1 M, 1000ml) until a OH\(^-\): M\(^{2+}\) ratio of 1 or a OH\(^-\): M\(^{3+}\) ratio of 2 was reached, in a nitrogen atmosphere. The solution was stirred and heated (depending on the cation) for a further 24 hours as a suspension was formed. This method was used in the synthesis of Cu, Zn, Ni, Co, Mn and La based LHSs including both nitrate and acetate analogues (Table 3.7).


### Table 3.7
A summary of the parent salts used, temperatures used and products recovered using the titration method.

<table>
<thead>
<tr>
<th>Parent salt</th>
<th>Colour of product</th>
<th>Temp (°C)</th>
<th>Parent salt</th>
<th>Colour of product</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NO)₂.3H₂O</td>
<td>Blue</td>
<td>Ambient</td>
<td>Cu(OAc)₂.2H₂O</td>
<td>No product</td>
<td>Ambient</td>
</tr>
<tr>
<td>Zn(NO)₂.6H₂O</td>
<td>White</td>
<td>Ambient</td>
<td>Zn(OAc)₂.2H₂O</td>
<td>No product</td>
<td>Ambient</td>
</tr>
<tr>
<td>Ni(NO)₂.6H₂O</td>
<td>Green</td>
<td>100</td>
<td>Ni(OAc)₂.4H₂O</td>
<td>No product</td>
<td>50</td>
</tr>
<tr>
<td>Co(NO)₂.6H₂O</td>
<td>Blue</td>
<td>Ambient</td>
<td>Co(OAc)₂.4H₂O</td>
<td>No product</td>
<td>Ambient</td>
</tr>
<tr>
<td>Mn(NO)₂.4H₂O</td>
<td>Pink</td>
<td>Ambient</td>
<td>Mn(OAc)₂.4H₂O</td>
<td>No product</td>
<td>Ambient</td>
</tr>
<tr>
<td>La(NO₃)₃.6H₂O</td>
<td>White</td>
<td>65</td>
<td>La(OAc)₃.6H₂O</td>
<td>No product</td>
<td>50</td>
</tr>
</tbody>
</table>

3.2.1.4 “Digestion” method

M²⁺O (0.025 mols) was dispersed into a solution of M²⁺(NO₃)₂ₙH₂O (0.25M, 200ml) contained within a crucible to give a M²⁺(NO₃)₂ₙH₂O:M²⁺O: ratio of 2. The suspension was then stirred for 20 days to allow full digestion of the metal oxide powder. This method was used in the synthesis of Cu and Zn based LHSs including both nitrate and acetate analogues (Table 3.8).

### Table 3.8
A summary of the parent salts / oxides used and products recovered using the digestion method.

<table>
<thead>
<tr>
<th>Parent salt and oxide</th>
<th>Colour of product</th>
<th>Parent salt and oxide</th>
<th>Colour of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NO)₂.3H₂O / CuO</td>
<td>Dark Blue</td>
<td>Cu(OAc)₂.2H₂O / CuO</td>
<td>Black</td>
</tr>
<tr>
<td>Zn(NO)₂.6H₂O / ZnO</td>
<td>White</td>
<td>Zn(OAc)₂.2H₂O / ZnO</td>
<td>White</td>
</tr>
<tr>
<td>Ni(NO)₂.6H₂O / NiO</td>
<td>Light green</td>
<td>Ni(OAc)₂.4H₂O / NiO</td>
<td>Light green</td>
</tr>
<tr>
<td>La(NO₃)₃.6H₂O / La₂O₃</td>
<td>White</td>
<td>La(OAc)₃.6H₂O / La₂O₃</td>
<td>White</td>
</tr>
</tbody>
</table>

3.2.1.5 “Autoclave” method

M²⁺ or M³⁺ metal dust (0.02mols) was dispersed in a saturated solution of M²⁺(X)₂ or M³⁺(X)₂ contained within a 20ml Teflon-lined autoclave. The sealed autoclave was then placed in an oven at 220°C for 2 days. This method was used in the synthesis of Cu, Zn, Ni, Co, Mn and La based LHSs including both nitrate and acetate analogues (Table 3.9).
<table>
<thead>
<tr>
<th>Parent salt and metal / metal oxide</th>
<th>Colour of powder</th>
<th>Parent salt and metal / metal oxide</th>
<th>Colour of powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NO)(_2)(_3)H(_2)O / Cu</td>
<td>Blue</td>
<td>Cu(OAc)(_2)(_2)H(_2)O / Cu</td>
<td>Black</td>
</tr>
<tr>
<td>Zn(NO)(_2)(_3)H(_2)O / Zn</td>
<td>White</td>
<td>Zn(OAc)(_2)(_2)H(_2)O / Zn</td>
<td>White</td>
</tr>
<tr>
<td>Ni(NO)(_2)(_3)H(_2)O / NiO</td>
<td>Light Green</td>
<td>Ni(OAc)(_2)(_2)H(_2)O / NiO</td>
<td>Dark Green</td>
</tr>
<tr>
<td>Co(NO)(_2)(_3)H(_2)O / COO</td>
<td>Blue</td>
<td>Co(OAc)(_2)(_2)H(_2)O / CoO</td>
<td>Black</td>
</tr>
<tr>
<td>Mn(NO)(_2)(_3)H(_2)O / MnO</td>
<td>Pink</td>
<td>Mn(OAc)(_2)(_2)H(_2)O / MnO</td>
<td>Dark green</td>
</tr>
<tr>
<td>La(NO(_3)(_3)(_3)H(_2)O / La</td>
<td>White</td>
<td>La(OAc)(_2)(_2)H(_2)O / La</td>
<td>White</td>
</tr>
</tbody>
</table>

Table 3.9 A summary of the parent salts / oxides used and products recovered using the autoclave method.

3.2.1.6 Characterisation

XRPD patterns and elemental analysis data were collected as previously described in chapter 2. XRPD patterns were collected from 5 - 55º 2θ with a step size of 0.014º, and patterns used for phase identification and to determine whether a change in the interlayer spacing occurred. Elemental analysis was used as a quantitative method to determine the amount of nitrate and acetate located within the interlayer spacing post exposure to a salt solution.

3.2.2 Results

3.2.2.1 Copper hydroxynitrate

A reflection at 12.99° 2θ is present in the diffraction pattern of all samples recovered. This indicates the formation of Cu\(_2\)HN with an interlayer spacing of 6.81 Å. Both monoclinic and orthorhombic Cu\(_2\)HN phases are present in samples obtained using hydrolysis and titration methods. The relative intensities of the reflections of the orthorhombic phase relative to those in the monoclinic phase are large enough to indicate a distinct presence of the orthorhombic phase within a majority monoclinic phase. The observed reflections are broad; this is due to the mixture of the two phases resulting in the overlap of two very similar diffraction patterns (Figure 3.6).

There is a slight sharpening of reflections observed in the diffraction pattern when using the oven method is used compared to the toluene method; however this is to be expected as the synthesis is carried out at a higher temperature which will increase crystallinity. When using the titration method, it can be seen that reflections indicating the presence of the orthorhombic phase are present, however relative to the intensity of reflections observed using hydrolysis methods, there is a distinct progression towards single monoclinic phase purity. The reflections observed in the material formed using the titration method are broader than those found using the hydrothermal routes, possibly due to synthesis at an ambient temperature. Previous reports have suggested that a strictly controlled OH/M ratio along with vigorous stirring and slow titration of the sodium hydroxide are vital in the reduction in MO and/or M(OH)\(_2\) formation. This was confirmed in earlier synthetic attempts whereby any titration speed of over 1 drop per second and a reduction in the volume of reaction medium (water) resulted in the formation of CuO and Cu(OH)\(_2\) impurities.
When considering the final two methods, it can be seen that there is a complete absence of any orthorhombic phase when using either the digestion method or the autoclave method. However, when copper hydroxynitrate was synthesised using the digestion at ambient temperature, even after 20 days there are still reflections indicating the presence of un-reacted CuO. The autoclave method...
produced sharp reflections indicating a crystalline product and single phase purity after just 1 day. The relative intensity of the basal spacing reflections (001) to others in the pattern generated from the sample using the autoclave method indicated the presence of some preferred orientation. This is probably expected since autoclaves are used to generate large crystals for single crystal studies and the product of the autoclave reactions are platy crystals. Interestingly, there is no trace of the mineral malachite present in any of the XRPD samples, indicating low carbonate content. It has previously been reported that atmospheric CO₂ that has been absorbed into a basic solution can inhibit the formation of layered material with incorporation of the carbonate anion in itself into the target structure.

Although the XRPD patterns seem to indicate that no carbonate phases are present in the sample, elemental analysis was used to confirm this observation (Table 3.10). If carbonate is replacing nitrate within the interlayer spacing, it can be expected that as the % C increases, the % N will decrease. This is due to a single atmospheric carbonate anion for every two nitrate anions being incorporated into the structure. When analysing the product of the toluene method, an extremely high % C (4.37) is observed, however the % N also remains relatively high (5.04) along with a higher than expected % H (1.31) (though the acceptable error on hydrogen analysis is in the order of 0.5%).

The XRPD pattern of the product indicates the presence of orthorhombic and monoclinic modifications only, therefore the high % C must be due to either the formation of an amorphous malachite-like phase during synthesis, and/or the toluene reaction medium interacting with copper hydroxynitrate. Further reactions in an inert nitrogen atmosphere presented little difference in the % C observed and so it can be assumed that there is a distinct toluene interaction. A carbon content of 0.25% in Cu₂HN recovered using the titration method is slightly higher than that found in the oven method (0.17 %) and digestion method (0.19 %). All three methods have different contributing factors that may encourage a higher % C. A high pH environment in the titration method, increased reaction time of 10 days in the digestion method and a higher temperature in the oven method most likely increase the formation of carbonate in solution. A lower carbon content of 0.05% is observed when using the bomb method. This is most likely due to the short reaction time and closed reaction vessel, consequently reducing the amount of carbonate present in solution. Despite subtle differences in carbon content between methodologies, values of 0.25 % and lower represent a very low value indicating that carbonate interference is minimal. The lower nitrogen content observed using oven, titration and toluene methods are as expected and correspond to the higher % C. A low nitrogen content observed using the digestion method is attributable to the presence of unreacted CuO, as confirmed by XRPD analysis. The bomb method yielded a lower than expected % N, despite a lower % C, indicating nitrate content is 0.72% less than expected. XRPD does not show the presence of any impurities and a low hydrogen content suggests that an increase in hydroxide stoichiometry is not the cause. The most likely impurity is the presence of an amorphous CuO phase.
Table 3.10  Elemental analysis of products recovered in the synthesis of copper hydroxynitrate. Approximate variation 0.2% C and N, 0.5% H.

<table>
<thead>
<tr>
<th>Method</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Structure</td>
<td>0.00</td>
<td>1.26</td>
<td>5.83</td>
</tr>
<tr>
<td>Toluene method</td>
<td>4.37</td>
<td>1.31</td>
<td>5.04</td>
</tr>
<tr>
<td>Oven method</td>
<td>0.17</td>
<td>1.13</td>
<td>5.31</td>
</tr>
<tr>
<td>Titration method</td>
<td>0.25</td>
<td>1.16</td>
<td>5.48</td>
</tr>
<tr>
<td>Digestion method</td>
<td>0.19</td>
<td>1.02</td>
<td>4.98</td>
</tr>
<tr>
<td>Bomb method</td>
<td>0.05</td>
<td>1.11</td>
<td>5.11</td>
</tr>
</tbody>
</table>

Previous literature has reported all the methods trialled successful in synthesising copper hydroxynitrate. There is a large amount of debate to whether the monoclinic phase is a meta-stable form, a high temperature form or purely synthetic form. Analysing the XRPD patterns and quantitative data obtained, it can be seen that only the autoclave method produces Cu$_2$HN that is purely single phase monoclinic with no orthorhombic or CuO impurities. The digestion method did produce the desired monoclinic phase however even after 10 days of reaction time; there was unreacted copper oxide still present. The autoclave method is effectively the same as the digestion method however using a sealed reaction vessel at a high temperature and pressure increases the rate of the reaction. The decomposition of copper hydroxynitrate starts to occur at around 170°C which is well below the temperature used in the bomb method, however due to the sealed reaction vessel, NO$_x$ is unable to escape and so the copper hydroxynitrate is stable. Increasing the temperature past the normal decomposition point in the bomb method markedly increases the crystallinity of the copper hydroxynitrate and SEM images show regular shaped particles that are smaller in size than those found when using other methods (Figure 3.7).

Figure 3.7  SEM images of copper hydroxynitrate.

When analysing the reason for the phase purity observed in digestion methods, temperature does not seem to be the determining factor. Precipitating Cu$_2$HN from a parent salt solution (as in the hydrolysis techniques) results in the formation of nitric acid. The amount of nitric acid produced when
copper hydroxynitrate is precipitated in the presence of a base is reduced, however excess nitrate anions are still present in solution along with sodium cations. Precipitation in the presence of a metal/metal oxide reduces both acidity and excess nitrate anions as shown in equation 3.2. These observations suggest an increase in acidity and excess nitrate anions promote the formation of the orthorhombic phase.

\[
\text{Hydrolysis} \quad 2\text{Cu(NO}_3\text{)}_2 + 3\text{H}_2\text{O} \rightarrow \text{Cu}_2\text{(OH)}_3(\text{NO}_3) + 3\text{HNO}_3
\]

\[
\text{Titration} \quad 2\text{Cu(NO}_3\text{)}_2 + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{(OH)}_3(\text{NO}_3) + \text{HNO}_3 + 2\text{NaNO}_3
\]

\[
\text{Digestion} \quad \text{Cu(NO}_3\text{)}_2 + \text{CuO} + 2\text{H}_2\text{O} \rightarrow \text{Cu}_2\text{(OH)}_3(\text{NO}_3) + \text{HNO}_3
\]

**Equation 3.4**  Reaction schemes using hydrolysis, titration and digestion techniques.

### 3.2.2.2 Zinc hydroxynitrate

From the XRPD patterns it is clear that a pure sample of zinc hydroxynitrate is difficult to obtain with an impurity observed in all but the oven method. Intense reflections at 31.92°, 34.58°, 36.37° and 47.66° 2θ identify this impurity as ZnO. The structure of the zinc hydroxynitrate differs depending on what synthetic procedure was used. An intense reflection at 12.83° 2θ when using hydrolysis methods indicates the formation of Zn\(_3\)HN\(_2\) with an interlayer spacing of 6.88 Å. The titration method favours the formation of Zn\(_3\)HN\(_2\) with an intense reflection at 9.31° 2θ showing a basal spacing of 9.47 Å. When using the bomb method, both compounds were obtained despite using identical synthetic procedures. With Zn\(_3\)HN\(_2\) obtained using toluene and oven methods, it stands to reason that Zn\(_3\)HN\(_2\) is preferentially formed at high temperatures and vice versa Zn\(_5\)HN\(_2\) formed at ambient temperatures. This hypothesis does not agree when considering the bomb method. This method uses the highest temperature with a considerable amount of pressure yet produces both Zn\(_3\)HN\(_2\) (80%) and Zn\(_5\)HN\(_2\) (20%) with neither containing an impurity of the other. It can be hypothesised that the low temperature synthesis forms Zn\(_3\)HN\(_2\) and as the temperature increases, the high temperature Zn\(_3\)HN\(_2\) structure is formed via the breakdown of Zn\(_5\)HN\(_2\). Another possible explanation for the formation of Zn\(_3\)HN using the titration method is the presence of OH\(^-\) anions. This may promote the formation of coordinated zinc atoms [Zn\(^{10+}\)\(\text{H}_2\text{O})\]^\(+\) located above and below a [Zn\(^{3+}\)oct(OH)\(_8\)]^\(-\) layer. Nitrate anions then locate between the layers but are not directly bonded to the zinc atom. When heat is applied to the Zn\(_3\)HN.2H\(_2\)O structure, it breaks down. The [Zn tet(H\(_2\)O)]^\(+\) layer is removed leaving the [Zn\(^{3+}\)oct(OH)\(_8\)]^\(-\) that is then dehydrated to [Zn\(_3\)(OH)\(_4\)]^\(+\), two nitrate anions then co-ordinate directly to the zinc centre and form Zn\(_3\)HN\(_2\). When using the autoclave method, Zn\(_3\)HN\(_2\) is synthesized more often than Zn\(_5\)HN\(_2\) so it can be assumed that the formation of Zn\(_3\)HN\(_2\) using the bomb method is simply an incomplete reaction. Stoichiometries of reagents were adjusted in an attempt to remove the ZnO impurity observed in samples, however this was unsuccessful.
Carbon content for zinc hydroxynitrate samples is relatively high when compared to that of copper hydroxynitrate. The XRPD pattern for the digestion method shows a large amount of zinc oxide present and this is further confirmed by the H% and N% being very low. Interestingly, the toluene method does not result in high carbon content, as in the copper modification. Nitrogen and hydrogen content is extremely low indicating as a result of the presence of a ZnO impurity. When looking at the oven method, nitrogen content is 0.48% less than expected whilst carbon content is 0.37%. This indicates that an amorphous hydroxide or oxide phase is unlikely to be present, as confirmed by XRPD. As expected, increased carbonate content is observed when using the titration method. CO$_2$ absorption is promoted by the increased basicity. Relatively low nitrogen content is observed in both Zn$_3$ and Zn$_5$ modifications synthesised using the bomb method. This is in agreement with XRPD data and observations when using the bomb method to synthesise a copper modification.
Table 3.11 Elemental analysis of products recovered in the synthesis of zinc hydroxynitrate. Approximate error variation 0.2% N and C, 0.5% H.

<table>
<thead>
<tr>
<th>Method</th>
<th>% C</th>
<th>H%</th>
<th>N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal structure (Zn₃(OH)₄(NO₃)₂)</td>
<td>0.00</td>
<td>1.04</td>
<td>7.12</td>
</tr>
<tr>
<td>Ideal structure (Zn₅(OH)₈(NO₃)₂.2H₂O)</td>
<td>0.00</td>
<td>1.94</td>
<td>4.50</td>
</tr>
<tr>
<td>Toluene method (Zn₃(OH)₄(NO₃)₂)</td>
<td>0.45</td>
<td>1.45</td>
<td>4.94</td>
</tr>
<tr>
<td>Oven method (Zn₃(OH)₄(NO₃)₂)</td>
<td>0.37</td>
<td>0.94</td>
<td>6.64</td>
</tr>
<tr>
<td>Titration method (Zn₅(OH)₈(NO₃)₂.H₂O)</td>
<td>0.52</td>
<td>1.02</td>
<td>3.23</td>
</tr>
<tr>
<td>Digestion method (ZnO)</td>
<td>0.01</td>
<td>0.12</td>
<td>0.36</td>
</tr>
<tr>
<td>Bomb method (Zn₃(OH)₄(NO₃)₂)</td>
<td>0.02</td>
<td>0.81</td>
<td>5.75</td>
</tr>
<tr>
<td>Bomb method (Zn₅(OH)₈(NO₃)₂.2H₂O)</td>
<td>0.04</td>
<td>0.88</td>
<td>3.44</td>
</tr>
</tbody>
</table>

3.2.2.3 Nickel hydroxynitrate

A basal spacing reflection at 12.82° 2θ is present when using the hydrolysis, titration and autoclave methods indicating an interlayer spacing of 6.89 Å. Both reported modifications of nickel hydroxynitrate, Ni₃HN₂ and Ni₂HN, have an interlayer spacing of ~6.9 Å. A diffraction pattern for Ni₃HN₂ present on the ICDD database does not agree with data collected in this study, however Ni₂HN synthesised by Pollard et al does display identical reflections. Intense reflections of Ni(NO₃)₂ are present when using the hydrolysis method indicating an incomplete reaction. A considerable amount of washing was required to remove the parent salt and even then a single phase Ni₂HN product was not present. Several reflections between ~16° to 24° 2θ indicate an impurity phase; however it has not been possible to identify this impurity phase. As expected the digestion method results in no reaction after 10 days. At an elevated temperature of 80°C, small reflections indicate the presence of some Ni₂HN, however this is most likely due to a hydrolysis mechanism. The autoclave method yielded an incomplete reaction and an impure product. Reflections at 44.8° and 52.4° 2θ show a marked presence of unreacted Ni. Various stoichiometries of Ni and Ni(NO₃)₂ were trialled; however a pure phase using the bomb method was unobtainable. XRPD patterns show that only the titration method yielded a single phase. Reflections are broad when compared to those displayed when synthesising other LHSs, indication crystallinity is inherently poor.
Figure 3.9 XRPD patterns comparing methods used to synthesize nickel hydroxynitrate (a = toluene method, b = oven method, c = titration method, d = digestion method, e = autoclave method) (green = Ni, blue = Ni$_2$(OH)$_3$(NO$_3$), green = NiNO$_3$ and purple = NiO)

<table>
<thead>
<tr>
<th>Method</th>
<th>% C</th>
<th>H %</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Structure Ni$_2$(OH)$_3$(NO$_3$)</td>
<td>0.00</td>
<td>1.31</td>
<td>6.08</td>
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<tr>
<td>Toluene method</td>
<td>2.33</td>
<td>0.61</td>
<td>5.56</td>
</tr>
<tr>
<td>Oven method</td>
<td>0.22</td>
<td>1.22</td>
<td>6.23</td>
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<tr>
<td>Titration method</td>
<td>0.31</td>
<td>1.16</td>
<td>5.94</td>
</tr>
<tr>
<td>Digestion method</td>
<td>0.01</td>
<td>0.12</td>
<td>0.51</td>
</tr>
<tr>
<td>Bomb method</td>
<td>0.08</td>
<td>1.07</td>
<td>5.15</td>
</tr>
</tbody>
</table>

Table 3.12 Elemental analysis of products recovered in the synthesis of nickel hydroxynitrate. Approximate error variation 0.2% C and N, 0.5% H.

Carbon content for nickel hydroxynitrate samples is similar to that observed in copper modifications. A general trend is observed in that the toluene method yields high carbon content as a result of an interaction between the organic solvent and the LHS (possibly by incomplete removal of solvent during synthesis). The titration method and oven methods have carbon contents of 0.22 % and 0.31 % respectively which show that a high reaction temperature and the presence of a base...
increase carbonate interference. A low carbon, hydrogen and nitrogen content are observed when using the digestion method, agreeing with XRPD analysis confirming the presence of NiO in the majority. The autoclave method produces low carbon content as a result of a closed reaction vessel. High nitrogen content and low hydrogen content when using the hydrolysis method indicates the presence of the un-reacted parent salt in the majority. The titration method has nitrogen and hydrogen contents that are very similar to those that are expected, despite a carbon content of 0.31 %. This again mirrors what is observed in copper morphologies. The bomb method yields a nitrogen content of 5.15 %, which is 0.93 % less than what is expected. This is most likely as a result of a considerable amount of un-reacted nickel present in the XRPD pattern.

3.2.2.4 Lanthanum hydroxynitrate

![XRPD patterns comparing methods used to synthesis lanthanum hydroxynitrate](image)

Figure 3.10 XRPD patterns comparing methods used to synthesis lanthanum hydroxynitrate (a = toluene method, b = oven method, c = titration method, d = digestion method, e = autoclave method)(red = La(OH)₃, blue = La(OH)₂(NO₃).H₂O and green = LaNO₃, * = La(OH)₂(NO₃), + = La₂O₃).
All methods except the toluene method were successful in producing lanthanum hydroxynitrate. Only the parent salt was present when using the toluene method, and when the temperature was elevated, lanthanum oxide was formed. A basal spacing reflection at 11.55° 2θ is present when using all other methods and shows that the hydrated lanthanum hydroxynitrate phase has an interlayer spacing of 7.62 Å. A reflection at 12.59° 2θ present when using the oven, titration and digestion indicates the presence of an anhydrous lanthanum hydroxynitrate phase with an interlayer spacing of 7.02 Å. The removal of water in the drying phase at 50°C is reversed when anhydrous LaHN is suspended in water, and so is not a concern to the exchange capabilities of the material. There are impurities present in all samples recovered. A La$_2$O$_3$ impurity is identified when using the oven, digestion and autoclave methods by an intense reflection at 27.4° 2θ. Although other reflections for La$_2$O$_3$ are expected in the range of the XRPD pattern, identifying them is difficult due to the presence of similarly located reflections attributed to LaHN. The intensity of the La$_2$O$_3$ reflection in the oven and digestion method indicates it is perhaps a majority phase within the sample recovered. The high temperature of the oven method and the use of La$_2$O$_3$ as a starting material for the digestion method are the likely sources. In the case of the autoclave method, the La$_2$O$_3$ reflection is slightly less intense indicating a lesser quantity within the sample. When using the titration method, a reflections show that La(OH)$_3$ is present within the sample. As lanthanum is a trivalent cation, the hydroxide ratio is double to that used in the divalent cations. This increases the likelihood of forming a pure hydroxide phase, and when the ratio is decrease closer to 1.5:1, the yield dramatically reduces.

<table>
<thead>
<tr>
<th></th>
<th>% C</th>
<th>H %</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Structure</td>
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<td>6.34</td>
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<tr>
<td>Toluene method</td>
<td>0.01</td>
<td>0.51</td>
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<tr>
<td>Oven method</td>
<td>0.37</td>
<td>1.22</td>
<td>4.23</td>
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<td>Titration method</td>
<td>0.41</td>
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</tr>
<tr>
<td>Digestion method</td>
<td>0.26</td>
<td>1.12</td>
<td>4.51</td>
</tr>
<tr>
<td>Bomb method</td>
<td>0.03</td>
<td>1.27</td>
<td>4.75</td>
</tr>
</tbody>
</table>

Table 3.13 Elemental analysis of products recovered in the synthesis of lanthanum hydroxynitrate. Approximate error variation of 0.2% C and N and 0.5% H.

Carbon content within samples of lanthanum hydroxynitrate is comparable to those found in zinc analogues. Once again a general trend whereby carbon content is increased when using the titration method is observed, however the nitrogen content is also relatively high. The presence of a distinct oxide phase is confirmed in the oven, digestion and bomb phase by a nitrogen content that is ~1.5-2 % lower than expected. XRPD pattern indicate that hydroxide phase is present when using the titration method, however with a nitrogen content of 5.75%, 0.48 % less than expected, the hydroxide phase must be a minority phase with the target hydroxynitrate phase in the majority.

### 3.2.2.5 Layered hydroxyacetates

Pure Cu$_2$HA.H$_2$O is identified by intense and sharp reflections at 9.48°, 18.92° and 28.60° 2θ with an interlayer spacing of 9.31Å. As expected the interlayer spacing is 2.50Å larger than that observed in the nitrate analogue as a result of the incorporation of both acetate and water. Some
reactions yielded small reflections in the diffraction pattern located at 12.31° and 7.10° 2θ. These can be attributed to the anhydrous form with an interlayer spacing of 7.22 Å and a higher hydrated form with an interlayer spacing of 12.44 Å. An intense reflection at 6.0° 2θ indicates the presence of zinc hydroxyacetate with an interlayer spacing of 12.61Å. Zn₅HA₂ has an interlayer spacing of 9.72Å, when comparing this to the interlayer spacing of the acetate sample produced, a 1.89Å increase in basal spacing, along with the titration method used, suggest a Zn₅HAc modification is formed and not Zn₅HAc₂.

![Figure 3.11 XRPD patterns for the attempted synthesis of (a) lanthanum hydroxyacetate, (b) nickel hydroxyacetate, (c) zinc hydroxyacetate and (d) copper hydroxyacetate.](image)

Other reflections in the sample of Zn₅HA are very low in intensity, most likely as a result of preferred orientation. The basal spacing reflection observed in lanthanum hydroxyacetate suggests an interlayer spacing similar to that observed in the zinc modification and is consistent with the observed increase in basal spacing over the nitrate analogue. A broad reflection at 9.2°2θ in the sample recovered in the nitrate hydroxyacetate sample seems to suggest a LHS is formed with an interlayer spacing of 9.63 Å, which is slightly larger than that observed in the copper modification. It should be noted that the measured 2θ values for the nickel hydroxyacetate sample are very unreliable as a result of a poor diffraction pattern. The instability of acetate based LHSs past 100°C was the primary reason only the titration method was expected to yield results. Synthesis using the oven method was attempted using a reaction temperature of 70°C, however oxide impurities were present. Interestingly in the case of lanthanum hydroxyacetate, no presence of a hydroxide impurity phase is
observed as with the nitrate analogue. It must be noted however that the poor crystallinity of the XRPD pattern may make identification of the impurity difficult.

Elemental analysis was used to gather a scope as to the acetate of the samples recovered, however it must be noted that some of the carbon content may be attributed to carbonate content. In the case of the copper analogue, carbon content is 0.39 % less than expected and hydrogen content is 0.06 % more than expected. This indicates that a small hydroxide impurity phase is present despite the XRPD pattern showing the product to be phase pure. Interestingly, the carbon content and hydrogen content of the zinc sample is 0.24 % and 0.28 % more respectively than expected. The presence of a Zn$_3$HN$_2$ phase would increase the nitrogen content, however XRPD suggested this phase is not present. The most probable cause is either the presence of a carbonate phase, or some dehydration of the zinc hydroxyacetate phase. The XRPD pattern of the nickel analogue is very poor and this is reflected in the poor agreement of the elemental analysis. Carbon content is very low (0.69 % less) with hydrogen content remaining relatively high (0.49 % less) indicating the presence of an amorphous hydroxide phase. In the case of lanthanum, carbon content and hydrogen content are approximately a third less than expected indicating the presence of an oxide impurity phase.

<table>
<thead>
<tr>
<th>% C</th>
<th>H %</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Structure Cu$_2$(OH)$_3$(Ac).H$_2$O</td>
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<td>3.16</td>
</tr>
<tr>
<td>Titration method</td>
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<td>3.22</td>
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<td>7.78</td>
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<td>Titration method</td>
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<tr>
<td>Titration method</td>
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<td>2.11</td>
</tr>
</tbody>
</table>

Table 3.14 Elemental analysis of products recovered in the synthesis of copper, zinc, nickel and lanthanum hydroxyacetate.

3.2.2.6 Cobalt and manganese based LHSs

XRPD patterns (Figure 3.12) of products recovered in the synthesis of both cobalt and manganese based LHS are very poor. Broad low intense reflections indicate the presence of MO in most samples recovered, however it is very difficult to identify the presence of a LHS. Manganese and cobalt atoms fluoresce when bombarded by Cu X-rays resulting in a very high background, which is most likely “hiding” LHS reflections. XRPD utilising a different X-ray source would alleviate this problem, however only a Cu X-ray tube was available. As ease of characterisation is one of the primary goals of this chapter, exchange reactions involving cobalt and manganese base LHSs were not carried out. This is does not necessarily imply manganese and cobalt based LHSs are unsuitable but only a reflection on the unsuitability of the equipment available.
3.2.3 Discussion

It is clear from the results obtained that no one method is best at producing a single phase product that is easily characterised. Most samples recovered have N % (in the case of nitrate analogues) or C % (in the case of acetate analogues) below what is expected, although in most cases this is within the tolerance levels of the technique. In some cases, XRPD shows clear reflections attributable to the presence of hydroxide and/or oxide impurities, however in some other examples, there is no clear indication. It is unclear whether the presence of an orthorhombic phase has any effect on the exchange capability of copper hydroxynitrate, therefore a sample recovered using the oven method will be used in the exchange reactions in Chapter 4. This sample does contain less exchangeable nitrogen (5.31 %) content compared to that of the sample recovered using the titration method (5.48 %), however XRPD patterns suggest a greater quantity of the orthorhombic phase is present. The product recovered using the autoclave method will also be used as this represents a phase pure sample. Although the sample recovered using the autoclave method does have lower nitrogen content (5.11 %) compared to the oven method, a good comparison of the effect of the orthorhombic phase on exchange capability can be assessed.

The two modifications of zinc hydroxynitrate will be used in exchange reactions. A Zn$_3$(OH)$_4$(NO$_3$)$_2$.H$_2$O phase recovered using the oven method offers an increase in nitrogen content (6.64 %) when compared to a sample recovered by the autoclave method (5.75 %). Carbon content (0.37 %) is higher when compared to the autoclave method (0.02 %), however the increase nitrogen content and more reliable synthesis path makes the sample recovered using the oven method more favourable. All samples recovered in the synthesis of Zn$_6$(OH)$_9$(NO$_3$)$_2$.H$_2$O have a ZnO impurity, however the sample recovered using the autoclave method has an increase nitrogen content (3.44 %) and reduced carbon content (0.04 %) when compared to other methods and will be used in exchange reactions.
In the case of nickel hydroxynitrate, it is clear that only the titration method gives a phase pure sample with a nitrogen content (5.94 %) that is higher than any other method used, and so will be used in exchange reactions. All products recovered when synthesising lanthanum hydroxynitrate display either an oxide or hydroxide impurity. Although the titration method has high nitrogen content (5.75 %) compared to the sample recovered using the autoclave method (4.75 %), the second sample will be used for exchange reactions. The presence of a hydroxide phase is more likely to result in the formation of a hydroxide phase during an exchange whereas, due to the relative success in the digestion technique, the presence of La$_2$O$_3$ is more likely to promote the formation of a LHS.

As only the titration technique was used in the synthesis of acetate analogues, all samples recovered will be used in exchange reactions.

4.2.3.1 IR analysis

IR analysis of the samples to be used in exchange reactions compares well to literature data. Broad absorption bands in the region 3700 – 3300 cm$^{-1}$ are indicative of O-H stretching vibrations of bridging and terminal hydroxides within the brucite like layers, as well as water located within the layers. Clear O-NO asymmetric stretches in the region 1415 – 1503 cm$^{-1}$ wave numbers, O-NO symmetric stretches in the region 1289 - 1316 cm$^{-1}$ wave numbers are observed in samples of Cu$_2$(OH)$_3$(NO$_3$)$_2$.H$_2$O, Zn$_3$(OH)$_4$(NO$_3$)$_2$.H$_2$O, Ni$_2$(OH)$_3$(NO$_3$)$_2$ and La(OH)$_2$(NO$_3$)$_2$.H$_2$O, indicating the nitrate anion has C$_{2v}$ symmetry as is bonded directly to the layers. A band located in the region 1368 – 1451 cm$^{-1}$ wave numbers is present in samples of Zn$_3$(OH)$_4$(NO$_3$)$_2$.H$_2$O, Zn$_5$(OH)$_8$(NO)$_2$.H$_2$O and La(OH)$_2$(NO$_3$)$_2$.H$_2$O. This band may be attributed to a NO$_3^-$ absorption which suggests a nitrate anion with $\nu_3$ symmetry is present and therefore not bonded to the layers. This band was expected in the case of Zn$_5$(OH)$_8$(NO)$_2$.H$_2$O showing that no nitrate is bonded to the layers. Interestingly the nitrate anions seems to display both bonded and free characteristics in samples of Zn$_3$(OH)$_4$(NO$_3$)$_2$.H$_2$O and La(OH)$_2$(NO$_3$)$_2$.H$_2$O. The difference in the asymmetric and symmetric stretches in the sample of Ni$_2$(OH)$_3$(NO$_3$)$_2$ (125 cm$^{-1}$) is less than that previously reported (187 cm$^{-1}$) indicating the strength of the N-O-M bond is weaker. Previous studies have attributed strong bonding of the nitrate anion to the layers as the reason behind its reduced exchange capability, however based on the IR spectrum recovered in this study, the nitrate anion does not seem to be as strongly bound to the layers. With an asymmetric and symmetric stretch difference of 175 cm$^{-1}$, it may be possible that the nitrate anion is strongly bonded to the layers in Zn$_3$(OH)$_4$(NO$_3$)$_2$.H$_2$O and its exchange capability is reduced.
Figure 3.13 FT-IR spectra of 1:1 exchange reactions of (a) Cu$_2$O, (b) Zn$_3$, (c) Zn$_5$, (d) Ni$_2$ and (e) La hydroxynitrate.

Table 3.15 FTIR data for several hydroxynitrates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wave number (cm$^{-1}$)</th>
<th>$a = \text{OH stretch}$</th>
<th>$c = \text{O-NO}_2$ asymmetric stretch, $v_4$</th>
<th>$d = \text{NO}_3^-$ absorption band, $v_3$</th>
<th>$e = \text{O-NO}_2$ symmetric stretch, $v_1$</th>
<th>$f = \text{N-O stretch, } v_2$</th>
<th>$v_4 - v_1$</th>
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</thead>
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<tr>
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<td>1415</td>
<td>1316</td>
<td>1047</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>Zn$_3$(OH)$_2$(NO$_3$)$_2$.2H$_2$O</td>
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<td>-</td>
<td>1378</td>
<td>1319</td>
<td>1010</td>
<td>174</td>
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</tr>
<tr>
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<td>-</td>
<td>1368</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ni$_2$(OH)$_3$NO$_3$</td>
<td>3546, 3538</td>
<td>-</td>
<td>1443</td>
<td>1318</td>
<td>1052</td>
<td>125</td>
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<tr>
<td>La(OH)$_2$NO$_3$.H$_2$O</td>
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<td>1289</td>
<td>1052</td>
<td>116</td>
<td>-</td>
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Broad absorption bands in the region 3700 – 3300 cm$^{-1}$ are indicative of O-H stretching vibrations of bridging and terminal hydroxides within the brucite like layers, as well as water located...
within the layers. This region is broader than that displayed in nitrate analogues indicating a greater presence of water located within the interlayer spacing. Two intense bands in the region 1581 – 1544 cm\(^{-1}\) and 1404 – 1373 cm\(^{-1}\) present in acetate analogous can be assigned to asymmetric and symmetric stretching vibrations of the acetate anion. The difference between these bands ranges from 192 cm\(^{-1}\) in the nickel analogue to 144 cm\(^{-1}\) in the lanthanum analogue. This difference would normally indicate bidentate coordination of the acetate anion, however previous structural refinements show that the acetate anion bonds in a unidentate fashion.

![Figure 3.14 FT-IR spectra of 1:1 exchange reactions of (a) Cu\(_2\), (b) Zn\(_5\), (c) Ni\(_2\) and (d) La hydroxyacetate.](image)

**Table 3.16 FTIR data for several hydroxyacetates.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wave number (cm(^{-1}))</th>
<th>(b = \text{COO}^-) symmetric stretch, (v_1)</th>
<th>(a = \text{COO}^-) asymmetric stretch, (v_2)</th>
<th>(v_4 - v_1)</th>
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<td>Cu(_2)(OH)(_3)(Ac).H(_2)O</td>
<td>3400 (b)</td>
<td>1597</td>
<td>1397</td>
<td>160</td>
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<tr>
<td>Zn(_5)(OH)(_8)(Ac)(_2).2H(_2)O</td>
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<td>192</td>
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<tr>
<td>La(OH)(_3)(Ac).H(_2)O</td>
<td>3608, 3400 (b)</td>
<td>1548</td>
<td>1404</td>
<td>144</td>
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</table>
3.3 Conclusion

The synthesis of nitrate and acetate analogues of copper, zinc, nickel and lanthanum layered hydroxysalts has been investigated. Single phase products of Cu$_2$(OH)$_3$(NO$_3$) (monoclinic), Cu$_2$(OH)$_3$(Ac).H$_2$O, Zn$_3$(OH)$_4$(NO$_3$)$_2$.2H$_2$O, Zn$_3$(OH)$_8$(Ac)$_2$.2H$_2$O, La(OH)$_2$(Ac).H$_2$O and Ni$_2$(OH)$_3$(NO$_3$) were easily recovered when using the correct synthetic method. Oxide impurities were present in samples of Zn$_3$(OH)$_8$(NO$_3$)$_2$.2H$_2$O and La(OH)$_2$(NO$_3$).H$_2$O irrelevant of the method used. In the case of Ni$_2$(OH)$_3$(Ac), the XRPD pattern was inconclusive, however subsequent elemental and FTIR analysis suggests the presence of a LHS. XRPD and FTIR analysis of the products recovered generally agreed with previously reported data. The only notable discrepancy was a reduction in the difference of the asymmetric and symmetric NO$_3^-$ absorption band observed in a sample of Ni$_2$(OH)$_3$(NO$_3$). This reduction suggests the nitrate anion is less strongly bound to the brucite like layers. The exchange capacity of products recovered will be tested in the Chapter 4.
3.4 References

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Chapter 4

Anion Exchange Capabilities of LHSs
This chapter investigates anion exchange reactions involving LHSs synthesised in Chapter 3 and is divided into 3 parts. Initially the exchange capabilities of LHSs in a standard iodide solution are assessed. Quantitative analysis is then performed on LHSs which seemed to have undergone ion exchange to determine their exchange capacity in the following section. Finally, the full anion exchange capabilities of suitable LHSs with anions of varying size, geometry and valency are investigated.

4.1 Introduction

Previous studies have shown that LHs are able to incorporate and substitute anions of varying size, shape and valency in the interlayer spacing \[1\]. Anions range from small monovalent single ion species such as the halides, \(X^- (X^- = F^-, Cl^-, Br^-, I^-)\), to polyatomic mono-, di- and tri-valent species of varying geometry (\(NO_3^-, XO_3^-, XO_4^-, CrO_4^{2-}, SO_4^{2-}, CO_3^{2-}, Cr_2O_7^{2-}, MnO_4^{2-}, VnO_4^{3-}, PO_4^{3-}\)), to large organic anionic species (RCOO\(^-\), ROSO\(^3^-\)). A large number of reviews have been published to illustrate the diversity of these reactions \[2, 3, 4, 5, 6\].

The anion-exchange properties of LDHs have been studied extensively and are well known. There are no apparent restrictions to the type of anion which may be incorporated within the interlayer spacing. The primary reason for this observation is the way in which anions are electrostatically incorporated within the interlayer spacing, with no covalent bond to a metal \[7, 8\]. Anion exchange reactions involving LDHs are generally non-selective, however there have been several papers suggesting that LDHs may be engineered to be selective towards certain anions. Li-Al LDHs have been shown to be highly selective towards certain isomers of organic anions. Exchange reactions involving LiAl\(_2\)(OH)\(_6\)Cl\(_n\)H\(_2\)O were shown to selectively incorporate 1,4-benzenedicarboxylate over 1,2 and 1,3 isomers with near 100% selectivity \[9\]. Selectivity between chiral molecules was also demonstrated using Mg-Al LDHs whereby incorporation of L-histidine was favoured over D-histidine with a ratio of 98:2 \[10\]. Exchange reactions involving non-organic molecules have not been as extensively studied. Exchanges of LDHs with halides and nitrates do not exhibit a high affinity for one particular anion, despite the specific examples shown above. Smaller anions were shown to exchange at a slightly faster rate than larger anions, however suspension in an equimolar solution of halides showed all iodide, bromide, chloride and fluoride analogues present \[11, 12\]. A common feature of exchange reaction involving LDHs is interference of carbonate. It has been shown that suspension of a LDH in a salt solution causes a rise in pH, which in turn promotes the solubility of CO\(_2\) from the atmosphere \[13\]. Although carbonate interference is often small, extra precautions, such as performing exchange reactions in an inert atmosphere have to be taken.

Anion exchange reactions involving LHSs have previously been reported successful using several metal modifications including copper, zinc, cobalt and lanthanum LHSs with respect to both inorganic and organic anions of monovalent valency \[14, 15, 16, 17\]. Substitution of anions in nickel and magnesium containing layered hydroxides have so far been reported unsuccessful, even at elevated temperatures of 60 °C. This lack of reactivity may be due to strong bonding of anions to the positively charged sheets and/or poor crystallinity of the hexagonal structure observed in these materials \[18\]. Double layered hydroxides of both acetate and nitrate analogues have recently been subjected to anion exchange reactions and in particular \(Cu_{1.6}Zn_{0.6}(OAc)(OH)\(_3\) has recently been reported
successful in exchanges with a variety of organic and inorganic anions (Cl, NO\textsubscript{3}, C\textsubscript{6}H\textsubscript{5}COO and CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}SO\textsubscript{3}) \textsuperscript{19}. An interesting feature of exchange reactions involving layered hydroxides is the reversibility and the selectivity of anions. When copper hydroxyacetate is exposed to a variety competitive anions (X\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, ClO\textsubscript{4}\textsuperscript{-} and OAc\textsuperscript{-}), it was discovered that nitrate, perchlorate and acetate anions were reversibly exchangeable with each other whereas halide anions irreversibly exchange (Figure 1) \textsuperscript{20}. This is of particular interest to this study as any material that is capable of irreversibly incorporating 129-iodine into its structure will have potential as a nuclear waste form.

Figure 4.1 Preferential anion exchange within a [Cu\textsubscript{2}(OH)\textsubscript{3}]\textsuperscript{+} framework.

Halides are practically irreversibly exchanged with layered hydroxyfluoride analogues being the most stable due to the small size of the fluoride anion. The theoretical anion-exchange capacities (assuming complete exchange of the interlayer nitrate anions) of the Zn, Cu, Ni, and La hydroxy nitrates are 320, 420, 430 and 400 g kg\textsuperscript{-1} respectively \textsuperscript{21}. The size of the interlayer spacing can dramatically change depending on the occupying anion. A large proportion of layered hydroxides reported contain nitrate as the exchangeable anion however examples of acetate, benzoate, sulphate and chloride containing materials have also been reported \textsuperscript{5}. In copper hydroxynitrate, the gallery spacing is ~6.9Å however when nitrate is replaced by the smaller chloride anion, the gallery spacing is reduced to ~5.7Å. The reduction of the interlayer spacing inhibits the ability of anions to enter the gallery spacing and access the exchangeable sites, which explains why halide exchange is irreversible. Similarly, LHSs synthesized using large exchangeable anions such benzoate, are less stable and prone to anion exchange with smaller species \textsuperscript{22}. An interesting feature of copper hydroxyacetate is the incorporation of water molecules within the structure. The exact effective anionic radius of the acetate anion is unknown, however it is expected to be of similar size to the nitrate anion at ~2.2Å. This theory is supported by comparing the acetate/nitrate species whereby anhydrous acetate analogues display a basal spacing of ~7.22Å which is only slightly larger than the nitrate analogue at ~6.9Å. Upon mono-hydration, the basal spacing of the acetate analogue increases dramatically to ~9.42Å. Some studies have suggested that a reflection at ~16.2Å is a higher hydration phase of CuHA, however this has been disputed by some authors as no phase with a higher level of hydration has been isolated. There has been some confusion as to the exact structure of Cu\textsubscript{2}HA with some models suggesting a similar structure to Zn\textsubscript{5}HN whereby the water molecules are bonded to the layers and the acetate anion is held electrostatically in the interlayer spacing. It is now generally accepted that the converse situation is true and that the hydrated phase of Cu\textsubscript{2}HA is favoured over the anhydrous phase. All synthetic methods produce the hydrated phase with heating at 140°C for several hours needed in order to drive the water out of the interlayer spacing, forming the anhydrous...
phase. The hydrated phase can easily be restored within 3 hours upon exposure to air with a humidity of 45% [23]. Carbonate interference is almost non-existent in exchange reactions of LHSs. This is partly due to a lower pH observed when LHSs are suspended in a salt solution (as a result of the proposed exchange mechanism explained below) and direct co-ordination of the occupying anion to the metal centre. Incorporation of carbonate within the interlayer spacing would require structure modification, which is not a true anion exchange, and thus potentially is less favourable.

### 4.1.1 Exchange mechanism

Two models have been proposed for the mechanism of anion exchanges in LHs. Topotactive exchange involves the direct exchange of anion within a metal hydroxide framework. Anion exchange reactions of LHSs are generally assumed to take place topotactically as a structural relationship between the parent and product is observed. The only structure modification as a result of anion exchange is a change in the interlayer spacing, which is in turn defined by the size and shape of the incoming anion (Figure 4.2) [24, 25].

![Figure 4.2 Topotactic exchange mechanism.](image)

The rate at which an exchange occurs depends on the size and how strongly bound the occupying anion is to the layers of the LH, with smaller and/or more strongly bound anions less likely to migrate out of the interlayer spacing.

Several authors have reported mass loss of a LDH during anion exchange reactions, which can be attributed to bulk dissolution. Rives and co-workers observed the formation of salts as impurity.
phases during anion exchange reactions. These observations tend to suggest that anion exchange is a two-step process—the LDH first dissolves and then re-precipitates with the incoming ion. This is known as the dissolution - re-precipitation mechanism \[26,27,28\] (Figure 4.3).

![Dissolution – re-precipitation exchange mechanism.](image)

**Figure 4.3** Dissolution – re-precipitation exchange mechanism.

### 4.1.2 Typical anion exchange reaction involving LHSs

A typical anion exchange reaction involves the suspension of a suitable material in a solution containing the relevant sodium or potassium salt dissolved in de-ionised water. The reaction vessel is then covered in laboratory grade parafilm and the suspension stirred for a period of time. The product is then retrieved via vacuum filtration and then washed with deionised water to remove any impurities (Equation 4.1).

\[
\begin{align*}
\text{Type Ia} & \quad M_2(OH)_3(X)\cdot nH_2O + NaY \rightarrow M_2(OH)_3(Y)\cdot nH_2O + NaX \\
\text{Type Ib} & \quad M_3(OH)_4(X)\cdot 2nH_2O + NaY \rightarrow M_3(OH)_4(Y)\cdot 2nH_2O + NaX \\
\text{Type II} & \quad M_5(OH)_8(X)\cdot 2nH_2O + NaY \rightarrow M_5(OH)_8(Y)\cdot 2nH_2O + NaX \\
\text{Type M}^{3+} & \quad M(OH)_2(X)\cdot nH_2O + NaY \rightarrow M(OH)_2(Y)\cdot nH_2O + NaX
\end{align*}
\]

**Equation 4.1** Generic anion exchange reactions when suspended in water

Previous studies have utilised XRPD, FT-IR and elemental analysis to qualitatively characterise exchange reactions. A common feature of LHSs is a basal spacing reflection of a particular 2θ angle which can be converted into a d-spacing value, which indicates the size of the interlayer spacing. A shift of this reflection post exposure of a LH to an anion indicates a change in...
the size of the interlayer spacing concomitant with the size of the anion. Quantitative analysis is often performed by comparing the intensities of relevant reflections indicating the size of the interlayer spacing. Unfortunately, due to the lamellar structure of LH materials preferred orientation of the 00l reflections can hinder monitoring the progress of the reaction. However, this method can offer a good indication to the success of an exchange reaction, since additional reflections appear as exchange occurs. Specific experimental exchange capacities of LHs have not, to our knowledge, been reported (Figure 4.4) or quantitatively determined previously.

FT-IR is also a useful tool in determining the progress of an exchange reaction, particularly those involving nitrate and organic molecules. Figure 4.5 shows FT-IR spectra of acetate, chloride and nitrate analogues of a copper LHS. In all LHs, strong and broad absorption bands are observed in the region 3300 – 3500 cm\(^{-1}\), which correlates to an O-H stretching vibration. For LHs that contain water molecules, this region is often broader and extends over a greater range as a result of hydrogen bonding (similar to hydrogen bonded alcohols).

Nitrate-containing LHs whereby the nitrate group is bonded to the metal cation display C\(_{2v}\) symmetry, which gives rise to four strong absorption bands over the region 900 – 1600 cm\(^{-1}\). In ascending order, these bands correlate to an N-O stretch, O-NO\(_2\) symmetrical stretch, NO\(_3^-\) absorption and O-NO\(_2\) asymmetrical stretch. For LHs where the nitrate anion is not bonded to the layer, a single absorption band at ~1370 cm\(^{-1}\) is observed.

The IR spectrum of the acetate analogue displays two intense bands in the region 1400 to 1600 cm\(^{-1}\) correlating to the asymmetric and symmetric stretching vibrations of acetate anion. Bidentate bonding is suggested because the difference between these bands is often in the region of
140 cm\(^{-1}\); however structural determination of this compound has shown that acetate has unidentate character. The presence of carbonate may also be determined by an absorption band at 1356 cm\(^{-1}\).

Elemental analysis is often used to determine the carbon, hydrogen and nitrate content within nitrate and organic analogues of LHSs. It is noted that carbonate interference within LHSs is less pronounced than in LDHs, this is often confirmed by determining carbon content within LHSs that are not expected to contain carbon, and attributing it to CO\(_3^{2-}\) anions.

### 4.2 Anion exchange reaction comparison of Cu, Zn, Ni and La LHSs

Anion exchange reactions of nitrate and acetate analogues of copper, zinc, nickel and lanthanum were investigated to determine exchange capabilities. Iodide is one of the anions of interest within the nuclear industry and was used as a standard to determine both the exchange capability and rate of a LHS. With an effective ionic radius of \(~2.20\) Å, iodide is smaller in comparison to both nitrate anion (\(~2.31\) Å) and acetate analogues, and therefore is expected to preferentially replace either occupying anion. Magnesium, cobalt and manganese modifications were not trialled as phase identification and characterisation was shown to be difficult in Chapter 3.
4.2.1 Experimental

LHSs were exposed to a solution containing an equimolar amount of iodide in a 1:1 ratio with the outgoing anion. All samples were placed in a ball mill for 2 h before exposure to iodide in order to reduce the particle size and increase surface area for exchange. All suspensions were filtered under suction, washed twice with deionised water and oven dried at 50°C, resulting in a fine powder.

4.2.1.1 Anion exchange reactions of type Ia $M_2(OH)_3(X).nH_2O$ LHSs

$M_2(OH)_3(X).nH_2O (0.002mols)(M = Cu^{2+}, Ni^{2+}, X = NO_3^-, OAc^-)$, prepared in chapter 2, was added slowly and under stirring to a solution containing an equimolar amount NaI (0.3g, 0.002M in 50ml). In the case of $Cu_2HN$, both monoclinic and orthorhombic (large impurity) modifications were trialled. A resulting suspension was left for 24 h under stirring. Table 4.1 shows the recorded colour of the exchange material before exposure, during suspension for 1 h and after exposure for comparison.

<table>
<thead>
<tr>
<th>$M_2(OH)_3(X).nH_2O$</th>
<th>Colour of exchange material</th>
<th>Colour of suspension after 1 hour</th>
<th>Colour of powder recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M = Cu, X = NO_3^-$ (monoclinic)</td>
<td>Dark blue</td>
<td>Dark blue</td>
<td>Dark blue-green</td>
</tr>
<tr>
<td>$M = Cu, X = NO_3^-$ (orthorhombic impurity)</td>
<td>Dark blue-green</td>
<td>Dark blue-green</td>
<td>Dark blue-green</td>
</tr>
<tr>
<td>$M = Cu, X = OAc^-$</td>
<td>Light blue</td>
<td>Green</td>
<td>Green</td>
</tr>
<tr>
<td>$M = Ni, X = NO_3^-$</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
</tr>
<tr>
<td>$M = Ni, X = OAc^-$</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
</tr>
</tbody>
</table>

Table 4.1 Colour of Type I $M_2(OH)_3(X).nH_2O$ powders pre, during and post exposure to iodide.

4.2.1.2 Anion exchange reactions of type Ib $M_3(OH)_4(X)_{2.n}H_2O$

$M_3(OH)_4(X)_{2.n}H_2O (0.002mols)(M = Zn^{2+}, X = NO_3^- or OAc^-)$, prepared in chapter 2, was added slowly and under stirring to a solution containing NaI (0.6g, 0.004M in 50ml). A resulting suspension was left for 24 h under stirring. Table 4.2 shows the recorded colour of the exchange material before exposure, during suspension for 1 h and after exposure.

<table>
<thead>
<tr>
<th>$M_3(OH)<em>4(X)</em>{2.n}H_2O$</th>
<th>Colour of exchange material</th>
<th>Colour of suspension after 1 hour</th>
<th>Colour of fine powder recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M = Zn, X = NO_3^-$</td>
<td>White</td>
<td>White</td>
<td>White</td>
</tr>
<tr>
<td>$M = Zn, X = OAc^-$</td>
<td>White</td>
<td>White</td>
<td>White</td>
</tr>
</tbody>
</table>

Table 4.2 Colour of Type I $M_3(OH)_4(X)_{2.n}H_2O$ powders pre, during and post exposure to iodide.
4.2.1.3 Anion exchange reactions of type II \( M_5(OH)_8(X)_2.nH_2O \)

\( M_5(OH)_8(X)_2.nH_2O \) (0.002mols)\((M = \text{Zn, } X = \text{NO}_3^- \text{ or } \text{OAc}^-)\), prepared in chapter 2, was added slowly and under stirring to a solution containing \( \text{NaI} \) (0.6g, 0.004M in 50 ml). The resulting suspension was left for 24 h under stirring. Table 4.3 shows the recorded colour of the exchange material before exposure, during suspension for 1 h and post exposure.

<table>
<thead>
<tr>
<th>( M_5(OH)_8(X)_2.nH_2O )</th>
<th>Colour of exchange material</th>
<th>Colour of suspension after 1 hour</th>
<th>Colour of fine powder recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M = \text{Zn, } X = \text{NO}_3^- )</td>
<td>White</td>
<td>White</td>
<td>White</td>
</tr>
<tr>
<td>( M = \text{Zn, } X = \text{OAc}^- )</td>
<td>White</td>
<td>White</td>
<td>White</td>
</tr>
</tbody>
</table>

Table 4.3 Colour of Type II \( M_5(OH)_8(X)_2.nH_2O \) powders pre, during and post exposure to iodide.

4.2.1.4 Anion exchange reactions of type \( M^{3+} M(OH)_2(X).nH_2O \)

\( M(OH)_2(X).nH_2O \) (0.002mols)\((M = \text{La, } X = \text{NO}_3^- \text{ or } \text{OAc}^-)\), prepared in chapter 2, was added slowly and under stirring to a solution containing \( \text{NaI} \) (0.020M in 50 ml). A resulting suspension formed was left for 24 h under stirring. Table 4.4 shows the recorded colour of the exchange material before exposure, during suspension for 1 hour and post exposure.

<table>
<thead>
<tr>
<th>( M(OH)_2(X).nH_2O )</th>
<th>Colour of exchange material</th>
<th>Colour of suspension after 1 hour</th>
<th>Colour of fine powder recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M = \text{La, } X = \text{NO}_3^- )</td>
<td>White</td>
<td>White</td>
<td>White</td>
</tr>
<tr>
<td>( M = \text{La, } X = \text{OAc}^- )</td>
<td>White</td>
<td>White</td>
<td>White</td>
</tr>
</tbody>
</table>

Table 4.4 Colour of \( M(OH)_2(X).nH_2O \) powders pre, during and post exposure to iodide.

4.2.1.5 Characterisation

PXRD patterns and elemental analysis data were collected as previously described in chapter 2. PXRD patterns were collected from 5 - 55º 2θ with a step size of 0.014º, and patterns used to determine for phase identification and to determine whether a change in the interlayer spacing has occurred. Elemental analysis was used as a quantitative method to determine the amount of nitrate and acetate located within the interlayer spacing post exposure to a salt solution.

4.2.2 Results and discussion

4.2.2.1 Cu modifications

Figure 4.6 shows the XRPD patterns of Cu\(_2\)HX samples. Products recovered for Cu\(_2\)HN analogues are not phase pure. Cu\(_2\)HN analogues only undergo a small amount of anion exchange when exposed to an equimolar amount of NaI for 24 h. The appearance of a basal spacing reflection at a higher 2θ angle \((^\circ = 13.8 ^\circ, 6.58 \text{ Å})\) indicates a reduction in the interlayer spacing, and therefore successful migration of iodide into the gallery spacing. The relative intensities of the two phases suggest that the nitrate analogue is still the major. The small reduction in intensity of the iodide basal spacing reflection observed when Cu\(_2\)HN (orthorhombic) is exposed to iodide indicates that the
presence of a phase impurity does have a small effect on the efficiency of an exchange. Full exchange of nitrate for iodide is observed after ~7-10 days in both samples of Cu₂HN with subsequent iodide basal spacing reflections being of similar intensity. This observation indicates that although an orthorhombic phase impurity does have an effect on the efficiency of an exchange, no detrimental effect to the overall exchange capacity is observed.

Figure 4.6 XRPD patterns of CuHN (pure monoclinic), CuHN (large orthorhombic impurity) and CuHA, and subsequent patterns post exposure to NaI for 1 day (* = A shift in the basal spacing reflection) (Vertical tick marks - blue = Cu₂(OH)₃NO₃ (orthorhombic); pink = Cu₂(OH)₃NO₃ (monoclinic); red = Cu₂(OH)₃(Ac).H₂O; green = Cu₂(OH)₃I).

In the case of Cu₂HA, exposure to iodide results in a complete shift in the observed basal spacing reflection from 9.8° (9.22 Å) to 13.8° (6.58 Å). This implies that complete substitution of iodide for acetate (and water) is observed. In some exchange reactions, a basal spacing reflection at 12.6° (7.19 Å) is observed indicating the presence of an intermediate anhydrous Cu₂(OH)₃(OAc) probably
generated in the drying step, however this reflection is extremely small in intensity and the addition of a small amount of additional NaI pushes the reaction to completion.

![Figure 4.7](image)

Figure 4.7 A picture of (a) Cu$_2$HA and (b) after exposure to an equimolar NaI solution for 4 minutes.

Figure 4.7 shows the colour change from acetate to iodide in a [Cu$_2$H]$^+$ matrix. It was noted that a distinct colour change from light blue to green was observed in exchange reactions involving Cu$_2$HN and Cu$_2$HA with iodide. This clear colour change is a useful way of determining the progression of a reaction and was observed when Cu$_2$HA was exposed to an equimolar amount of NaI in solution after only 4 minutes.

The increased exchange rate of acetate over the nitrate analogue is due to the larger basal spacing required to incorporate both acetate and water molecules. It was noted that suspension of Cu$_2$HA in distilled water results in the formation of a black powder, probably suggesting the formation of CuO on decomposition of the parent material. XRPD patterns do not show the presence of CuO, therefore it must form as an amorphous crust on particles with the acetate phase still present within. No black powder formation was observed when Cu$_2$HN is suspended in distilled water. The formation of CuO indicates migration of the larger acetate anion out of the [Cu$_2$H]$^+$ framework occurs when suspended in solution, and with no incoming anion present in solution (outgoing acetate anions are diluted in solution), CuO forms along with Cu(OAc)$_2$ (indicated by a blue solution present post exposure). These observations perhaps suggest a dissolution/re-precipitation mechanism is responsible, however no significant change in the pH of the solution was observed. When iodide is present in solution, it replaces acetate as the occupying anion. The reduction in interlayer spacing is too small to allow re-migration of acetate anions back into the interlayer spacing. The reduction in exchange rate of nitrate analogues is due to the similar effective ionic radii of nitrate (2.31Å) and iodide (2.20Å) anions. Migration of iodide into a smaller interlayer spacing (compared to Cu$_2$HA)
occurs at a slower rate. It should also be noted that once iodide is incorporated into the layers, re-
exchange for the nitrate anion does not occur even when the sodium nitrate is in very high excess,
indicating a topotactic exchange mechanism.

<table>
<thead>
<tr>
<th>Structure</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Structure Cu₂(OH)₃(NO₃)</td>
<td>0.00</td>
<td>1.26</td>
<td>5.86</td>
</tr>
<tr>
<td>Ideal Structure Cu₂(OH)₃(OAc).H₂O</td>
<td>9.41</td>
<td>3.16</td>
<td>0.00</td>
</tr>
<tr>
<td>Ideal Structure Cu₂(OH)₃I</td>
<td>0.00</td>
<td>0.99</td>
<td>0.00</td>
</tr>
<tr>
<td>Cu₂HN (monoclinic)</td>
<td>0.05</td>
<td>1.11</td>
<td>5.11</td>
</tr>
<tr>
<td>Cu₂HN (monoclinic) + NaI 1 day</td>
<td>0.12</td>
<td>1.11</td>
<td>4.05</td>
</tr>
<tr>
<td>Cu₂HN (monoclinic) + NaI 10 days</td>
<td>0.19</td>
<td>1.12</td>
<td>0.31</td>
</tr>
<tr>
<td>Cu₂HN (orthorhombic)</td>
<td>0.17</td>
<td>1.13</td>
<td>5.31</td>
</tr>
<tr>
<td>Cu₂HN (orthorhombic) + NaI 1 day</td>
<td>0.20</td>
<td>1.09</td>
<td>4.63</td>
</tr>
<tr>
<td>Cu₂HN (orthorhombic) + NaI 10 days</td>
<td>0.21</td>
<td>1.14</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu₂HAc</td>
<td>9.02</td>
<td>3.22</td>
<td>0.00</td>
</tr>
<tr>
<td>Cu₂HAc + NaI 1 day</td>
<td>0.51</td>
<td>1.05</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 4.5 Elemental analysis of Cu modifications. Approximate error margin 0.2% C and N and 0.5% H.

Table 4.5 shows the elemental data of Cu₂HX samples. A NO₃⁻ loss of ~21% and ~13% respectively is observed when a monoclinic sample and mixed phase sample are exposed to iodide for 24 h. These figure increase to ~94% and ~93% respectively after 10 days exposure. These data agree with the XRPD patterns indicating that the rate of exchange in phase pure monoclinic Cu₂HN is increased compared to Cu₂HN with a large orthorhombic impurity. Interestingly, the carbon content does rise slowly, the longer Cu₂HN is suspended in water, however values of 0.19% and 0.21% after 10 days indicate that carbonate interference is extremely small and much lower that observed in LDHs. In the case of Cu₂HAc, a reduction in carbon content from 9.02% to 0.51% indicates a 95% loss of acetate anions when exposure to I⁻ for one day. This figure is likely to be slightly higher as some of the 0.51% carbon content is likely to be attributed to CO₃²⁻.

4.2.2.2 Zn modifications

Figure 4.8 shows the XRPD patterns of Zn₅HX samples. Both analogues of the Zn₅HX.nH₂O and Zn₅HAc are still present post exposure to iodide, however hydrolysis into Zn(OH)₂ also occurs. The reported ability of both forms of zinc hydroxyxinitrate to undergo anion exchange with iodide has not been consistently reproduced. This study has shown that Zn₅HN is capable of anion exchange, however the d₀₀₁ reflection expected for an iodide analogue is weak in intensity compared to the starting material after 1 day exposure. Newman and Silverman reported successful exchange of nitrate for chloride with similar structures apart from a difference in coordination to the zinc centre. In the nitrate analogue, zinc atoms form a tetrahedral net of 6.14 x 5.52 Å, however in the chloride analogue, a hexagonal net with length of 6.34 Å is formed. This indicates substantial structure modification, however the exact reason for the slow rate of exchange of nitrate for iodide is not apparent. Newman and Jones noted that whilst a [Zn₅H]²⁺ framework was able to exchange with
organic anions such as benzoate and terephthalate, exposure to acetate resulted in hydrolysis to Zn(OH)$_2$.

Figure 4.8 XRPD patterns of Zn$_5$HN, Zn$_3$HN and Zn$_3$HAc, and subsequent patterns post exposure to NaI for 1 day (* = A shift in the basal spacing reflection) (Vertical tick marks -green = Zn$_5$HN; red = Zn$_3$HN; pink = ZnO; blue = Zn(OH)$_2$).
No obvious reasons for this outcome were identified, especially considering Zn$_3$H$_4$ can be easily prepared via direct precipitation of zinc acetate salt against a basic solution, indicating the predictability of exchanges within a [Zn$_3$H$_4$]$^{2+}$ framework are inconsistent. In the case if Zn$_3$HN, it has been shown that during exposure to anions, Zn$_3$HN hydrolyses forming a zinc hydroxide intermediate, that undergoes further structural modification to form the appropriate LHS. The reaction is therefore not a true anion exchange and a hydrolysed intermediate is observed in the case of Zn$_3$HN indicating an incomplete reaction.

Table 4.6 shows the elemental data of Zn$_n$HX samples. Elemental analysis indicates a decrease in carbon and nitrogen content with an increase in hydrogen content when Zn$_3$HN is exposed to iodide. A 97 % N loss is observed after 10 days indicating an almost complete migration of NO$_3^-$ out of the layers, however a large increase in hydrogen content to 1.45 %, 0.33 % more than expected though within error limits, agrees with XRPD data that exchange with iodide does not occur and a hydroxide / oxide phase is formed. When Zn$_3$HN is exposed to NaI, after one day a nitrate loss of 29% is observed, increasing to 72% after 10 days. An increase in carbonate content is also observed from 0.19% to 0.44% after 10 days exposure. Although no trace of a ZnHCO$_3$ phase is observed in XRPD patterns, the presence of CO$_3^{2-}$ is most likely due to the method of incorporating anions found within zinc LHSs, whereby anions are held electrostatically within the layers, as in LDHs. In the case of Zn$_3$HA, a reduction from 9.02% to 5.11% indicates a loss of acetate from the layers; however the hydrogen content remains relatively stable. This is agreeable with the XRPD whereby no traces of an iodide phase is present and hydrolysis of Zn$_3$HA into Zn(OH)$_2$ occurs.

<table>
<thead>
<tr>
<th></th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal structure (Zn$_3$(OH)$_4$(NO)$_2$)</td>
<td>0.00</td>
<td>1.04</td>
<td>7.12</td>
</tr>
<tr>
<td>Ideal structure (Zn$_5$(OH)$_8$(NO$_3$)$_2$-2H$_2$O)</td>
<td>0.00</td>
<td>1.94</td>
<td>4.50</td>
</tr>
<tr>
<td>Ideal structure (Zn$_5$(OH)$_8$(OAc)$_2$.2H$_2$O)</td>
<td>7.78</td>
<td>2.94</td>
<td>0.00</td>
</tr>
<tr>
<td>Ideal Structure (Zn$_3$(OH)$_4$(I)$_2$)</td>
<td>0.00</td>
<td>0.78</td>
<td>0.00</td>
</tr>
<tr>
<td>Ideal structure (Zn$_5$(OH)$_8$(I)$_2$)</td>
<td>0.00</td>
<td>1.12</td>
<td>0.00</td>
</tr>
<tr>
<td>Zn$_3$HN</td>
<td>0.37</td>
<td>0.94</td>
<td>6.64</td>
</tr>
<tr>
<td>Zn$_3$HN + NaI 1 day</td>
<td>0.20</td>
<td>1.41</td>
<td>0.23</td>
</tr>
<tr>
<td>Zn$_3$HN + NaI 10 days</td>
<td>0.23</td>
<td>1.45</td>
<td>0.19</td>
</tr>
<tr>
<td>Zn$_3$HN</td>
<td>0.19</td>
<td>0.88</td>
<td>3.44</td>
</tr>
<tr>
<td>Zn$_3$HN + NaI 1 day</td>
<td>0.24</td>
<td>0.91</td>
<td>2.43</td>
</tr>
<tr>
<td>Zn$_3$HN + NaI 10 days</td>
<td>0.44</td>
<td>1.01</td>
<td>0.98</td>
</tr>
<tr>
<td>Zn$_3$HAc</td>
<td>9.02</td>
<td>3.22</td>
<td>0.00</td>
</tr>
<tr>
<td>Zn$_3$HAc + NaI 1 days</td>
<td>5.11</td>
<td>3.03</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 4.6 Elemental analysis of Zn modifications. Approximate error margin 0.2% for C and N and 0.5% for H.

4.2.2.3 Ni modifications

Figure 4.9 shows the XRPD patterns of Ni$_2$HX samples. A reduction of the basal spacing reflection from ~13.2° 2θ (6.91 Å) to ~14.1° 2θ (6.44 Å) when Ni$_2$HN is exposed to an equimolar
amount of iodide indicates a reduction in the interlayer spacing and incorporation of iodide. From the relative intensities of the nitrate and iodide basal spacing reflections, it is likely that iodide is in the majority in a ratio of ~10:1 with nitrate, with full exchange observed after 10 days, however due to the high atomic number of iodine and the possibility of preferred orientation from the lamellar arrangement, this finding is not entirely conclusive. A large NiO impurity is also noted with intense reflections at 37.1° 2θ and 44.8° 2θ. Previous studies have shown that Ni LHS either do not interact with anion or hydrolyse into Ni(OH)₂, however in this study no hydrolysed product is observed. In the case of the acetate analogue, an extremely broad reflection at 7.1° 2θ completely disappears post exposure to iodide indicating an interaction has taken place, however the quality of the XRPD patterns make it difficult to determine whether an exchange has taken place.

Table 4.7 shows elemental data for Ni modifications. A 97 % loss of NO₃⁻ upon exposure of Ni₂HN to sodium iodide for 10 days is observed indicating full exchange of iodide for nitrate. A large NiO impurity is observed in the XRPD patterns and this observed in elemental analysis by a very low hydrogen content of 0.52% (0.94% expected). A reduction in carbonated content also agrees with XRPD patterns whereby a large portion of NiHN is oxidised into NiO. In the case of the acetate

![Figure 4.9 XRPD patterns of Ni₂HN and Ni₂HA, and subsequent patterns post exposure to NaI for 1 day (* = A shift in the basal spacing reflection) (Vertical tick marks - blue = Ni₂(OH)₃(NO₃); pink = NiO).]

Table 4.7 shows elemental data for Ni modifications. A 97 % loss of NO₃⁻ upon exposure of Ni₂HN to sodium iodide for 10 days is observed indicating full exchange of iodide for nitrate. A large NiO impurity is observed in the XRPD patterns and this observed in elemental analysis by a very low hydrogen content of 0.52% (0.94% expected). A reduction in carbonated content also agrees with XRPD patterns whereby a large portion of NiHN is oxidised into NiO. In the case of the acetate
analogue, exposure to an equimolar solution of sodium iodide does result in a 32% loss of carbonate after 10 days. This would suggest incorporation of iodide occurs, however an increase in hydrogen content from 2.03% to 2.31% indicates formation of a hydroxide phase.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal structure (Ni$_2$(OH)$_3$(NO$_3$))</td>
<td>0.00</td>
<td>1.31</td>
<td>6.08</td>
</tr>
<tr>
<td>Ideal structure (Ni$_2$(OH)$_3$(OAc))</td>
<td>9.79</td>
<td>3.28</td>
<td>0.00</td>
</tr>
<tr>
<td>Ideal Structure (Ni$_2$(OH)$_3$I)</td>
<td>0.00</td>
<td>0.78</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni$_2$HN</td>
<td>0.31</td>
<td>1.16</td>
<td>5.94</td>
</tr>
<tr>
<td>Ni$_2$HN + NaI 1 day</td>
<td>0.20</td>
<td>0.56</td>
<td>0.87</td>
</tr>
<tr>
<td>Ni$_2$HN + NaI 10 days</td>
<td>0.23</td>
<td>0.52</td>
<td>0.19</td>
</tr>
<tr>
<td>Ni$_2$HAc</td>
<td>3.11</td>
<td>2.03</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni$_2$HAc + NaI 1 days</td>
<td>2.55</td>
<td>2.23</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni$_2$HAc + NaI 10 days</td>
<td>2.13</td>
<td>2.31</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 4.7 Elemental analysis of Ni modifications. Approximate error margin 0.2% C and N and 0.5% H.

4.2.2.4 La modifications

![Figure 4.10 XRPD patterns of LaHN and LaHA, and subsequent patterns post exposure to NaI for 1 day (* = A shift in the basal spacing reflection) (blue = La(OH)$_2$(NO$_3$).H$_2$O).]
This suggests that lanthanum LHS are most susceptible to exchange and more stable with larger organic anions than smaller inorganic anions.

Figure 4.11 Proposed structures of LaHI and LaHA based on work by Pollard et al.

Figure 4.11 shows the structure of lanthanum LHS based on a model proposed by Pollard et al. The structure of La LHS differs from that of the structure found when divalent anions are occluded by water being directly bound to the tetrahedra protruding into the interlayer spacing and the anion being bonded slightly deeper within the layers. When a small inorganic anion is bonded to the layers, the tetrahedra containing the bonded water molecule is likely to come in close proximity to the opposing tetrahedra causing steric hindrance. When a larger inorganic anion such as acetate is bonded, the opposing protruding tetrahedra are further apart causing less steric hindrance.

<table>
<thead>
<tr>
<th></th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal structure (La(OH)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}.H\textsubscript{2}O)</td>
<td>0.00</td>
<td>1.59</td>
<td>5.54</td>
</tr>
<tr>
<td>Ideal structure (La(OH)\textsubscript{2}(OAc)\textsubscript{2}.H\textsubscript{2}O)</td>
<td>9.61</td>
<td>2.82</td>
<td>0.00</td>
</tr>
<tr>
<td>Ideal structure (La(OH)\textsubscript{2}I\textsubscript{2}.H\textsubscript{2}O)</td>
<td>0.00</td>
<td>1.27</td>
<td>0.00</td>
</tr>
<tr>
<td>LaHN</td>
<td>0.41</td>
<td>1.67</td>
<td>5.75</td>
</tr>
<tr>
<td>LaHN + NaI 1 day</td>
<td>0.42</td>
<td>1.52</td>
<td>5.11</td>
</tr>
<tr>
<td>LaHN + NaI 10 days</td>
<td>0.40</td>
<td>1.42</td>
<td>4.83</td>
</tr>
<tr>
<td>LaHA</td>
<td>6.77</td>
<td>2.11</td>
<td>0.00</td>
</tr>
<tr>
<td>LaHA + NaI 1 days</td>
<td>6.75</td>
<td>2.12</td>
<td>0.00</td>
</tr>
<tr>
<td>LaHA + NaI 10 days</td>
<td>6.74</td>
<td>2.10</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 4.8 Elemental analysis of La modifications. Approximate error margin 0.2% for C and N and 0.5% H.

Table 4.8 shows elemental analysis for LaHX samples. Elemental analysis confirms that when LaHN is exposed to an equimolar solution containing NaI, an interaction occurs (0.16% loss in nitrogen) however it is difficult to determine whether an exchange has taken place. Elemental analysis
on the acetate analogue shows that very little change has occurred in the carbon and hydrogen content during exchange, in full agreement with the XRPD data.

### 4.2.3 Conclusion

From the results obtained, it can be seen that an orthorhombic impurity in synthetic Cu$_2$HN would affect the rate at which an exchange reaction progresses, however the overall exchange capacity does not seem to be affected. These results indicate that both forms of CuHN exhibit exchange capabilities, but a simple disruption in the long range order of the layers due to the mixing of phases may be the cause of a decreased rate of exchange. Exposure to iodide results in full conversion of copper hydroxyacetate into its iodide analogue. This is due to the instability of the unbound acetate anion located between the copper hydroxide layers as a result of coordination of water to the positive layer. In the case of Zn LHSs, both Zn$_3$ and Zn$_5$ modifications have been reported to undergo anion exchange, however in this study only the Zn$_5$HN modification exhibited some degree of exchange capability with iodide whereas Zn$_3$HA and Zn$_5$HN modifications underwent full and partial hydrolysis into Zn(OH)$_2$, respectively. In the case of Zn$_5$ modifications, it has been shown that anions are held electrostatically within the layers and basal spacings are slightly larger in size and comparable to those found in LDHs. This may explain the slow reaction time, as selectivity for smaller anions is less of a determining factor in LDHs. Pollard et al has previously reported that exchange of acetate into a [Zn$_5$H]$_2^+$ framework as unsuccessful despite the acetate analogue being easily prepared via the direct precipitation of the copper acetate salt against sodium hydroxide solution. This is in agreement with observations in this study whereby Zn$_5$HA is easily prepared, however when it is placed in a solution of iodide, it hydrolyses into Zn(OH)$_2$. There does not seem to be any particular reason why iodide does not replace acetate, however the slightly smaller basal spacing associated with incorporating iodide may bring the opposing layers too close as described earlier with La LHSs. It was previously reported that, when exposed to a salt solution, Ni$_2$HN hydrolyses to form Ni(OH)$_2$. Upon exposure to an equimolar NaI solution, the basal spacing reflection for nitrate disappears completely after 10 days indicating complete exchange, however intense reflections and XRPD analyses indicate a large NiO impurity. Anion exchange of nitrate or acetate analogues of lanthanum LHS with iodide results in very little alteration to the parent structure. It was previously reported that a lanthanum hydroxide framework was able to incorporate larger organic molecules, however this has not been shown with respect to iodide. In terms of reproducibility and ease of characterisation, the nitrate analogues of Cu$_2$, Zn$_5$ and Ni$_2$ and the acetate analogue of the Cu$_2$ modification show the most potential for use as anion exchangers within the nuclear industry.

### 4.3 Efficiency of anion exchange reactions

It has been shown that only nitrate and acetate analogues of the copper hydroxy phases and nitrate analogues of Ni hydroxy phases give both reliable and reproducible exchanges in respect to iodide. It is clear that Cu$_2$HA.H$_2$O shows a greater rate of exchange compared to that of other LHSs. The main concerns pertaining to the use of Zn$_5$HN$_2$.H$_2$O as an ion exchange material is its slow exchange rate, the inability to determine an exact reason for the instability of its acetate analogue and the reduced inherent exchange capacity as a result of a ZnO presence from the synthetic stage. In the case of Ni$_2$HN, a slightly faster rate of exchange is observed compared to the Cu analogue; however the formation of NiO reduces the exchange capacity and presents a carcinogenic risk to the
user. When comparing the different copper phases, both analogues form a phase pure iodide product; however the acetate analogue clearly presents an advantage in terms of exchange rate. In this part of the investigation, only Cu$_2$HA.$\text{H}_2\text{O}$ was used as the ion exchange starting material. Previous studies have primarily used relative intensities of basal spacing reflections to quantify an exchange reaction. Although this provides a good estimate to the progression of an exchange, true quantitative measurements have not been taken as extensively. Thomas (2012) used ion chromatography to quantify the amount of anions present in the supernatant post exposure of Cu$_2$HN and Cu$_2$HA to a variety of anions. It was discovered that 99% exchange of acetate for chloride, bromide, iodide and sulphate was achieved after only 4 days exposure. Exposure of Cu$_2$HA to chloride, bromide, iodide and acetate resulted in 71%, 17%, 19 and 2% exchange after 2 days exposure. These values increased to 99%, 99%, 95% and 3% respectively after 4 days exposure.

4.3.1 Experimental

A sample of Cu$_2$HA was exposed to a solution containing an equimolar amount of iodide in solution in a 1:1 ratio with the outgoing anion. All suspensions were filtered under suction, washed twice with deionised water and oven dried at 50°C resulting in a fine powder.

4.3.1.1 Ion specific probe

This experiment was performed by Marijana Dragosavac in the Chemical Engineering Dept at Loughborough University. A sample of Cu$_2$HA, 2.5g (0.0080 mols) was exposed to a solution containing 2000 ppm NaI solution (0.0080 mols in 1000ml). A resulting suspension was placed in a constant stirred tank (CST) and the concentration of iodide in solution tracked over a period of 3 h.

4.3.1.2 Gravimetric analysis

A sample of Cu$_2$HI prepared by anion exchange was analysed using gravimetric analysis. A small amount of this sample (12 mg) was analysed using thermogravimetric analysis. The rest of this sample was dissolved in a nitric acid solution containing an excess of silver nitrate to release occupying anions into solution and form AgI. Equation 4.2 shows the reaction.

\[
\text{Cu}_2(\text{OH})_3\text{I(s)} + 3\text{HNO}_3(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgI(s)} + 2\text{Cu(NO}_3)_2(\text{aq}) + 3\text{H}_2\text{O(l)}
\]

Equation 4.2 Gravimetric analysis equation of Cu$_2$HI.

4.3.1.3 Characterisation

Quantitative analysis was carried out using the anion specific probe (4.3.1.1) and based on mass measurements (4.3.1.2). In the case of gravimetric analysis, XRPD patterns were collected from 5 - 55° 2θ with a step size of 0.014° and used to determine the phase of the solid present post exposure to the acid/silver nitrate solution. A sample was dried in an oven at 60 °C to remove any surface water. TGA analysis was carried out from 100 – 400 °C with a heat rate of 1 °C/min.
4.3.2 Results and discussion

4.3.2.1 Ion specific probe

Figure 4.12 shows the colour change when Cu$_2$HA is added to a solution of NaI over a 4 minute period. It was noted that within 30 seconds of addition of Cu$_2$HA, a small colour change from light blue to light blue - yellow was observed indicating a reaction was already taking place. After 4 minutes exposure, a strong yellow green colour persists until the conclusion of the experiment after 3 hours.

![Colour change images]

Figure 4.12 Colour change when Cu$_2$HA is added to a solution of NaI over a 4 minute period.

![Iodide concentration plot]

Figure 4.13 A plot tracking iodide concentration in solution when exposed to an equimolar amount of Cu$_2$HI under CST conditions.
Figure 4.13 shows the concentration of iodide in solution as a function of time when exposed to Cu₂HA. The rate of exchange is very fast and uniform up until ~80% replacement of acetate for iodide after 3300s (55 minutes) exposure. Past this point the rate of exchange decreases until a maximum value of 92.9% exchange of acetate for iodide after 9800s (163.3 minutes) is observed. Extending the trend line past the experimental 3 hours does show that 95.1% exchange of iodide for acetate is calculated to occur after 4 days exposure. It was previously reported that in a 6 times molar excess of iodide for acetate, 99% exchange occurs as determined by IC after 4 days. It must be noted that the reduced number of available anions for exchange and the lower concentration of iodide are the most likely reasons for this slightly reduced exchange capacity.

4.3.2.2 Gravimetric analysis

Table 4.9 shows the gravimetric analysis for a sample of Cu₂Hl. Based on gravimetric analysis, an average iodide content of 92.20% is observed. This is slightly lower than what is observed using the ion specific probe (92.9%). More importantly, this indicates the carbonate content observed in elemental analysis of Cu₂Hl prepared from Cu₂HA is probably attributable to residual acetate, rather than carbonate. XRPD patterns and elemental analysis of the solid product indicates the presence of AgI only with no carbonate phase present.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Attempt</th>
<th>Ideal mass of AgI (g)</th>
<th>Actual mass of AgI (g)</th>
<th>% of ideal I⁻ content</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuHl</td>
<td>1.0054</td>
<td>0.8035</td>
<td>0.7376</td>
<td>91.81</td>
</tr>
<tr>
<td></td>
<td>1.0013</td>
<td>0.7707</td>
<td>0.7116</td>
<td>92.34</td>
</tr>
<tr>
<td></td>
<td>0.9980</td>
<td>0.7681</td>
<td>0.7101</td>
<td>92.46</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td>92.20%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>σ = 0.28%</td>
</tr>
</tbody>
</table>

Table 4.9 Gravimetric analysis of CuHl prepared via anion exchange (Mₐ Cu₂(OH)₃I = 305.02 g/M, Mₐ AgI = 234.77 g/M, solubility AgI = 3 x 10⁻⁶ g/l).

Halide containing type I LHSs are expected to decompose in two well defined steps: first through de-hydroxylation followed by loss of the halogen as either HX or X₂ gas. TGA data indicates thermal decomposition of Cu₂Hl occurs in one well defined step. A XRPD diffraction pattern collected of the decomposition product indicates the presence of CuI₀ and CuI only. Bromide, chloride and fluoride containing Cu LHSs easily form copper(II) based halide salts whereas the iodide analogue is very unstable and quickly decomposes into copper(I) iodide and iodine gas.

Figure 4.14 XRPD pattern of the thermal decomposition product of Cu₂Hl (blue = CuO, red = CuI).
Cul is more thermally stable than Cu(X)$_2$ (X = Br, Cl, F) and decomposition is reported to occur at 1290 °C. The formation of Cul and CuO after de-hydroxylation terminates the decomposition path of Cu$_2$HI (at least in the temperature range we are interested in) after one step with a weight loss of 29.66% (Equation 4.3).

\[
2\text{Cu}_2\text{(OH)}_3\text{I}_3(s) \rightarrow 3\text{CuO}_3(s) + \text{Cul}_3(s) + 3\text{H}_2\text{O}_3(g) + \frac{1}{2}\text{I}_2(g) \quad \text{Mass loss = 29.66%}
\]

Equation 4.3 One step thermal decomposition route of Cu$_2$HI.

The TGA trace (Figure 4.15) indicates the sample of Cu$_2$HI prepared via the addition of Cu$_2$HAc.H$_2$O to an equimolar solution of NaI loses 24.14% mass between 145 – 246 °C. This loss is 5.52 % less than expected.

![TGA trace for the thermal decomposition product of Cu$_2$HI in air.](image)

One possible explanation for this less than expected weight loss is further reduction of copper and formation of more Cul. The expected weight loss of this alternative thermal decomposition route is calculated to 11.42% which is 12.72% less than that observed (Equation 4.4). It is therefore more likely that the actual Cul content present in the decomposition product is somewhere in between the amount proposed in two decomposition routes. Quantitative analysis has determined that iodide content is only 92% of that expected, therefore another possible explanation is the formation of more CuO than expected as a result of the low iodide content.

\[
2\text{Cu}_2\text{(OH)}_3\text{I}_3(s) \rightarrow 2\text{CuO}_3(s) + 2\text{Cul}_3(s) + 3\text{H}_2\text{O}_3(g) + \frac{1}{2}\text{O}_2(g) \quad \text{Mass loss = 11.42%}
\]

Equation 4.4 Alternative one step thermal decomposition route of Cu$_2$HI.
4.3.3 Conclusion

Experiments have been carried out to show that iodide ions lost from solution (via the ion specific probe) are occluded within the layers of LHS. The key point being to show that it is the LHS which removes the iodide ions from solution, rather than any other secondary phase.

The ion specific probe has shown that the concentration of iodide in solution decreases by 92.9% when exposed to an equimolar amount of Cu$_2$HA.H$_2$O. The ion specific probe experiment presumes that all iodide anions leaving solution are located within the layers of the LHS, however a gravimetric measurement provided an insight to the quantity of iodide actually located within the layers, since the weight loss associated with breakdown of the LHS can be directly measured. Gravimetric analysis showed an iodide content of 92.2% directly attributable to the breakdown of the LHS. These values are in good agreement; a slightly higher iodide loss from solution using the ion specific probe may be attributable to physisorption onto the surface of the exchange material.

4.4 Full exchange capabilities of Cu$_2$(OH)$_3$(OAc).H$_2$O

It has been shown that exchange of acetate with iodide within a layered [Cu$_2$(OH)$_3$] framework occurs with ~92-93% efficiency with an equimolar amount of iodide in solution. The exchange capability of CuHA with a variety of other anionic species was carried out to determine the effect, if any, of the geometry, effective ionic radius and charge on exchange capabilities. Sodium or potassium salts of single ion monovalent (F$, \text{Cl}$, Br$, \text{I}$), linear monovalent (OH$^-$), trigonal planar monovalent (NO$_3^-$, SbO$_3^-$) trigonal pyramidal monovalent (IO$_3^-$), tetrahedral monovalent (ClO$_4^-$, IO$_4^-$, ReO$_4^-$), trigonal planar divalent (CO$_3^{2-}$), tetrahedral divalent (CrO$_4^{2-}$, SeO$_3^{2-}$) and tetrahedral trivalent (PO$_4^{3-}$) anions provided a wide range of geometries, sizes and charges to investigate.

4.4.1 Experimental

A sample of Cu$_2$HA was added to a slightly molar excess solution containing a relevant sodium or potassium salt as performed the initial section of this chapter.

4.4.1.1 Anion exchange reaction between Cu$_2$(OH)$_3$(OAc).H$_2$O and Na$_x$Y$^{m-}$

Cu$_2$(OH)$_3$(OAc).H$_2$O (0.002mols) was added slowly and under stirring to a solution containing Na$_x$Y$^{m-}$ ($Y = \text{F}$, Cl, Br, I, OH, NO$_3^-$, SbO$_3^-$, IO$_3^-$, ClO$_4^-$, IO$_4^-$, ReO$_4^-$, CO$_3^{2-}$, CrO$_4^{2-}$, SeO$_3^{2-}$, PO$_4^{3-}$) (0.0025 in 50ml). A resulting suspension was left for one hour under stirring. The colour of the exchange material before exposure, during suspension for 10 min and after exposure was recorded for comparison. All suspensions were filtered under suction, washed twice with deionised water and oven dried at 50°C resulting in a fine powder. Table 4.10 shows the recorded colour of the exchange material before exposure, during suspension for 10 min and after exposure.

4.4.1.2 Characterisation

XRPD patterns and FT-IR spectra were collected as previously described in Chapter 2. PXRD patterns were collected from 5 - 60° 2θ with a step size of 0.014°, and used for phase identification and to determine whether a change in the interlayer spacing had occurred. FT-IR data were collected over 4000-400cm$^{-1}$ wavenumbers, not only to determine the loss of acetate post exchange but also to determine the presence, if any, of a band indicating carbonate.
<table>
<thead>
<tr>
<th>Cu₂(OH)₃(Y)·nH₂O</th>
<th>Colour of exchange material</th>
<th>Colour of suspension after 10 mins</th>
<th>Colour of powder recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁻</td>
<td>Light blue</td>
<td>Light blue</td>
<td>Light blue</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Light blue</td>
<td>Blue</td>
<td>Blue</td>
</tr>
<tr>
<td>Br⁻</td>
<td>Light blue</td>
<td>Blue</td>
<td>Blue</td>
</tr>
<tr>
<td>I⁻</td>
<td>Light blue</td>
<td>Green</td>
<td>Green</td>
</tr>
<tr>
<td>OH⁻</td>
<td>Light blue</td>
<td>Light blue</td>
<td>Light blue</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>Light blue</td>
<td>Blue</td>
<td>Blue</td>
</tr>
<tr>
<td>SbO₃⁻</td>
<td>Light blue</td>
<td>Light blue</td>
<td>Light blue</td>
</tr>
<tr>
<td>IO₃⁻</td>
<td>Light blue</td>
<td>Dark blue</td>
<td>Black</td>
</tr>
<tr>
<td>IO₄⁻</td>
<td>Light blue</td>
<td>Green</td>
<td>Light Green</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>Light blue</td>
<td>Blue</td>
<td>Dark Blue</td>
</tr>
<tr>
<td>ReO₄⁻</td>
<td>Light blue</td>
<td>Blue</td>
<td>Blue</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>Light blue</td>
<td>Light blue</td>
<td>Dark blue</td>
</tr>
<tr>
<td>CrO₄²⁻</td>
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<td>Dark blue</td>
</tr>
<tr>
<td>SeO₃²⁻</td>
<td>Light blue</td>
<td>Green</td>
<td>Dark green</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>Light blue</td>
<td>Blue</td>
<td>Dark blue</td>
</tr>
</tbody>
</table>

Table 4.10 Colour of Cu₂(OH)₃(Y) powders pre, during and post exposure to a variety of anions.

4.4.2 Results and discussion

4.4.2.1 XRPD analysis

Figure 4.16 show XRPD patterns of Cu₂HA when exposed to several salt solutions for 1 h. A shift in the basal spacing reflection from 9.80° to a higher 2θ angle occurs when Cu₂HA is exposed to F⁻, Cl⁻, Br⁻, I⁻, OH⁻, NO₃⁻, IO₄⁻, ClO₄⁻ and SbO₃⁻, indicating an exchange has taken place. Reflections of the starting CuHA material are present in exchanges with SbO₃⁻ and ClO₄⁻, suggesting full exchange has not occurred. Although an exchange is observed upon exposure to SbO₃⁻, the XRPD pattern indicates a full exchange is not observed after 1 h. Although this would indicate incorporation of SbO₃⁻ anions is slower than in other anions, poor solubility of the sodium salt leads to a reduction in available anions for exchange and is a more likely explanation as similarly shaped trigonal nitrate is easily exchanged. There seems to be no reason why ClO₄⁻ anions, especially given successful exchange reactions with IO₄⁻ anions, only partially substitutes for the acetate anions. The intensities of basal spacing reflection indicate that acetate anions are still the majority anion occupying the interlayer spacing. Sharp reflections indicate only KReO₄ is present post exposure of CuHA to the potassium salt with no trace of the starting material. ReO₄⁻ has the same valency and same shape as periodate and perchlorate, so the exact reason why this phenomena is observed is unknown.
Figure 4.16 XRPD patterns of 1:2 exchange reactions of Cu$_2$(OH)$_3$(OAc).H$_2$O with various anions (* = reaction has taken place).

Another disparity with respect to ClO$_4^-$ is the appearance of the basal spacing reflection at a higher 2θ angle than that observed with the IO$_4^-$ analogue. This indicates a basal spacing in the
perchlorate analogue of 7.26Å compared to 7.07Å in the periodate analogue. Despite the occurrence of \( \text{Cu}_2(\text{OH})_3(\text{IO}_3) \) in nature, exchanges with iodate have proved unsuccessful. A possible reason for this inhibited migration of the iodate anion into the gallery spacing is the stereoactive lone pair of electrons present in the pyramidal shape. This electron rich lone pair may inhibit the ability of the iodate anion to enter the negatively charged interlayer spacing. Sharp reflections indicate only \( \text{KReO}_4 \) is present post exposure of \( \text{CuHA} \) to the potassium salt with no trace of the starting material. \( \text{ReO}_4^- \) has the same valency and same shape as periodate and perchlorate, so the exact reason why this phenomena is observed is unknown.

Monovalent anions of varying size and geometry are easily exchanged with acetate in solution to form new LHSs. The only monovalent anion that was unable to be incorporated into the gallery spacing was \( \text{IO}_3^- \). When looking at the geometry and bonding mode (monodentate) of an anion, spherical, trigonal planar and tetrahedral anions show no apparent steric hindrance. Trigonal pyramidal anions, such as \( \text{IO}_3^- \), would create steric hindrance between non coordinated oxygen atoms and the copper hydroxide layer (Figure 4.17).

![Schematic representations of possible molecular geometries located within the interlayer spacing of a \([\text{Cu}_2(\text{OH})_3]^-\) framework.](image)

Upon exposure of copper hydroxyacetate to \( \text{PO}_4^{3-} \), a reflection observed at 7.80º 2θ (~11.31Å) is at lower angle than the starting materials. The reflections observed indicate the formation of an insoluble copper phosphate phase. No change in the basal spacing reflection is observed upon
exposure of CuHA to $\text{CO}_3^{2-}$, $\text{CrO}_4^{2-}$ and $\text{SeO}_3^{2-}$, indicating no exchange has taken place. The incorporation of these divalent and trivalent anions into a copper hydroxide framework would require significant structure modification and so would not be a true anion exchange. It is clear that, in a slightly excess molar solution at least, that the Cu$_2$HA is more favourable than the formation of the relevant LHS containing carbonate, chromate and selenate anions.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Charge</th>
<th>Geometry</th>
<th>d spacing (Å)</th>
<th>Eff radius (Å)</th>
</tr>
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<tbody>
<tr>
<td>PO$_4$</td>
<td>3-</td>
<td>Tetrahedral</td>
<td>No shift</td>
<td>2.38</td>
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<tr>
<td>SeO$_3$</td>
<td>2-</td>
<td>Tetrahedral</td>
<td>No shift</td>
<td>No data</td>
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<tr>
<td>CrO$_4$</td>
<td>2-</td>
<td>Tetrahedral</td>
<td>No shift</td>
<td>2.40</td>
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<tr>
<td>CO$_3$</td>
<td>2-</td>
<td>Trigonal planar</td>
<td>No shift</td>
<td>1.85</td>
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<tr>
<td>CH$_3$CO$_2$H$_2$O</td>
<td>1-</td>
<td>Organic</td>
<td>9.28</td>
<td>3.49</td>
</tr>
<tr>
<td>CH$_3$CO$_2$</td>
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<td>Organic</td>
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<td>2.51</td>
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<tr>
<td>ReO$_4$</td>
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<td>Tetrahedral</td>
<td>No shift</td>
<td>No data</td>
</tr>
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<td>2.36</td>
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<td>SbO$_3$</td>
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<td>IO$_4$</td>
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<td>2.44</td>
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<tr>
<td>IO$_3$</td>
<td>1-</td>
<td>Trigonal pyramidal</td>
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<td>No data</td>
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<tr>
<td>NO$_3$</td>
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<td>I</td>
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<td>Spherical</td>
<td>6.57</td>
<td>2.20</td>
</tr>
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<td>Br</td>
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<td>Spherical</td>
<td>6.08</td>
<td>1.96</td>
</tr>
<tr>
<td>Cl</td>
<td>1-</td>
<td>Spherical</td>
<td>5.73</td>
<td>1.81</td>
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<tr>
<td>OH</td>
<td>1-</td>
<td>Linear</td>
<td>5.23</td>
<td>1.40</td>
</tr>
<tr>
<td>F</td>
<td>1-</td>
<td>Spherical</td>
<td>4.63</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Table 4.11 The relationship between effective anionic radius (if known) and the d spacing of the corresponding Cu LHS (red = calculated from this study, blue = reported by Shannon (1976)[30] and Manku (1980))[31].

It is clear from basal spacings that a reduction of the basal reflection is observed in the order $\text{Ac}^- \cdot \text{H}_2\text{O} > \text{Ac}^- > \text{ClO}_4^- > \text{SbO}_3^- > \text{IO}_4^- > \text{NO}_3^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{OH}^- > \text{F}^-$. As previously stated, monionic effective anionic radius values have been widely reported, however more than one source has been used to collect data for NO$_3^-$, OH$^-$ and ClO$_4^-$ anions. Figure 4.18 shows the relationship between effective anionic radius of an anion its subsequent basal spacing when incorporated into a [Cu$_2$H]$^+$. 
Figure 4.18  A graph showing the relationship between effective ionic radius (Å) and size of the interlayer spacing (Å) (red = calculated from this study, blue = reported by Shannon (1976) and Manku (1980), green = see below).

From the graph, a clear linear relationship between effective anionic radius of the halides and nitrate anions with subsequent interlayer spacing of the layered copper hydroxide LHS is observed. The hydroxide anion has a smaller than expected basal spacing with XRPD data indicating the formation of the mineral spertiniite. Figure 4.19 shows the crystal structure of spertiniite and Cu$_2$HCl.

Figure 4.19  The crystal structure of (left) Cu$_2$HCl and (right) Cu(OH)$_2$ (green = Cu, blue = O, light green = Cl and white = O).

The structure of spertiniite is considerably different from that of the other Cu based LHSs and explains the smaller than expected basal spacing observed. In the case of ClO$_4^-$, a basal spacing reflection indicates an interlayer spacing of 7.26 which is larger than expected. One author has suggested that this larger than expected basal spacing is as a result of the formation of a Cu$_2$HCl$_{0.43}$(ClO$_4$)$_{0.57}$ in which perchlorate and hydroxide anions are randomly located in the layer coordination sites, thus increasing the interlayer spacing. The same arrangement is not observed.
when periodate is incorporated into the gallery spacing with the basal spacing reflection indicating an interlayer spacing of 7.07Å. Based on the equation of the trend line observed when comparing the basal spacing and subsequent known effective anionic radius of the halides and nitrate anions, the anionic radii of acetate monohydrate, acetate, antimonite, and iodate are predicted to be 3.49 Å, 2.51Å, 2.47Å and 2.44Å respectively.

4.4.2.2 FT-IR analysis

Figure 4.20 and 4.21 show FT-IR data for exchanged products. A total loss of bands at 1541 cm\(^{-1}\), 1407 cm\(^{-1}\) and 1345 cm\(^{-1}\) is observed when CuHA is exposed to \(X^-, NO_3^-, IO_4^-, ClO_4^-\), PO\(_4^-\) and ReO\(_4^-\), with a reduction in transmittance noted in exchanges with ClO\(_4^-\) and SbO\(_4^-\). The loss or a reduced transmittance of these bands indicates either a total or partial loss of acetate respectively from the recovered product. This would indicate a successful exchange (except in the case of phosphate) agreeing with XRPD observations. A almost total loss of hydroxide character is observed in the FT-IR spectra when phosphate is exposed to Cu\(_2\)HA, and along with strong absorption bands in the region 1250 cm\(^{-1}\) – 1050 cm\(^{-1}\) wavenumbers characteristic of P=O stretching, confirms the formation of copper phosphate. In the case of IO\(_3^-\), bands observed in the region 3700cm\(^{-1}\) – 3200cm\(^{-1}\) wavenumbers seem to have notably reduced in broadness compared to that of the parent Cu\(_2\)HA material. There also seems to be alteration in the bands observed in the fingerprint region, however the acetate bands still remain. These data are contrary to the XRPD results, which indicate no structural modification. The loss of acetate bands and the retention of hydroxide character in the case of ReO\(_4^-\) indicates an interaction has taken place. When comparing the FT-IR spectra of the KReO\(_4\) salt and the recovered product post exposure to Cu\(_2\)HA, extra absorption bands in the region 1000cm\(^{-1}\) to 350cm\(^{-1}\) wavenumbers are observed. It is difficult to determine whether these bands indicate the formation of a LHS, however a band located at ~930 cm\(^{-1}\) wavenumbers may indicate the presence of a downshifted ReO\(_4^-\) – \(\nu_1\) stretching mode as a result of a lowering of the symmetry from T\(_d\) (free anion) to C\(_{3v}\) (monodentate coordination to the copper metal, through an oxygen atom).

![Figure 4.20](image-url) FT-IR spectra of 1:2 exchange reactions of Cu\(_2\)(OH)\(_2\)(OAc).H\(_2\)O with various anions.
Figure 4.21  FT-IR spectra of 1:2 exchange reactions of Cu$_2$(OH)$_3$(OAc).H$_2$O with various anions (red circle = partial acetate loss, blue circle = no acetate loss).
4.4.3 Conclusion

The ability of an anion to exchange with acetate within a [Cu₂H]⁺ framework based on its valency, size and geometry has been investigated. Unsurprisingly, the size of the interlayer spacing generally increases as the size of the anion incorporated increases. Based on the known effective anionic radii of the halides and nitrate anions, this progression is shown to occur in a predictable linear fashion. The only anion shown not to adhere with this trend is ClO₄⁻, however previous studies have suggested that a larger than expected increase in interlayer spacing is as a result of the formation of a hydroxide rich phase. The main disadvantages of LDHs are reduced in LH materials i.e. poor selectivity and susceptibility to carbonate anion ingress. In this study, exchanges with anions of greater charge than -1 have been mostly unsuccessful. When exposed to an equimolar amount of carbonate, selenate and chromate, no modification to the Cu₂HA structure was observed. In the presence of the phosphate anion, the parent Cu₂HA material decomposed forming copper phosphate. The iodate anion was not successfully incorporated into the interlayer spacing when exposed to Cu₂HA. Previous studies have shown that exchange reactions involving chlorate anions were also unsuccessful, further strengthening the theory that a trigonal pyramidal anion would create steric hindrance.

4.5 Neutron diffraction data

Powder neutron diffraction (PND) data were collected on deuterated samples of Cu₂(OD)₃X (X = Cl, Br, I) using experimental parameters described in chapter 2. GSAS-EXPGUI and WINPLOTR were used to analyse the PND data.

4.5.1 Preparation of Cu₂(OD)₃X (X = Cl, Br, I) and analysis using neutron diffraction

All glass equipment was dried at 80°C for 1 week prior to the synthesis in order to remove any water before use. All experiments were performed in an atmosphere controlled bag under nitrogen. A Cu₂(OD)₃(Ac).D₂O precursor was prepared by the standard titration technique. NaOD (99% D, 40% wt. % in D₂O) was added slowly and under stirring to a solution of Cu(Ac)₂ dissolved in D₂O (99.9% D)(0.1M, 1000ml) until a Cu:OD ratio of 1 was achieved. The solution was stirred for a further 24 hours as a suspension was formed. The blue powder was retrieved by vacuum filtration and dried under suction. Deuterated samples of Cu₂(OD)₃X (X = Cl, Br, I) were prepared by anion exchange. Cu₂(OD)₃(Ac).D₂O (0.002mols) was added slowly and under stirring to a D₂O (99.9% D) solution containing an 3x molar excess amount of NaX (0.9g, 0.006mols in 50ml). The resulting suspensions were left for 24 h under stirring and retrieved by vacuum filtration. Powders retrieved were stored in a small sample vile within a larger sample vile containing drying silica gel. The larger sample vile was sealed under a N₂ atmosphere.

4.5.2 Results

Figure 4.22 shows the NPD data collected for samples of Cu₂(OD)₃X.nH₂O (X = Cl, Br, I, Ac). No reflections indicative of the parent Cu₂(OD₃)(Ac).D₂O material are present post exchange with Cl⁻, Br⁻ and I⁻. Tick marks have been generated based on unit cell data reported by Zheng (2006)³³ for chloride and Oswald (1961)³⁴ for bromide and iodide analogues. Although this data were collected using XRPD data, they provide a good basis for comparison of the raw data. Reflections present for samples of Cu₂(OD)₃X (X = Cl, Br, I) generally agree well with the tick marks. A broad reflection at
103.4 msec in the chloride analogue does not agree with calculated data and does not agree with any observed reflections for the acetate precursor, therefore the exact origin of this apparent impurity is not obvious. The broadening of some reflections is likely to be a result of formation at low temperature which in turn promotes poor crystallinity resulting from disorder between the layers but order within them.

Figure 4.22 NPD patterns of Cu$_2$(OD)$_3$X (X = Cl, Br, I) using HRPD bank no. = 1 at 2θ = 168.33 with expected reflections marked.

4.5.3 Rietveld refinement

A Rietveld intensity extraction method was used with a convergence criterion and Marquardt damping of 0.01. The background profiles were initially fitted using the function type 1 (shifted Chebyschev polynomial). A reasonable model was obtained using 8 terms with no dampening required in order to stabilise the refinements. The background was then fixed for the rest of the
refinement until the final stages when a better model was obtained. An attempt to fit the background graphically yielded a slightly better initial curve; however, using advice from the GSAS-EXPGUI help function, a refined background function was preferred as Rietveld refinements usually achieve better fits when the background is optimised and provided a better feel for the interaction between background values and displacement (thermal) parameters. Diffractometer constants (DIFC = 48283.87, DIFA = 2.09 and Zero = 8.00) were provided by the ISIS HRPD scientist and fixed to these values. Unit cell data based on work by Zheng (2006)\(^{35}\) for chloride and Oswald (1961)\(^{36}\) for bromide and iodide analogues were then refined with no dampening factor. Profile parameters were refined using the standard type 3 function with a peak cutoff of 10\(^{-4}\). A damping factor of 5 was used with the chloride analogue profile function in order to stabilise the refinement. For the chloride, bromide and iodide analogue a total of 4400, 4244 and 4400 powder profile points were processed respectively. Profile function diffractometer constants (alp = 0.183554, bet-0 = 0.223152 x10\(^{-3}\) and bet-1 = 0.723694 x10\(^{-2}\)) were provided as described above by the ISIS HRPD scientist and fixed to these values. Gaussian peak shape functions sig-1 and sig-2 and Lorentzian peak shape function gam-1 were refined independently until the R\(^2\) value remained constant. In the case of bromide and iodide, significant problems arose when refining the Lorentzian peak shape function whereby a reduction in the R\(^2\) value corresponded to an overly Gaussian peak shape when examining the calculated plot. To solve this problem, a gam-1 value obtained for the chloride peak shape refinement was used as starting point at which to refine the Lorentzian peak shape for the bromide and iodide analogues. Once all profile functions refined independently gave a stable R\(^2\) value and a good calculated fit, both Gaussian and Lorentzian peak shape functions were refined co-dependently. The final profile functions were fixed before the next step in refinement. Thermal parameters (U\(_{ISO}\)) fixed at 0.0125 Å\(^2\) prior to refining atomic position co-ordinates. Atomic positions were refined independently with a damping factor of 5 in the order Cu(1), Cu(2), X, O(1), O(2), D(1) then D(2). The process was repeated until no further reduction in the R\(^2\) was observed. The atomic position co-ordinates were then fixed and the thermal parameters (U\(_{ISO}\)) refined independently as above. The background function type 1 was finally further refined using 8 terms to conclude the Rietveld refinement.

4.5.3.1 Cu\(_2\)(OD)\(_3\)Cl

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Cu(_2)(OD)(_3)Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>216.58</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>monoclinic, P2(_1)/m</td>
</tr>
<tr>
<td>Refined Unit cell parameters</td>
<td></td>
</tr>
<tr>
<td>a = 5.7255(5)</td>
<td></td>
</tr>
<tr>
<td>b = 6.1253(3)</td>
<td></td>
</tr>
<tr>
<td>c = 5.6336(3) Å</td>
<td></td>
</tr>
<tr>
<td>β = 93.100(7)˚</td>
<td></td>
</tr>
<tr>
<td>Cell volume (Z)</td>
<td>197.28(2) Å(^3) (2)</td>
</tr>
<tr>
<td>Chi(^2)</td>
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</tr>
<tr>
<td>Scale factor</td>
<td>73.258</td>
</tr>
<tr>
<td>Sig-1</td>
<td>0.154412 x10(^5)</td>
</tr>
<tr>
<td>Sig-2</td>
<td>0.264568 x10(^4)</td>
</tr>
<tr>
<td>Gam-1</td>
<td>0.508996 x10(^2)</td>
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</table>
The refined atomic co-ordinates and thermal parameters are shown in table 4.12 and selected calculated bond lengths (Å) and selected bond angles (˚) are reported in tables 4.13 and 4.14; ESDs are given in parenthesis.

<table>
<thead>
<tr>
<th>Wychoff</th>
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<th>y</th>
<th>Z</th>
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Table 4.12  Refined atomic positions and thermal parameters for Cu₂(OD)₃Cl.

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<th>Bond</th>
<th>Length (Å)</th>
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<td>O₁_D₁</td>
<td>1.0239(1)</td>
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<tr>
<td>Cu₁_O₁</td>
<td>2.3227(1)</td>
<td>Cu₂_O₁</td>
<td>1.9219(1) x2</td>
<td>O₂_D₂</td>
<td>0.8984(1)</td>
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<td>1.9568(1) x2</td>
<td>Cu₂_O₂</td>
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<td></td>
<td></td>
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<tr>
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Table 4.13  Selected bond lengths (Å) of Cu₂(OD)₃Cl.
Table 4.14  Selected bond angles (°) of Cu$_2$(OD)$_3$Cl.

<table>
<thead>
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<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Angle (°)</th>
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4.5.3.2 Cu$_2$(OD)$_3$Br

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Formula weight     261.04
Crystal system, space group monoclinic, P2$_1$/m
Refined Unit cell parameters
  a = 6.0847(7) Å
  b = 6.1440(4) Å
  c = 5.6502(4) Å
  β = 93.593(10)°
Cell volume (Z) 210.81(3) Å$^3$ (2)
Chi$^2$ 11.51
Scale factor 123.08
Sig-1 0.306423 x10$^6$
Sig-2 0.457207 x10$^3$
Gam-1 0.766606 x10$^2$

Figure 4.24  Observed (red), calculated (green) and difference (purple) profiles from Reitveld refinement of NPD data collected on Cu$_2$(OD)$_3$Br.
The refined atomic co-ordinates and thermal parameters are shown in table 4.14 and selected calculated bond lengths (Å) and selected bond angles (˚) are reported in tables 4.15 and 4.16; ESDs are given in parenthesis.

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<th>Wychoff</th>
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<th>z</th>
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<th>Occupancy</th>
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<tr>
<td>Cu2</td>
<td>2d</td>
<td>0.5</td>
<td>0.0</td>
<td>0.5</td>
<td>1</td>
<td>0.0081(14)</td>
</tr>
<tr>
<td>Br1</td>
<td>2e</td>
<td>0.1201(16)</td>
<td>0.25</td>
<td>0.2849(15)</td>
<td>1</td>
<td>0.0157(17)</td>
</tr>
<tr>
<td>O1</td>
<td>2e</td>
<td>0.6573(15)</td>
<td>0.25</td>
<td>0.6215(15)</td>
<td>1</td>
<td>0.0033(16)</td>
</tr>
<tr>
<td>O2</td>
<td>4f</td>
<td>0.6342(9)</td>
<td>0.0086(14)</td>
<td>0.1888(9)</td>
<td>1</td>
<td>0.0059(12)</td>
</tr>
<tr>
<td>D1</td>
<td>2e</td>
<td>0.8100(17)</td>
<td>0.25</td>
<td>0.6046(17)</td>
<td>1</td>
<td>0.0300(24)</td>
</tr>
<tr>
<td>D2</td>
<td>4f</td>
<td>0.7886(9)</td>
<td>0.0148(13)</td>
<td>0.2016(9)</td>
<td>1</td>
<td>0.0193(14)</td>
</tr>
</tbody>
</table>

Table 4.14  Refined atomic positions and thermal parameters for Cu2(OD)3Br.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1_Br1</td>
<td>2.905(14)</td>
<td>Cu2_Br1</td>
<td>2.971(8)</td>
<td>O1_D1</td>
<td>0.940(13)</td>
</tr>
<tr>
<td>Cu1_O1</td>
<td>2.376(15)</td>
<td>Cu2_O1</td>
<td>1.914(6)</td>
<td>O2_D1</td>
<td>0.939(7)</td>
</tr>
<tr>
<td>Cu1_O2</td>
<td>1.994(11)</td>
<td>Cu2_O2</td>
<td>1.985(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu1_O2'</td>
<td>2.0034(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.15  Selected bond lengths (Å) of Cu2(OD)3Br.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (˚)</th>
<th>Bond</th>
<th>Angle (˚)</th>
<th>Bond</th>
<th>Angle (˚)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2_Cu1_O2</td>
<td>176.60(50)</td>
<td>O1_Cu2_O1</td>
<td>180.0</td>
<td>Cu2_O1_D1</td>
<td>116.02(2)</td>
</tr>
<tr>
<td>O2_Cu1_O2'</td>
<td>80.60(23)</td>
<td>O1_Cu2_O2</td>
<td>94.14(29)</td>
<td>Cu1_O2_D2</td>
<td>113.17(7)</td>
</tr>
<tr>
<td>O2_Cu1_O2''</td>
<td>102.71(53)</td>
<td>O1_Cu2_O2'</td>
<td>85.86(29)</td>
<td>Cu1_O2_D2</td>
<td>115.64(10)</td>
</tr>
<tr>
<td>O2_Cu1_O2'''</td>
<td>96.15(49)</td>
<td>O2_Cu2_O2</td>
<td>180.0</td>
<td>Cu2_O2_D2</td>
<td>113.45(5)</td>
</tr>
</tbody>
</table>

Table 4.16  Selected bond angles (˚) of Cu2(OD)3Br.

4.5.3.3 Cu2(OD)3I
Chemical formula  Cu2(OD)3I
Formula weight  308.04
Crystal system, space group  monoclinic, P2_1/m
Refined Unit cell parameters  
\[ a = 6.5865(6) \]
\[ b = 6.17880(33) \]
\[ c = 5.6803(4) \, Å \]
\[ \beta = 95.044(8) \, ^\circ \]
Cell volume (Z)  230.27(2) Å³ (2)
Chi²  2.321
Figure 4.25  Reitveld refinement of Cu$_2$(OD)$_3$I.

The refined atomic co-ordinates and thermal parameters are shown in table 4.17 and selected calculated bond lengths (Å) and selected bond angles (°) are reported in table 4.18 and 4.19; ESDs are given in parenthesis.

<table>
<thead>
<tr>
<th>Wychoff</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>U$_{ISO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1</td>
<td>2e</td>
<td>0.4897(11)</td>
<td>0.25</td>
<td>0.9967(14)</td>
<td>1</td>
</tr>
<tr>
<td>Cu2</td>
<td>2d</td>
<td>0.5</td>
<td>0.0</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>I1</td>
<td>2e</td>
<td>0.1071(14)</td>
<td>0.25</td>
<td>0.2797(15)</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>2e</td>
<td>0.6385(12)</td>
<td>0.25</td>
<td>0.6244(12)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>4f</td>
<td>0.6194(7)</td>
<td>0.0070(12)</td>
<td>0.1888(8)</td>
<td>1</td>
</tr>
<tr>
<td>D1</td>
<td>2e</td>
<td>0.7692(17)</td>
<td>0.25</td>
<td>0.6095(17)</td>
<td>1</td>
</tr>
<tr>
<td>D2</td>
<td>4f</td>
<td>0.7741(8)</td>
<td>0.0148(11)</td>
<td>0.2075(7)</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4.17  Positional parameters for Cu$_2$(OD)$_3$I.
## 4.5.4 Discussion

From the unit cell data, a slight expansion is observed when Cu$_2$(OD)$_3$X is synthesised using anion exchange compared to data reported in the literature that was analyzed using XRPD and not synthesized using anion exchange (Table 4.20). Although this expansion may be due to the synthetic method, comparisons hydrated vs deuterated and XRPD vs NPD data may not draw this assumption conclusively.

When comparing the bond lengths, Cu-X increases steadily (in the order of 0.1-0.2 Å) as the size of the occupying anion increases. This is increase also agrees well with the observed increase (in the order of 0.4-0.5 Å) in the unit cell along the a axis and progresses in a linear progression. An increased Cu_X bond length reduces stability of that bond and an increased anionic radius in turn increases the unit cell along the a axis which increases the interlayer spacing which ultimately allows easier migration of an anion into the interlayer spacing, this further decreasing stability. Interestingly a relatively smaller increase (in the order 0.01- 0.05 Å) in Cu1_O1 and Cu1_O2 bond lengths accounts for a slight increase in unit cell (in the order of 0.01-0.03 Å) along the b and c axis (Figure 4.26).
There are regions of the datasets that are poorly fitted by the refined model. Analysis of the hkl values of peaks shows that the peak shape is very anisotropic. Figure 4.27 highlights selected regions of the 3 NPD datasets showing the 0k0 and 0kl peaks are sharper than other reflections, with an h component. As the stacking direction of the layers is along the h00 direction, we suggest there is more disorder along this direction which is observed in broader h00, hk0 and hkl type reflections. To improve the fit of the data, a new model is required that takes this anisotropy into account. The areas of poorly fitted data above and below the ideal calculated pattern roughly equal out and it is expected that although a better model may help the peak shape function, the refined cell data will actually remain relatively stable.
Figure 4.27 Selected 70-80 msec region of the Cu$_2$(OD)$_2$X (X = Cl, Br, I) datasets showing the 0k0 and 0kl peaks are sharper than other reflections.

4.6 Conclusions on All Ion Exchange Experiments

Copper based layered hydroxysalts have been shown to be effective as anion exchange materials with respect to a variety of anions, more specifically I$^-$ and Cl$^-$. If these materials are to be seriously considered as an option in the long term separation and immobilisation of radioactive anions, its long term stability in chemically and radiolytically diverse environments must be evaluated. The most obvious factor to be considered is the presence of radiation, not only originating from the target anion, but originating from other active sources in close proximity to the exchange material. The
current preferred option is to mix treated waste within a concrete matrix before being placed in an underground depository for long term storage. The caustic, high pH environment of concrete can be considered as a serious long term obstacle when evaluating the stability of any materials used in the separation of radio-anions. The final variable to consider is the effect of underground water movements on the repository as a whole. Radiolytic and caustic stability are variables that directly affect the stability of the waste form and its contents directly from the moment it is fabricated. Movement of underground water causing the waste from the break down is a variable that is most likely to happen in the long run with heavily engineered waste form canisters and repository vaults being specifically designed to resist these affects.
4.6 References

5. A. Khan and D. O’Hare, *J. Mater. Chem.*, 12, 3191
Chapter 5

Stability and Applications of Copper Hydroxyacetate to the Nuclear Industry
Based on work in chapter 4 in this thesis, copper based layered hydroxysalts have been shown to be effective as anion exchange materials with respect to a variety of anions, more specifically I⁻ and Cl⁻. If this material is to be seriously considered as an option in the long term separation and immobilisation of radioactive anions, its long term stability in chemically and radiolytically diverse environments must be tested. The most obvious hurdle is the presence of radiation, not only originating from the target anion, but also from other active sources in close proximity. The current preferred option for dealing with active material is to mix treated waste with a concrete matrix before placing it in an underground repository for long term storage. The caustic, high pH environment of concrete can be considered as a serious long term obstacle for the stability of any materials used in the sequestration of radio-anions since the extreme alkalinity can cause breakdown of many conventional ion exchangers. Radiolytic and caustic stability are variables that directly affect the stability of the waste form and its contents directly from the moment it is fabricated. The final variable to consider is the effect of underground water movements on the repository as a whole. Movement of underground water causing the waste form to break down is a variable that is most likely to happen in the long run with heavily engineered waste form canisters and repository vaults being specifically designed to resist these affects.

5.1 Introduction

As discussed in chapter 1, the United Kingdom currently has a substantial legacy of both civil and defence related radioactive waste. A small amount of this waste is in long term storage, but most is either part of an existing facility or in a short term storage facility, such as a storage pond. The best course of management for this waste is separation and immobilisation of individual active constituents and depending on the radioactive level and structure, encapsulation of them within a substrate such as cement, polymer, glass, metals or sorbent material. This represents the final waste form and the primary barrier to the release of the radionuclides, which may be subject to various degradation mechanisms, into the geosphere.

5.1.1 Properties of cement

Cement is a material that is used in the production of concrete and mortar. It can be broadly categorised as either hydraulic or non-hydraulic. Hydraulic cement, such as Portland cement, is one that hardens upon hydration when anhydrous cement powder is mixed with water forming insoluble hydrates, allowing the cement to set even when under water. Non-hydraulic cements are made using materials such as non-hydraulic lime and gypsum plasters, and cannot harden while in contact with water [1, 2, 3].

5.1.1.1 Production of Portland Cement

The cement manufacturing process uses a lot of energy and there are currently two main methods used to initially mix the raw materials (Figure 5.1). The dry process uses more energy in grinding but less in the kiln, whereas the wet process conversely uses water to aid mixing with more energy used in the kiln to remove water. The two processes provide adequate mixing of the starting materials. Clinkering is a step which is characteristic of Portland cement; finely ground material is dried, heated (to enable the sintering reactions to take place) and then cooled down again [4, 5].
Immediately following the kiln is a large cooler designed to drop the temperature of the clinker (as the fused material is now called) from 1000°C to 150°C. At this stage all the raw materials have been transformed into all the required minerals to make cement. A retarder, such as gypsum (CaSO₄·2H₂O), is then added and ground for approximately 30 mins in large tube mills to produce a fine powder known as Portland cement [6, 7].

There are four primary minerals present in a Portland cement; tricalcium silicate (Ca₃SiO₅), dicalcium silicate (Ca₂SiO₄), tricalcium aluminate (Ca₃Al₂O₅) and calcium aluminoferrite (Ca₄AlₙFe₂₋ₙO₇). Cement chemists use abbreviated nomenclature based on oxides of various elements to indicate chemical formulae of relevant species, C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃ [2, 7, 8], and this nomenclature will be used for the remainder of this chapter.

It is the hydration of the calcium silicate, calcium aluminate, and aluminoferrite minerals that causes the setting of cement. The ratio of C3S to C2S determines how fast the cement will set, with slower setting occurring with lower C3S contents. Higher amounts of ferrite lead to slower hydration and it is the ferrite phase which causes the brownish grey colour in cements, so that “white cements” (those that are low in C4AF) are often used for aesthetic purposes. The C4AF phase forms around the other mineral crystallites, as the iron containing species act as a fluxing agent in the rotary kiln during cement production. This process means that C4AF is the last phase to solidify (around the others) [2].

5.1.1.2 Formation of concrete

Portland cement is a basic ingredient of concrete, mortar and most non-specialty grouts. Concrete is a composite material consisting of aggregate (gravel and sand), cement, and water. As a
construction material, concrete can be cast in almost any shape desired, and once hardened, can become a structural element. When cement is mixed with water, its constituents are hydrated, with the calcium silicates forming calcium silicate hydrate, calcium hydroxide and heat. These products contribute to the strength of the concrete. Tricalcium silicate reacts quickly producing a lot of heat whereas dicalcium silicate reacts more slowly and produces less heat (Equation 5.1).

\[
\text{Dissolution: } \quad \text{Ca}_3\text{SiO}_5 + 3\text{H}_2\text{O} \rightarrow 3\text{Ca}^{2+} + \text{H}_2\text{SiO}_4^{2-} + 4\text{OH}^- \\
\text{Formation of C-S-H: } \quad x\text{Ca}^{2+} + \text{H}_2\text{SiO}_4^{2-} + 2(x-1)\text{OH}^- \rightarrow \text{Ca}_x\text{SiO}_2\cdot\text{H}_2\text{O} \\
\text{Formation of Portlandite: } \quad \text{Ca}^{2+} + 2\text{OH}^- \rightarrow \text{Ca(OH)}_2
\]

Equation 5.1 Dissolution of calcium silicate upon exposure to water and subsequent formation of calcium silicate hydrate and portlandite.

When calcium silicates come into contact with water, an exothermic reaction occurs in which calcium cations form and water molecules break down to form hydroxide anions. As the reaction progresses, sparingly soluble calcium hydroxide soon becomes saturated in solution and precipitates. Simultaneously, calcium silicate hydrate also precipitates out of solution forming fine solid particles. A network of strong Si-O-Si bonds is formed between the particles in which the aggregates are trapped. Some weak bonds are formed to the aggregates directly with the strength of this bond further decreasing for smooth, inert and hard aggregates. After an initial expansion of the concrete, these reactions continue to take place for some time (depending on the composition of the cement) until the material shrinks as unreacted water is lost. As long as water is in contact with the cement, these reactions continue but they get slower and slower, and can take several years to reach full strength. The aggregates form a surface for the solids to form on, this process is rapid at first owing to the large areas of water and cement mixed together, however as more solids form, the amount of space between the grains of aggregate and silicate hydrate for the water to migrate decreases. The strength of concrete increases as less water is added in comparison to the amount of cement. This optimal strength mixture of concrete does not flow very well and is difficult to pour, consequently a compromise between strength and flow properties is reached when choosing an appropriate composition [9, 10, 11].

Admixtures are chemicals that can be added to a cement mix to alter properties to suit the function cement will serve. Minerals such as fly ash (also known as pulverized fuel ash or PFA) and synthetic polymer chemicals such as superplasticisers are sometimes added to improve the workability and plasticity of the concrete so that less water is needed, thus improving the strength. Other admixtures help construction forms adapt to different environmental factors. Retarding admixtures such as sugar are added to delay the setting time in hot climates and conversely accelerating admixtures such as calcium chloride and ammonium hydroxide are added to speed up setting time in colder climates [12, 13, 14, 15, 16, 17].

5.1.1.3 Use of concrete in the nuclear industry

Concrete is currently the most accepted material for use in an underground repository, ranging from the encapsulation of nuclear waste and backfilling of the repository, to applications in grout for sealing cracks and bolts. Concrete provides a matrix that has a low permeability which aids the long
term immobilisation of waste whilst providing structural strength to the repository. Underground repositories for ILW and HLW are generally considered the most cost effective and safest way of storing waste long term. The concept is to locate a geologically stable expansive underground location and excavate a tunnel 30–1,000 meters below the surface. Rooms or vaults may be constructed and used for waste disposal and long term storage, depending on the waste and geology of the area. Using this method it may be possible to permanently isolate the waste from the geosphere and biosphere \(^{[18, 19]}\). Although this method is very popular among scientists, many of the general public remains uncomfortable with the immediate stewardship cessation of land based disposal. The main concern with this method is the presence of radioactive species possessing half-lives of over 1 million years \(^{[20, 21]}\). Species such as \(^{129}\)I, raise concerns due to prolonged half-lives and therefore even an extremely low container leakage causes a problem as more than one half-life may be required until some nuclear wastes lose enough radioactivity to be considered no longer biologically active.

5.1.1.4 Long term underground repository storage

Near surface disposal facilities are used in several countries for short lived (usually with a half-life shorter than 30 years) LLW and ILW. These facilities consist of concrete vaults at shallow depths or rock caverns and boreholes at the depth of tens of meters. Near surface disposal facilities can provide the required isolation of radioactive substances for hundreds of years and are generally suitable for solid and solidified radioactive waste. Near surface disposal isolate waste forms by engineered or natural barriers \(^{[20]}\). Engineered barriers include the waste package, vaults, covers, linings, grouts and backfill material. All these barriers are intended to prevent or delay radionuclide migration from the disposal facility into the geosphere. Liquid wastes are usually solidified and/or immobilised within a matrix using materials such as cement, polymers and bitumen. The treatment of waste and fabrication of waste packages will most likely be carried out at a different location to that of the disposal facility \(^{[22, 23, 24, 25]}\).

Figure 5.3 Arrangement of near surface and deep geological disposal vaults.
Waste containing a large amount of radionuclides with either long half-lives or higher activity requires longer period of separation. These wastes include intermediate and high level waste originating from reprocessing of spent fuel elements, spent fuel when declared as waste and long lived alpha bearing waste. Deep geological formations of very low permeability or formations covered by overburdens of very low permeability (e.g. thick clayish layers) offer the greatest potential for long term isolation of such waste. A national waste management strategy may require that long lived waste and all other types of radioactive waste be emplaced in a geological repository, bypassing the near surface disposal option. Many disposal concepts are possible in different host rocks such as granite, clay, tuff or salt with a minimum depth of a few hundred meters. In the design of geological repositories, the characteristics of the site, host rock, and the properties of the waste packages should be taken into account. Geological repository design is an iterative process and the design may be modified as new data about the site are generated during the above ground and underground characterisation. By definition, disposal means that there is no intention to retrieve the disposed waste \(^{[20]}\).

Nevertheless, retrievable disposal concepts may also be considered (e.g. in order to enhance public acceptance or to provide for unforeseen developments). Retrieval has implications on the design of waste packages and the repository. Geological disposal programmes are in progress in various countries. Technological capability for the construction of geological repositories based on current drilling, tunnelling, backfilling and sealing technology is available \(^{[26, 27, 28]}\).

![Figure 5.4 Structure of a deposition vault.](image)

After closure of the repository, site surveillance, within a predefined period of institutional control, is generally implemented. Site monitoring and surveillance may include such operations as restriction of access, maintenance, documentation and remedial actions including waste retrieval and repackaging.
5.1.1.5 Interaction of waste packages and repositories with moving ground water

If Portland cement was to be used in underground repositories, any contact with the ground waters would create a plume leachate with a pH >13. The hyper-alkaline solution produced is due to the presence of NaOH and KOH with the pH then controlled by the dissolution of portlandite (Ca(OH)$_2$), one of the main phases of Portland cement. The concerns with the use of Portland cement and subsequent production of highly caustic plume water are; contact with UO$_2$ may increase radionuclide solubility and mobility, superplasticisers in the concrete could form organic acids that increase radionuclide transport via the formation of colloids, the presence of organics and gypsum may promote the growth of microbes that increase the rate of corrosion of waste packets and, perhaps the principle concern, the plume leachate may perturb the engineered bentonite barrier. It is these concerns that have led to a great deal of research and development into the use of low-pH cementitious materials for use in underground repositories [13, 29, 30, 31, 32, 33].

5.1.2 Radioactivity and subsequent interaction with materials

All ionizing radiation can be broadly classed into either charged or neutral particles. Charged particles include beta, protons, alpha and fission fragment ions, whereas neutral particles include gamma, X-rays and neutrons. The penetration and energy radiation depends on the mass and relative speed of a particular particle. Beta particles travel at 94% the speed of light (c) whereas alpha particles travel at only 2.3% c. This slower speed of heavier particles means they are more easily stopped and deposit their entire energy in a shorter distance (Table 5.1) [34].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Alpha (α)</th>
<th>Proton (p)</th>
<th>Beta (β)</th>
<th>Gamma and X ray (γ)</th>
<th>Neutron (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>$^2\alpha$ or He$^{2+}$</td>
<td>$^1\ p$ or H$^{1+}$</td>
<td>$^0\ e$ or $\beta$</td>
<td>$^0\gamma$</td>
<td>$^1n$</td>
</tr>
<tr>
<td>Charge</td>
<td>+2</td>
<td>+1</td>
<td>-1</td>
<td>neutral</td>
<td>Neutral</td>
</tr>
<tr>
<td>Mass (amu)</td>
<td>4.001506</td>
<td>1.007276</td>
<td>0.0054858</td>
<td>-</td>
<td>1.008665</td>
</tr>
<tr>
<td>Velocity (% of c)</td>
<td>2.3</td>
<td>4.6</td>
<td>94.1</td>
<td>100</td>
<td>4.6</td>
</tr>
<tr>
<td>Range in Air</td>
<td>0.0056m</td>
<td>0.0181m</td>
<td>0.3190m</td>
<td>820.00m</td>
<td>392.50m</td>
</tr>
<tr>
<td>Ionisation</td>
<td>Direct</td>
<td>Direct</td>
<td>Direct</td>
<td>Indirect</td>
<td>Indirect</td>
</tr>
</tbody>
</table>

Table 5.1 Comparison of ionizing radiation.

The behaviour of charged particles (α, β, p) passing through matter is fundamentally different from that of the neutral radiation (n, γ) (Figure 5.5). Charged particles strongly interact with the orbital electrons of the material through which the particles move, and so are classified as directly ionizing. Charged particle interactions can be further subdivided into two cases based on mass. Heavy charged particles include alphas and protons, whereas light electrons include both positrons and negatrons [34, 35].
Figure 5.5 Penetration and energy dissipation of alpha particles, beta particles and gamma and x rays through tissue \[34\].

Heavy moving particles initially lose small amounts of energy as a result of interactions with the electrons in the material through which it passes. This process continues until the heavy particle loses enough energy to the point at which it no longer has sufficient energy to excite an electron. The heavy particle subsequently loses additional energy by nuclear collisions. As heavy particles slow, they capture electrons to form a neutral atom until it slows down almost entirely due to coulombic interactions with the atomic electrons. Due to the large size of heavy particles, ions are not easily deflected by atomic electrons, travel in a straight-line path and have a well-defined range of only a few centimeters in air. Passage of light charged radiation such as beta particles leads to several possible processes. Ionisation may occur in which the energy loss mechanism is similar to that for heavy charged particles, Bremsstrahlung is the process in which X-rays are created from electron deceleration and elastic scattering from nuclear and electronic interactions. Scattering is more important in the case of beta particles than with heavy charged particles in which the path of an electron is not linear, and its range is greater, but its path is not well defined \[36, 37, 38, 39\].

5.1.2.1 The effect of radiation on atoms and bonds

Radiation effects on materials on a micro scale can be classified into atomic displacement, ionisation, impurity production and large energy release. Atomic displacement can either occur ballistically as a result of kinetic energy transfer, or radiolytically by the conversion of radiation induced excitation into atomic motion. As a charged particle passes through matter, particle energy dissipates by elastic collisions with the material nuclei ejecting an atom from its normal lattice position, and by exciting orbital electrons. The ejected atom, known as a primary knock-on, may in turn cause a cascade of atomic displacements with the displacement atom becoming an interstitial, and the position formerly occupied by the atom becoming a vacancy. The interstitial and vacancy are referred to collectively as a Frenkel pair. Secondary displacement occurs when the primary displaced atom collides with and replaces another atom in the material. Displacement damage is the result of nuclear interactions such as scattering and the cumulative long-term non-ionizing damage from the ionizing radiation. The collision between an incoming particle and a lattice atom subsequently displaces the atom which causes lattice defects \[34, 39\].
Ionisation is the process of adding or removing an electron from a neutral atom creating an ion. Electron excitation is a less energetic process whereby the energy level of an electron raised, rather than it being removed. Ionizing radiation tends to be increasingly damaging from metallic (least damaged) to ionic bonds to covalent bond (most damaging). Metallic bonding consists of positive ions with free valence electrons, holding the ions together. Ionizing radiation increases the kinetic energy of the electrons or excites the electron to a higher energy level, but they shortly return to their normal energy level. In either case, there is no permanent damage from ionisation, only temporary internal heat produced. Ionic bonding involves the transfer of electrons from one element to another element resulting in positive (cation) and negative (anion) ions which attract one another. Overall, the electrostatic attractive and repulsive forces between the ions lead to well-ordered, three-dimensional arrangements of the ions in crystalline substances. Ionisation of a positively charge ion leads to an increase in its overall charge that will continue to attract anions, however conversely, ionisation of a negatively charged anion leads to the formation of a neutral atom that will no longer be attracted to cations. Radiation causes only temporary ionisation of the lattice atoms, which soon become neutral. Some of the outer electrons in a covalently bonded compound may be shared between atoms in the compound and no longer uniquely associated with a particular atom. Covalently bonded molecules' atoms do not attract one another to any degree and are typical of gases, liquids and organic materials. Covalent bond energies are in the low eV range and so radiation of sufficient energy to overcome the covalent bond can permanently separate the molecule into its constituent atoms or radicals, permanently changing the chemical composition of the material [34, 42].

Radiation induced impurity production is caused when radiation interacts with bonds and atoms cause structural imperfections in a crystal, which can alter electrical and mechanical properties of the material as a whole. Beta particles, gamma rays and X-rays do not directly cause impurity production, however they may indirectly cause impurity production through chemical bond breakage. It is the effects of neutron and ion irradiation that causes a significant amount of structural damage. As discussed earlier, incident ions will eventually slow and capture the necessary electrons to render them neutral with protons becoming hydrogen and alpha particles becoming helium. It is this production of a gas that exerts pressure on its neighbouring atoms causing internal pressurisation that has been observed to cause swelling in the material. Neutron and ion irradiation can also form radioactive species. Neutron capture by a nucleus does not necessarily change the chemical element present, but does change the isotope present. The new isotopes produced may be radioactive and decay by one of several schemes, which can change the chemical element present [34, 40, 41, 42].

All types of radiation cause energy deposition within the absorbing material through the ionisation process. In water and organics, most of the absorbed ionisation energy breaks chemical bonds whereas in metals, almost all of the absorbed energy from ionisation appears as heat. It is the kinetic energy deposition that generally manifests itself as thermal heating of the material. The corresponding temperature rise can change a number of material properties.

5.2 Effects of radiation exposure on Cu LHS

Of the two main radio-anions of interest (I⁻ and TcO₄⁻), stable ¹²⁷I⁻ has been used as surrogate for active ¹²⁹I⁻ and ¹³¹I⁻. Technetium is the lowest atomic number element with no stable isotopes,
consequently until recently ReO$_4^-$ has been used as a surrogate anion. The tetrahedral shape of the ReO$_4^-$ anion is the same as that of TcO$_4^-$; however it has a smaller ionic radii (1.88 Å). In fact TcO$_4^-$ has an anionic radius more comparable to that of I$^-$ (2.2 Å). Cu$_2$HA is able to exchange with a variety of monovalent anions, including I$^-$, efficiently and the subsequent materials formed are stable in air. The same cannot be said for reactions involving ReO$_4^-$ whereby its potassium salt remains present despite multiple washing, as seen in chapter 4. It is assumed that the chemical properties of any stable isotope will be identical to those of a radioactive isotope; however the emission of β and γ radiation by a radioactive species may disrupt the crystal structure of the exchange material and consequently facilitate the release of previously immobilised anions. $^{129}$I and $^{131}$I possess half-lives of 1.57 million years and 8 days respectively. When considering an isotope to use experimentally in the lab, these represent values which are too long to be used safely and too short to give a valid result respectively. $^{125}$I has a half-life of 60 days which is more useful when considering the effects of radiolytic decay on crystal structures and hence is used as the basis of the radioactive anion experiments described in this chapter. Sodium salts of $^{99}$TcO$_4^-$ are readily available and will be used to not only investigate the effect of radiation on a copper based LHS, but also to determine whether TcO$_4^-$ behaves in a similar fashion to ReO$_4^-$.

A bonus of using radioactive species to examine structural effects is that the activity itself can be used as a way to qualitatively measure the activity (and therefore amount of an anion) lost in solution as a result of exposure to the exchange material. Since the radioactivity of a solution of comparable strength to those used in the previous ion exchange experiments would be too high, a way to limited the exposure had to be devised. Exchange reaction were performed with a 1:1 exchange material to target anion ratio as used in previous experiments, however only a 10 % spike of the radioactive anion was used added in a solution containing the majority non-active isotope. Active isotopes may also be used as tracers, particularly in assessing the uptake from, and leaching back into, solution of I$^-$ and TcO$_4^-$.  

5.2.1 Experimental  
5.2.1.1 Exposure of Cu$_2$HA to an equimolar solution containing active $^{125}$I$^-$ and $^{97}$TcO$_4^-$  
A solution containing Na$^{127}$I (0.7714g, 25ml) was prepared, to which a 10 % spike of active $^{125}$I$^-$ (0.3821g, 114 kBq) in the form of the ammonium salt solution was introduced. A sample (100µl) of this solution was collected in order to determine the activity of $^{125}$I$^-$ in solution pre-exposure to the exchange material. Cu$_2$(OH)$_3$(OAc).H$_2$O (1.2g) was suspended in the spiked solution and stirred for 60 mins. A 100µl aliquot was removed to determine the activity of $^{125}$I$^-$ in solution after 10 mins exposure to the exchange materials. After 60 mins, the exchange material was filtered, washed with 20ml of distilled water and dried in an oven at 50°C for 2 h. A 180µl aliquot of the filtered solution was taken to determine the activity of the solution post exchange. The same procedure was repeated but using a 10 % spike of $^{99}$TcO$_4^-$ (0.0501g, 925 kBq) in the form of a sodium salt solution, whilst still maintaining $^{127}$I$^-$ as the bulk exchange anion (Equation 5.2). 

$$\text{Cu}_2(\text{OH})_3(\text{OAc}).\text{H}_2\text{O} + 0.9 \text{ Na}^{127}\text{I} + 0.1 \text{ NH}_4^{125}\text{I} \rightarrow \text{Cu}_2(\text{OH})_3(127\text{I})^{0.9}(125\text{I})^{0.1}$$

$$\text{Cu}_2(\text{OH})_3(\text{OAc}).\text{H}_2\text{O} + 0.9 \text{ Na}^{127}\text{I} + 0.1 \text{ Na}^{99}\text{TcO}_4 \rightarrow \text{Cu}_2(\text{OH})_3(127\text{I})^{0.9}(99\text{TcO}_4)^{0.1}$$

Equation 5.2  Exchange reactions of Cu$_2$(OH)$_3$(OAc).H$_2$O with (1) $^{127}$I$^-$ and (2) $^{99}$TcO$_4^-$ using $^{129}$I$^-$ as the bulk exchange anion.
In order to analyse and quantify the amount of iodide contained within the exchanged material, a sample was exposed to a 3:1 molar acidic solution in order to break the Cu LHS down, thus releasing the anions back into solution. A sample (100μl) of the resulting solution was then taken as a comparator (Equation 5.3).

\[
2\text{Cu}_2(\text{OH})_3((^{127}\text{I})_{0.9}(\text{X})_{0.1})_{(s)} + 6\text{HNO}_3(\text{aq}) \rightarrow \text{Cu}((^{127}\text{I})_{0.9}(\text{X})_{0.1})_{2(\text{aq})} + 3\text{Cu(NO}_3)_2(\text{aq}) + 6\text{H}_2\text{O}(l)
\]

Equation 5.3 Exchange reactions of Cu$_2$(OH)$_3$(OAc).H$_2$O with (1) $^{127}$I$^{-}$ and (2) $^{99}$TcO$_4$$^{-}$ using $^{129}$I$^{-}$ as the bulk exchange anion.

5.2.1.2 Characterisation

XRPD patterns and radioactivity counting data were collected as previously described in chapter 2. Before XRPD analysis, samples were left for 60 days to allow radiation effects to take place and, in the case of iodide, to allow the activity to reduce enough (1 half-life) to be handled in a X-ray diffractometer. $^{99}$Tc has a half-life of 211,000 years and so time to allow at least 1 half-life to pass is impossible. The specific activity of $^{99}$Tc is low enough and safe enough (with precautions) to allow handling of a sample in an X-ray diffractometer. XRPD patterns were collected from 5 - 60º 2θ with a step size of 0.014º. Patterns were used for phase identification to determine the effect, if any, of the presence of active species. The experiment was repeated 3 times using samples of Cu$_2$HA from the same batch, and activity counting performed in order to compare 3 different data sets.

5.2.2 Results and discussion

5.2.2.1 XRPD analysis
Figure 5.6 Powder XRD pattern of Cu$_2$(OH)$_3$(OAc).H$_2$O exchanged 1 to 1 with stable $^{127}$I spiking with 10% $^{125}$I- and stable $^{127}$I spiked with 10% $^{99}$TcO$_4^-$ after 60 days.

The PXRD data (Figure 5.6) collected on the samples of iodide and pertechnetate spiked are very similar and match well to the iodide exchanged material Cu$_2$(OH)$_3$I. The position and sharpness of the reflections are almost identical, however the intensity of some reflections are subtly different. The greatest difference in intensity of a reflection between samples occurs in the basal spacing reflection. The basal spacing reflection for the pertechnetate sample is slightly lower in intensity when compared to the same reflection observed in the iodide sample. Although this may indicate lower iodide content, the most likely explanation is preferred orientation in the iodide sample, as the intensity of the remaining reflections in both samples remains relatively similar. The phase purity and crystallinity of the LHSs do not seem to be effected by the presence of radiation.

5.2.2.2 Quantitative analysis of radiation

A gamma counter was used to determine the activity of $^{125}$I$^-$ and a liquid scintillation counter used to determine the activity of $^{99}$TcO$_4^-$ present in the solution pre and post exposure to Cu$_2$HA. Four aliquots of solution were taken; before exposure, after 10 min exposure, after retrieval of the exchange materials solid and after treatment with acid. The samples containing $^{125}$I$^-$ were diluted using distilled water (2ml) before being placed into the gamma counter, whereas the samples containing $^{99}$TcO$_4^-$ were added to a scintillation cocktail (10ml) (Table 5.2).
Chapter 5 - Stability and Applications of Copper Hydroxyacetate to the Nuclear Industry

<table>
<thead>
<tr>
<th></th>
<th>10% NH$_4$$^{125}$I, cpm (% error)</th>
<th>10% Na$^{99}$TcO$_4^-$, cpm (% error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counts pre exposure to Cu$_2$HA in solution.</td>
<td>742.8 (2.1%)</td>
<td>1305.2 (1.9%)</td>
</tr>
<tr>
<td>Counts after 10 mins post exposure to Cu$_2$HA in solution.</td>
<td>107.2 (4.1%)</td>
<td>326.1 (3.7%)</td>
</tr>
<tr>
<td>Counts after 60 mins post exposure to Cu$_2$HA in solution.</td>
<td>60.0 (4.8%)</td>
<td>157.1 (5.1%)</td>
</tr>
<tr>
<td>% loss of radionuclide from solution after 10 mins.</td>
<td>85.6 %</td>
<td>74.9%</td>
</tr>
<tr>
<td>% loss of radionuclide from solution after 60 mins.</td>
<td>9.19 %</td>
<td>88.0%</td>
</tr>
<tr>
<td>Radionuclide counts in solution post exposure to acid solution.</td>
<td>673.7 (2.8%)</td>
<td>1134.8 (2.2%)</td>
</tr>
<tr>
<td>% difference</td>
<td>90.7 %</td>
<td>86.9%</td>
</tr>
</tbody>
</table>

Table 5.2 Activity (cpm) of spiked iodide and pertechnetate solutions (background corrected).

After 10 min exposure, 85.6% of $^{125}$I has been lost from solution increasing further to 91.9% after 60 mins. This value agrees with previous gravimetric analysis (92.2 %) and data collected using the ion specific probe (92.9%), indicating that the calculated exchange capacity of copper hydroxysalts with respect to an equimolar amount of iodide is approximately 92%. In the case of $^{99}$TcO$_4^-$, initially 75.0% of the activity in solution is lost, increasing to 88.0% after 60 mins. The similar relative anionic radius of the two anions gives reason to think the rate of exchange will be similar; however after 10 min 6% more $^{125}$I is immobilised compared to that of $^{99}$TcO$_4^-$ . This initial reduction in uptake is most likely due to a preferred migration of iodide into the gallery spacing over pertechnetate, owing to slightly decreased anionic radius of iodide. The comparative uptakes 89.7% and 91.9% after 60 mins are more agreeable. When samples are broken down with acid to release the active species back into solution, this quantity is less than what was taken out of solution originally. Both experiments were performed within 2 hours of each other; therefore loss of activity as a result of decay will be minimal. A 1.2 % and 1.1 % difference in iodide and pertechnetate respectively constitutes a significant loss. When trying to find an explanation for this observation, comparisons with quantitative results obtained in chapter 4 can be drawn. For the iodide analogue, wet samples analysed using the ion specific probe and gamma counting gave iodide loss from solution as 92.9% and 91.9% respectively. When these results are compared to quantitative values obtained using samples that have been washed and dried, an iodide content of 92.2 % using the gravimetric analysis and 90.7 % using a gamma counter is observed. A difference of 0.7 % and 1.2 % correspondingly is most likely as a result of physisorption of the anion to the exchange material. Analysis of wet samples accounts for physisorption by registering a loss of iodide from solution, whereas samples that have been washed and dried do not account for physisorption as the anion has been removed.

5.3 Stability of Cu LHSs in a chemically diverse caustic environment

As previously discussed, the most probable disposal route for solid waste is via encapsulation in a cementitious environment and subsequent storage in an underground repository. The basic nature of copper hydroxysalts was one the main reasons it was selected as a potential storage material, however unlike LDHs, LHSs perform less well at high pH (as a result of hydroxide deficiencies) and are more likely to break down thus releasing the trapped anion. The selection of
cement used in the encapsulation of solid waste is vital to the application of LHSs in the long term storage of radio-anions. In order to determine the effect of pH on LHSs, several experiments were designed specifically to gain both a quantitative loss of anions as a function of pH and how the crystal structure of the copper hydroxysalt is affected.

5.3.1 Experimental

5.3.1.1 Effects of high pH

Solutions of NaHCO₃ (0.05M) with the pH adjusted using NaOH (0.1M) ranging from pH 9 to pH 12.5 (via 0.5 intervals) (10ml) were prepared. Cu₂(OH)₃(I) (0.0015M) was suspended and stirred in each solution (along with a pH 7 standard solution) for 16 days. The resulting suspensions were washed with deionised water, filtered under suction and dried at 50°C.

In addition to this, 10% spiked samples containing active ¹²⁵I and ⁹⁷TcO₄ were prepared as described previously. These samples (~90mg) were suspended in similar solutions (3ml) as above and left for 16 days with occasional agitations. Samples (100µl) of the solutions were taken after 2 days, 4 days, 6 days, 8 days, 10 days and 16 days to identify the effect of the presence of (OH)⁻ anions have on Cu₂(OH)₃Cl.

5.3.1.2 Stability as a Function of carbonate

![Figure 5.7 Apparatus used to saturate a solution using CO₂ gas.](image)
Samples of Cu₂(OH)₃X (X = I, Cl and NO₃) were prepared and added to a saturated solution of CO₃²⁻ to determine the effect of large concentrations on carbonated anions on the stability of a LHS. CO₂ gas was bubbled through a sealed vessel of deionised water (20ml) for 1 day to enable a solution containing CO₃²⁻ to form. Samples of Cu₂(OH)₃I (0.0015M) were suspended and stirred in solution for 1 day whilst still maintaining a steady flow of CO₂ gas (Figure 5.7). The resulting suspensions were washed with deionised water, filtered under suction and dried at 50°C.

### 5.3.1.3 Stability in the presence of other anions

Equimolar solutions of NaCl and NaNO₃ (3.5% and 5.25% by mass) were prepared. Several volumes of the solution were measured into vessels (1.0 ml, 1.5 ml, 2.5 ml, 5.0 ml, 10.0 ml and 25ml). Samples of Cu₂(OH)₃I (0.4575g, 0.0015M) were suspended with minimal shaking and the reaction vessel sealed for 1 day. The resulting suspensions were washed with deionised water, filtered under suction and dried at 50°C. Exposure of Cu₂(OH)₃I to ground water movements has the potential to introduce anions, such as chloride, which may exchange with an occupying radio-anion. A chloride solution of 3.5% was chosen as this represents the average salt content of sea water and presents an extreme environment to determine the amount of contact with sea water needed to facilitate a release. Nitrate anions at 5.25% mass were chosen to represent a comparison with a larger anion at an identical molarity (Table 5.3).

![Table 5.3](image)

<table>
<thead>
<tr>
<th>Amount of 3.5% NaCl and 5.25% NaNO₃ solution (ml)</th>
<th>% Cl⁻ or NO₃⁻ in solution compared to I⁻ anions in CuHI used.</th>
<th>Molar equivalence (I⁻ : X⁻ (X = NO₃⁻ or Cl⁻))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>2.5:1</td>
</tr>
<tr>
<td>1.5</td>
<td>60</td>
<td>1.6:1</td>
</tr>
<tr>
<td>2.5</td>
<td>100</td>
<td>1:1</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>1:2</td>
</tr>
<tr>
<td>10</td>
<td>400</td>
<td>1:4</td>
</tr>
<tr>
<td>25</td>
<td>1000</td>
<td>1:10</td>
</tr>
</tbody>
</table>

Table 5.3 % chloride and nitrate in increasing quantities of 3.5% NaCl and 5.25% NaNO₃ solutions of iodide present in CuHI.

### 5.3.1.4 Characterisation

XRPD patterns, IR spectra and activity counting data were collected as previously described in chapter 2. XRPD patterns were collected from 5 - 60° 2θ with a step size of 0.014°. FT-IR data were collected from 4000cm⁻¹ to 400cm⁻¹ wavenumbers over 16 datasets.

### 5.3.2 Results

#### 5.3.2.1 Effects of high pH

Comparing the colour of the samples after 16 days, no real change can be noted from pH 7 to pH 10 whereby a bright green colour is maintained. At pH 11, the sample darkens slightly; however from pH 11.5 onwards, a drastic colour change from bright green to dark brown to black is observed.
This colour change seems to suggest the formation of copper oxide and/or copper iodide, and not copper hydroxide (Figure 5.8).

Figure 5.8 A photo showing the colour of the product recovered when Cu₂HI is exposed to solutions of varying pH.

Figure 5.9 XRPD pattern of (a) Cu₂(OH)₃I post exposure to a variety of pH solutions (*=CuO).

XRPD patterns (Figure 5.9) show that Cu₂HI reflections decrease in intensity and broaden slowly as the pH is increase from 9 - 12. Reflections do seem to reduce more dramatically between pH 10 and pH 11, and as the pH increases above 12, Cu₂HI reflections disappear completely. At pH 12, broad and weak reflections indicate the formation of CuO. Reflections at pH 12.5 indicate the presence of CuO only, consistent with the black substance formed. This experiment seems to
suggest that the exchanged Cu$_2$HI material is stable up to pH 10. Past pH 11.0, Cu$_2$HI breaks down to form copper oxide. Interestingly no trace of a carbonate or hydroxide containing phase is observed despite earlier exchange reactions in chapter 4 of this study between the hydroxide anion being successful.

![Figure 5.10 FTIR spectra of Cu$_2$(OH)$_3$I post exposure to a variety of pH solutions.](image)

FTIR data (Figure 5.10) seems to agree with XRPD data whereby the intensity of the absorption bands are unchanged until pH 10. Past pH 11, the intensity of the bands decreases steadily until only trace amounts of the LHS remains from pH 12 onwards. The reduction of the hydroxide bands in the region 3600 – 3400 cm$^{-1}$ indicates that no exchange of iodide for hydroxide occurs. Absence of a band in the region 1600 – 1400 cm$^{-1}$ confirms no carbonate is present in the product recovered. The colour of the products recovered, XRPD data and FT-IR analysis all suggest that Cu$_2$(OH)$_3$I breaks down forming copper oxide.

Previous exchange reactions in chapter 4 involving equimolar amounts of copper hydroxyacetate with hydroxide anions resulted in the formation of copper hydroxide and sodium acetate. When copper hydroxyiodide is exposed to solutions of up to pH 10, a decreased interlayer spacing and increased stability means that the formation of copper hydroxide is inhibited. When the quantity of hydroxide anions increases to excess (a ratio of OH$^-$ to I$^-$ of greater than 1:1), copper hydroxide is formed as with the acetate analogue; however a further reaction with hydroxide anions results in the formation of copper oxide and water (Equation 5.4).
Hydroxide formation  \[ \text{Cu}_2(\text{OH})_3\text{I} \text{ + NaOH } \rightarrow 2\text{Cu(OH)}_2 \text{ + NaI} \]

Oxide formation  \[ 2\text{Cu(OH)}_2 \text{ + NaOH } \rightarrow 2\text{CuO} \text{ + 2H}_2\text{O} \text{ + NaOH} \]

Equation 5.4  Copper oxide formation in a highly basic solution.

Quantitative analysis of the activity of \(^{125}\text{I}\) and \(^{99}\text{TcO}_4^-\) in solution when active samples are exposed to various pH solutions offers a better insight into the loss of iodide and pertechnetate as a function of pH (Table 5.4).

<table>
<thead>
<tr>
<th>pH</th>
<th>2 days (cpm)</th>
<th>4 days (cpm)</th>
<th>6 days (cpm)</th>
<th>9 days (cpm)</th>
<th>16 days (cpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>79.82(12.2)</td>
<td>120.17(11.2)</td>
<td>101.18(11.5)</td>
<td>128.69(10.8)</td>
<td>152.69(10.1)</td>
</tr>
<tr>
<td>9.5</td>
<td>109.25(10.4)</td>
<td>129.55(10.8)</td>
<td>242.70(8.44)</td>
<td>346.21(8.25)</td>
<td>427.99(6.88)</td>
</tr>
<tr>
<td>10</td>
<td>128.40(10.2)</td>
<td>144.85(8.87)</td>
<td>262.98(8.84)</td>
<td>384.86(8.45)</td>
<td>437.57(6.79)</td>
</tr>
<tr>
<td>10.4</td>
<td>134.38(8.80)</td>
<td>177.65(8.39)</td>
<td>302.43(7.72)</td>
<td>349.28(6.80)</td>
<td>440.60(6.06)</td>
</tr>
<tr>
<td>11</td>
<td>174.31(7.16)</td>
<td>292.97(7.33)</td>
<td>319.86(6.76)</td>
<td>432.82(6.44)</td>
<td>475.55(5.73)</td>
</tr>
<tr>
<td>11.6</td>
<td>330.08(6.64)</td>
<td>331.09(6.58)</td>
<td>393.96(6.07)</td>
<td>521.59(5.42)</td>
<td>595.16(5.34)</td>
</tr>
<tr>
<td>12.2</td>
<td>402.33(6.17)</td>
<td>526.35(5.49)</td>
<td>614.15(5.35)</td>
<td>635.39(5.08)</td>
<td>638.83(5.16)</td>
</tr>
</tbody>
</table>

Table 5.4  Activity counts when \(\text{Cu}_2(\text{OH})_3^{(127}\text{I})_{0.9(125}\text{I})_{0.1}\) is exposed to solutions ranging from pH 7 to pH 12.2 over 16 days (maximum = 755 cpm) (errors in %)

From the plotted graph (Figure 5.11), it is clear that even in a neutral solution, iodide loss occurs steadily over 16 days to maximum of 20.22%. It was previously noted that when suspended in de-ionised water, copper hydroxyacetate turns from pale blue to black indicating the formation of copper oxide. XRPD and IR analysis however indicated the presence of the parent acetate LHS only. This seemed to suggest that the oxide phase forms on the surface of the particles as a result of acetate migration out of the layer. Since the iodide analogue has a smaller interlayer spacing, this effect was assumed to be reduced if not completely absent. It is noted that in de-ionised water, \(\text{Cu}_2\text{HI}\) undergoes no colour change suggesting this assumption is correct. However a 20.3% loss of iodide represents a significant amount. From pH 9.5 - pH 11.0, iodide loss increases slowly and at a similar rate ranging from 14.5% to 23.0% after 2 days, from 42.9% to 62.9% after 9 days and from 56.7% to 63.0% after 16 days. At pH 11.6, the initial loss of iodide after 2 days, 43.7%, is significantly bigger than that observed in lower pH solutions. After 16 days, the total loss of iodide at pH 11.5 levels out somewhat, 78.8%, however the loss observed is significantly higher than that observed in lower pH solutions. A significant increase in iodide loss is observed when the pH is increased above 12.2. After just 2 days exposure to pH 12.2 solutions, a loss of 53.2% is observed. When in a pH 12.2 solution, iodide loss increases at a steady rate over the next 7 days to a value of 84.1%. This value remains relatively stable over the next 7 days to a maximum of 84.6%.
Figure 5.11 A graph showing activity counts when Cu$_2$(OH)$_3$(I$^{127}$)(I$^{125}$) is exposed to solutions ranging from pH 7 to pH 12.2 over 16 days.
Table 5.5 Activity counts when Cu$_2$(OH)$_3$(127$I$)$_{0.9}$(99TcO$_4$)$_{0.1}$ is exposed to solutions ranging from pH 7 to pH 12.2 over 16 days (max = 1351 cpm)(% errors shown).

<table>
<thead>
<tr>
<th>pH</th>
<th>2 days (cpm)</th>
<th>4 days (cpm)</th>
<th>6 days (cpm)</th>
<th>9 days (cpm)</th>
<th>16 days (cpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>164.42(5.23)</td>
<td>243.54(4.53)</td>
<td>330.01(3.88)</td>
<td>360.29(3.86)</td>
<td>334.34(3.42)</td>
</tr>
<tr>
<td>9</td>
<td>387.07(3.36)</td>
<td>498.20(2.93)</td>
<td>764.06(2.36)</td>
<td>863.11(2.27)</td>
<td>995.82(2.09)</td>
</tr>
<tr>
<td>9.5</td>
<td>369.77(3.56)</td>
<td>463.61(3.28)</td>
<td>764.43(2.59)</td>
<td>937.75(2.22)</td>
<td>1071.2(2.06)</td>
</tr>
<tr>
<td>10</td>
<td>383.04(3.46)</td>
<td>713.39(2.54)</td>
<td>826.61(2.26)</td>
<td>940.83(2.19)</td>
<td>1056.3(2.08)</td>
</tr>
<tr>
<td>10.4</td>
<td>487.73(3.02)</td>
<td>478.87(3.01)</td>
<td>938.50(2.13)</td>
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<td>1234.5(2.00)</td>
<td>1264.5(2.00)</td>
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</tr>
</tbody>
</table>

When samples of Cu$_2$(OH)$_3$(127$I$)$_{0.9}$(99TcO$_4$)$_{0.1}$ are exposed to solutions ranging from pH 7 to pH 12.5 for 16 days, a different pattern of TcO$_4^-$ loss is observed compared to iodide (Table 5.5). From the plotted graph (Figure 5.12), TcO$_4^-$ loss increases steadily from 12.6% - 17.9% from 2 to 4 days respectively in a neutral solution. This value then remains stable over the next 12 days to a maximum of 25.6%. This value represents an increased TcO$_4^-$ loss of 5.3% over I$. Giving that the % errors in these experiments range from 2-10%, a difference of 5.3% may not be enough to be considered significant. Upon exposure to solutions of pH 9 – 10.4, pertechnetate loss is relatively consistent. After 2 days, TcO$_4^-$ loss ranges from 28.6% at pH 9 to 29.7% at pH 10.4. These values increase to 73.36% and 81.0% correspondingly after 16 days. These values represent a significant increase in TcO$_4^-$ loss compared to I$. At pH 11, an initial loss of 39.7% is 10% greater than that observed at pH 10.4. After 16 days, the quantity of pertechnetate lost at pH 11 is only 3.6% greater than that observed at pH 10.4. When the pH is increased to 12.5, an initial loss of 90.1% is observed after 2 days with this figure increasing to 99.1% after 16 days.
Figure 5.12  A graph showing activity counts when Cu$_2$(OH)$_3$(I$^{127}$)(TcO$_4$) is exposed to solutions ranging from pH 7 to pH 12.5 over 16 days.
It is clear from these results that the pertechnetate analogue is less stable as a function of basicity compared to iodide. When tracking the initial uptake into the exchange materials, it was noted that the rate of exchange for $\text{TcO}_4^-$ was slower than that observed with $\Gamma^-$. This observation was attributed to $\text{TcO}_4^-$ having a slightly larger anionic radius than $\Gamma^-$. This same reasoning can be used to explain the increased loss of $\text{TcO}_4^-$. It is also clear that XRPD and FTIR are not effective methods for estimating the quantity of an anion located within the interlayer spacing of a LHS. No obvious changes in either XRPD patterns or FTIR spectra are observed until Cu$_2$HI is exposed to a pH 11 solution. According to quantitative analysis, at this point ~60% of the immobilised iodide anion has been released back into solution. From the quantitative analysis it is noted that at pH 12.2, the released iodide levels in solution remain relatively stable from 6 days onwards whereas an increase in iodide levels up until 16 days is observed in all other pH solutions. This relative stability of the solution at pH 12.2 may allow CuO to form and thus be more apparent on the diffraction pattern. The presence of any amorphous CuO would be difficult to detect by PXRD techniques other than an increase in background counts in the 2theta regions, as well as a decrease in intensity of the Cu$_2$HI reflections; neither of these effects are obvious from analysis of the XRD data. XRPD and FTIR seem to suggest the material is stable until pH 11 with respect to the iodide analogue; however quantitative analysis of both the $\text{TcO}_4^-$ and $\Gamma^-$ analogues clearly shows that the material is not affective at retaining the immobilised anion even in a pH 7 solution.

### 5.3.2.2 Stability as a function of carbonate

![Figure 5.13 XRPD patterns of samples of Cu$_2$HI, Cu$_2$HCl (botallackite) and Cu$_2$HNO$_3$ post exposure to a saturated CO$_3^{2-}$ solution for 1 week (blue = Cu$_2$(OH)$_2$(CO$_3$), green = CuI, red = Cu$_2$HCl (botallackite))](image)

From the XRPD patterns, it is clear that the presence of an excess amount of CO$_3^{2-}$ has a large influence on the stability these samples. In the case of Cu$_2$HNO$_3$, broad reflections show the presence of malachite (Cu(OH)$_2$(CO$_3$)) only. When CuHI is exposed to CO$_3^{2-}$, broad reflections indicating the presence of malachite are present as well as sharp reflections for CuI. The relative
intensities show that CuI seems to be in the majority. The botallackite structure remains largely intact, however broad reflections of low intensity also show the presence of malachite in minority. The relative stability of the LHSs indicates that as expected, chloride with a reduced interlayer spacing is more stable than iodide and acetate analogues. Interestingly when Cu₂HI is exposed to a saturated carbonate solution, insoluble CuI is produced. Upon exposure of Cu₂(OH)₃X (X= Cl, I, NO₃) to a saturated carbonate solution, malachite is formed along with a soluble Cu₅X₂ salt. In the case of the iodide analogue, Cu₅I₂ is unstable. Either in solution or upon drying, two iodides oxidise to form iodine and 2 electrons. One of these electrons reduces CuI to Cu and the other reduces half the amount of iodine produced earlier to form I⁻. CuI then reacts with I⁻ to form CuI (Equation 5.5).

Malachite formation

\[ 4\text{Cu}_2(\text{OH})_3X(s) + 3\text{H}_2\text{CO}_3(aq) \rightarrow 2\text{Cu}X_2(s) + 3\text{Cu}_2(\text{OH})_2(\text{CO}_3)(s) + 6\text{H}_2\text{O}(l) \]

Cul formation

\[ \text{CuI}_2(aq) \rightarrow \text{Cu}^{2+}(aq) + 2\text{I}^-(aq) \rightarrow \text{Cu}^{2+}(aq) + I_2(l) + 2e^- \rightarrow \text{Cu}^{+}(aq) + \frac{1}{2}I_2(g) + \text{I}^-(l) \rightarrow \text{CuI}(s) + \frac{1}{2}I_2(g) \]

Equation 5.5 Malachite and Cul formation in a saturated carbonate solution.

Figure 5.14 FTIR spectra of Cu₂(OH)₃X (X = NO₃, I, Cl) and post exposure to a saturated carbonate solution for 7 days (blue line = bands indicative of the \( \nu_3 \) stretching mode of the carbonate anion in malachite).

FT-IR data for the nitrate analogue shows that post exposure to a saturated carbonate solution, broad hydroxide bands in the region 3600 – 3000 cm⁻¹ remain. Three bands indicative of the nitrate anion located at 1415, 1307 and 1046 cm⁻¹ disappear and are replaced by two bands located at 1490 and 1383 cm⁻¹ that represent \( \nu_3 \) stretching modes of the carbonate anion. The FTIR pattern
obtained for the sample of Cu₂HI exposed to a saturated carbonate solution is almost identical to the pattern obtained for the nitrate analogue. In the case of the chloride analogue, a small reduction in intensity of the IR bands indicates some loss of the LHS structure and this is consistent with the appearance of bands indicative of malachite (Figure 5.14).

From the data obtained, it is clear that in a high carbonate environment, LHSs are not stable. Exchange reactions involving an equimolar amount of carbonate were unsuccessful earlier in this study; however in a saturated solution, nitrate and iodide analogues completely decompose whereas the chloride analogue undergoes partial decomposition. This indicates that the decreased interlayer spacing of the chloride analogue increases stability. The fact that CuI is formed as a result of carbonate exposure may be regarded as a positive result with respect to possible applications in the nuclear industry. The formation of an insoluble immobilised copper iodide phase still serves the purpose, however based on the equation for the decomposition of Cu₂HI, some iodine must still remain in solution.

5.3.2.3 Stability in the presence of other anions

When Cu₂HI is exposed to increasing quantities of 3.5% NaCl solution, XRPD patterns indicate that exchange of Cl⁻ for I⁻ occurs in only 1ml 3.5% NaCl solution when the iodide to chloride ratio is only 2.5:1. The iodide basal spacing reduces by approximately 50% with a small broad reflection indicating chlorite is exchanged into the layers. The basal spacings of the iodide and chloride analogues are in ratio of ~ 4:1. When Cu₂Hi is added to a 1.5ml NaCl solution (1.6:1), the iodide and chloride basal spacing reduce and intensify respectively to a ratio of ~ 1:1. In a 2.5 ml (1:1) NaCl solution, the chloride basal spacing intensifies to a ratio of ~ 9:1 with respect to the iodide basal spacing. Doubling the volume of the NaCl solution to 5ml (1:2) and 10ml (1:4) results in the complete disappearance of the iodide basal spacing, with the chloride basal spacing becoming the most prominent. This suggests there is enough Cl⁻ in the solution for complete exchange of I⁻ with Cl⁻ producing a botallackite phase.

Figure 5.15 XRPD patterns of Cu₂HI when exposed to several volumes of 3.5% NaCl solution for 1 day (Green line = Cu₂HI, blue line = Cu₂HCl)(ratios shown as I⁻ : Cl⁻).
FTIR data shows a progressive loss and gain of absorption bands indicative of Cu₂HI and Cu₂HCl respectively. Several bands overlap, however it is clear that two bands attributed to the iodide analogue at 827 cm⁻¹ and 645 cm⁻¹ slowly reduce in intensity as the volume increases. Both bands completely disappear when Cu₂HI is exposed to 10ml 3.5% NaCl solution. Two bands at 860 cm⁻¹ and 690 cm⁻¹ indicate the presence of the chloride analogue. These bands are present at 1 ml and slowly increase in transmittance as the volume is increased.

Figure 5.16 FTIR spectra of Cu₂HI when exposed to several volumes of 3.5% NaCl solution for 1 day (Green line = Cu₂HI, blue line = Cu₂HCl)(ratios shown as I⁻ : Cl⁻).

Figure 5.17 XRPD patterns of Cu₂HI when exposed to several volumes of 5.25% NaNO₃ solution for 1 day (Green line = Cu₂HI, blue line = Cu₂HNO₃). (ratios shown as I⁻ : NO₃⁻).
When Cu₂HI is exposed to increasing quantities of 5.25% NaNO₃ solution, XRPD patterns indicate that exchange of NO₃⁻ for I⁻ does not occur until exposed to 5ml, representing an iodide to nitrate ratio of 1:2. Interestingly a progressive shift of the basal spacing reflection along the x axis is observed rather than the appearance of a separate basal spacing reflection for the nitrate analogue. The shift progresses as the volume of solution used increases until it reaches the expected 2θ value of the nitrate analogue at 12.99º at a volume of 25ml. This represents a nitrate to iodide ratio of 10:1 until full exchange is achieved.

![Figure 5.18 FTIR spectra of Cu₂HI when exposed to several volumes of 5.25% NaNO₃ solution for 1 day (Green line = Cu₂HI, blue line = Cu₂HNO₃). (ratios shown as I⁻ : NO₃⁻).](image)

Strong bands at 1413 cm⁻¹, 1315 cm⁻¹ and 1043 cm⁻¹ indicate the nitrate anion is bound to the layers in volume 5ml – 25ml. The intensity of these bands does increase a little, however this may just be due to experimental differences rather than a quantitative difference. As with the chloride analogue, overlapping of bands is observed in the fingerprint region, however a band located at 825 cm⁻¹ indicative of the iodide analogue does decrease in intensity from 2.5 ml to 5 ml and disappears at 10ml.

From the results obtained it is clear that Cu₂HI is more stable with respect to nitrate than chloride. Exchange of available chloride for iodide is apparent in ratio of 1:2.5 whereas a nitrate ratio of 2:1 is required before PXRD and FTIR data suggests an exchange has occurred. Complete iodide release with respect to chloride and nitrate is observed in a ratio of 1:4 and 1:10 respectively. This is...
as expected because the smaller chloride anion can migrate into the interlayer spacing of the iodide LHS easier than the larger nitrate anion.

5.4 Conclusion

The primary aim of this chapter was to determine the stability of Cu$_2$HI in caustic, carbonated and high chloride / nitrate solutions. The primary concern associated with LHSs is stability in high pH conditions due to an inherent hydroxide deficiency. PXRD and FTIR analysis suggests that the use of low pH cements with a pH range of 9-11 is not caustic enough to facilitate a release of the immobilised anion into the geosphere. Quantitative radiometric analysis however seems to suggest that even low pH cements (pH 9-11) would significantly interact with a LHS. It seems that the presence of hydroxide anions exchange with iodide with almost 100% efficiency, and even in a neutral pH 7 solution, causes migration of iodide and pertechnetate out of the interlayer spacing. Carbonate present in high amounts in solution also has a significant interaction with LHSs. In a 1:1 exchange reaction, LHS have no interaction with carbonate indicating relative stability when compared to LDHs [43]. Exchange of carbonate for the occupying anion in LDHs has been shown to occur even in small amounts. The interaction of a high amount of carbonate with a copper based LHS results in the formation of a non-layered compound malachite. This reaction is therefore not a true anion exchange, as observed with other anions of di- or tri- valency. Finally, stability of Cu$_2$HI with respect to other anions has been investigated. As expected, chloride anions easily replace iodide in the interlayer spacing with almost direct 1:1 exchange observed. Stability of Cu$_2$HI with respect to nitrate is increased, however it is clear that with enough nitrate present (10:1), full exchange may be achieved. From these results it is clear that LHSs are not stable in a cementitious environment and the long term immobilisation of iodide cannot be achieved. The use of LHSs in the separation of anionic waste into well defined streams is definitely a route that may be considered. Much in the same way that TPPB is used to temporarily separate $^{99}$TcO$_4^-$ until a better long-term storage solution is found, LHSs may be used as a safer non-organic alternative to TPPB. This would not only be applicable to pertechnetate, but a whole range of radio-anions. The long term stability of LHSs when kept in a dry has been proven and, when considering an appropriate anion exchange material for use in extracting particularly iodide out of nuclear waste streams, LHSs seem like a very good option for current and future nuclear waste needs.
5.5 References

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Chapter 6

Polymorphism of Cu$_2$(OH)$_3$Cl
This chapter further investigates the LHS Cu₂(OH)₃Cl (botallackite) synthesised in chapter 4 and its relationship to the other polymorphs of Cu₂(OH)₃Cl. The purpose of this chapter is two-fold: firstly to investigate and contrast reported synthetic techniques for polymorphs with the composition Cu₂(OH)₃Cl, and compare the crystalinity of synthetic samples to mineral samples; secondly to study the interconversion of Cu₂(OH)₃Cl polymorphs in a bid to reinvestigate previously reported data and propose a simpler conversion route/mechanism for synthesis.

6.1 Introduction

As demonstrated in chapter four, the anion exchange reaction of copper (II) hydroxyacetate with sodium chloride in water forms a modification of copper hydroxychloride, Cu₂(OH)₃Cl, known as botallackite. Cu₂(OH)₃Cl is known to exist naturally as four polymorphic minerals; atacamite, botallackite, clinoatacamite and anatacamite [1, 2, 3, 4]. The polymorphism exhibited by Cu₂(OH)₃Cl is unique amongst the basic copper hydroxyhalide series. To date, atacatmite, botallackite and clinoatacamite have been synthesised in the laboratory, whereas no synthetic version of anatacamite has been reported [5, 6, 7, 8, 9]. Synthetic atacamite and synthetic botallackite have previously been reported as unstable with respect to clinoatacamite both when suspended in solution and when heated in air [10, 11, 12]. This is contradictory to the stability shown by botallackite synthesised earlier in this study via anion exchange, which remained stable when suspended in solution and when heated in air. This result led to further investigation into the synthesis and stability of polymorphous Cu₂(OH)₃Cl, as well as possible applications for the immobilisation of the radio anion ³⁶Cl⁻.

6.1.1 Relevance to the nuclear waste industry

Graphite is a material often used in the nuclear industry with applications as a moderator in magnox or advanced cooling towers. Prior to its use, graphite is exposed to chlorine gas or chloride containing compounds at temperatures up to 2775K in order to remove boron and other impurities. This treatment leaves a residue of chlorine that, when exposed to a radioactive environment, forms the radio isotope ³⁶Cl (t½ = 3 x 10⁵ years). Any possible contact of waste graphite with water could lead to the release of ³⁶Cl, which as ³⁶Cl⁻, would be extremely mobile in the geosphere and a danger to the biosphere [13, 14, 15]. In this study, Cl⁻ has been shown to undergo an exchange reaction with OAc⁻ using [Cu₂(OH)₃]⁺ as the carrier cation. There is a possible application of this reaction in the trapping of potentially dangerous ³⁶Cl⁻ as botallackite. However, due to the reported poor stability of botallackite, subsequent exchanges and/or decomposition may occur, thus releasing ³⁶Cl⁻ back into the environment.

6.1.2 Occurrence and crystal structure of atacamite

Atacamite was first documented by Haüy in 1801 [16] and its crystal structure solved by Wells in 1949 [1]. It is a green-blue cross-linked layered material crystallising with an orthorhombic unit cell in the space group Pmcn, with lattice parameters a = 6.84 Å, b = 9.13 Å, c = 6.01 Å. Atacamite is named after the locality of discovery in the Atacama Desert, Chile, and tends to form as a secondary copper mineral through oxidation of other copper minerals, especially under arid, saline conditions. It also forms as a surface deposit on calcite and magnesite spar crystals that are submersed in water with a high chloride concentration, in
fumarolic deposits as a weathering product of sulfides in subsea black smoker deposits and as an alteration product of bronze and copper objects of antiquity \[^17, 18\].

Figure 6.1 shows the crystal structure of atacamite, consisting of layers with distorted octagonal vacancies linked by single octahedra. Atacamite has two Cu sites both with octahedral coordination, but of differing compositions; Cu(1) \([\text{Cu}_2(\text{OH})_4\text{Cl}_2]\) and Cu(2) \([\text{Cu}(\text{OH})_5\text{Cl}]\). A \((4 + 2)\) distortion is observed with respect to the \([\text{Cu}_2(\text{OH})_4\text{Cl}_2]\) octahedron with Cu-O bonds being shorter than those of Cu-Cl. The second \([\text{Cu}(\text{OH})_5\text{Cl}]\) octahedron shows \((4 + 2)\) distortion with a single chlorine and oxygen apical atoms \[^{19, 20, 21}\].

![Crystal structure of atacamite](image)

**Figure 6.1** a) Crystal structure of atacamite: bc projection showing 2 crystallographically unique Cu sites with octahedral co-ordination; b) Cu(1) \([\text{Cu}_2(\text{OH})_4\text{Cl}_2]\) and Cu(2) \([\text{Cu}(\text{OH})_5\text{Cl}]\)

### 6.1.3 Occurrence and crystal structure of botallackite

Botallackite is a mineral that was first reported by Church in 1865 \[^4\] and its crystal structure solved by Frodel et al in 1958 \[^22\], then further refined by Hawthorne in 1985 \[^23\] and Kraus in 2006 \[^24\]. It is a blue layered material with a monoclinic crystal system that crystallises in the space group \(P2_1/m\), with lattice parameters \(a = 5.715\ \text{Å},\ b = 6.126\ \text{Å},\ c = 5.632\ \text{Å},\ \beta = 93.07^\circ\). Botallackite can be broadly classed in the same structure type as its layered nitrate analogue, rouaite \((\text{Cu}_2(\text{OH})_3(\text{NO}_3))\), as well as many other monoclinic anhydrous divalent metal layered hydroxyides (e.g.) with the chlorine atom bonded directly to the \((\text{Cu}_2(\text{OH})_3)^+\) layer. It is named after the type locality of the mineral in the Botallack mines, England. Botallackite tends to form as a secondary copper mineral in deposits exposed to high chloride concentrations (typically sea water). It has also been found as a reaction product of slag immersed in seawater as weathering product of sulfides in subsea black smoker deposits \[^{25, 26}\].
Figure 6.2 shows the crystal structure of botallackite, which has 2 crystallographically unique copper sites, both with octahedral co-ordination: \( \text{Cu}(1)[\text{Cu}(OH)\text{Cl}] \) and \( \text{Cu}(2)[\text{Cu}_2(OH)_4\text{Cl}_2] \). The structure consists of edge sharing octahedral sheets in the \( bc \) plane that are linked along the \( a \) direction via hydrogen bonding. As in atacamite, both copper atoms have short equatorial bonds in a square-planar arrangement with either two chlorine or one chlorine and one hydroxyl group bonded axially, exhibiting strong Jahn-Teller \(^{27}\).

Natural samples of botallackite are often found with a small amount of zinc and, to a lesser extent, magnesium substituted for copper. Substitution of \( \text{Zn}^{2+} \) or \( \text{Mg}^{2+} \) for \( \text{Cu}^{2+} \) past 25 atom\% forms two distinct mineral phases, the zincian kapellasite (triganol) or magnesian haydeeite (triganol) \(^{28}\).

![Figure 6.2](image)

**Figure 6.2** a) Crystal structure of botallackite: \( ac \) projection showing hydrogen bonding (blue line) between octahedral sheets and 2 crystallographically unique Cu sites with octahedral co-ordination; b) \( \text{Cu}(1)[\text{Cu}_2(OH)_4\text{Cl}_2] \) and \( \text{Cu}(2)[\text{Cu}(OH)_5\text{Cl}] \)

### 6.1.4 Occurrence and crystal structures of paratacamite, clinoatacamite and anatacamite

A third mineral, paratacamite, was first discovered by Herbert Smith in 1905 \(^{29}\) and then further examined and confirmed as a mineral phase by Frondel in 1950 \(^{30}\). Both studies used the same natural samples collected from the Herminia and Generosa mine, Sierra Gorda, and the Bolaco mine, San Cristóbal, Chile. Herbert Smith initially described paratacamite, \( \text{Cu}_4(OH)_6\text{Cl}_2 \), as a new polymorph of atacamite, with a rhombohedral morphology. This was confirmed by Frondel and its structure determined as rhombohedral in space group \( R-3m \). Single crystal X-ray Diffraction studies re-determined the structure of paratacamite as rhombohedral in space group \( R-3 \) with \( R-3m \) substructure \(^{31}\). It is named after its structural and chemical relationship to atacamite, and has been classed with a structure type \( \text{Cu}_{2+n}X_n(OH)_3\text{Cl} \) \( (X = \text{Zn} \text{ or Ni}, n =0.2-1.2) \). Paratacamite is a blue-green mineral that crystallises into the space group \( R-3 \), with lattice parameters \( a = 13.654 \text{ Å} \), \( c = 14.041 \text{ Å} \). It has been suggested by Jambor et al. \(^{32}\) that a partial substitution of up to 6
atom% copper with a non Jahn-Teller distorting divalent cation of similar in size (usually Zn, Ni or Co) is needed to stabilise the paratacamite structure. Substitution of Zn and Ni for copper with more than 6 atom% leads to the formation of the distinct mineral phases; herbertsmithitite (trigonal), Cu$_3$Zn(OH)$_6$Cl$_2$, Gillardite (trigonal), Cu$_3$Ni(OH)$_6$Cl$_2$, whereas with levels of substitution of Co >6 atom% a mixture of cobaltian paratacamite and Co(OH)$_3$Cl (rhombohedral) is observed.

The mineral now known as clinoatacamite was first recognized as a different species to that of paratacamite by Grice et al [33] and was named with reference to its monoclinic morphology and relationship to atacamite. Clinoatacamite is a blue mineral that crystallises with a monoclinic crystal unit cell in space group P2$_1$/n and lattice parameters $a = 6.157$ Å, $b = 6.814$ Å, $c = 9.104$ Å, $\beta = 99.65^\circ$. Clinoatacamite tends to form as a secondary copper mineral through oxidation of other copper minerals, especially in arid and saline conditions.

This structure has 3 crystallographically unique Cu sites, which are all octahedrally coordinated with the compositions: Cu(1) [Cu(OH)$_6$], Cu(2) [Cu(OH)$_4$Cl$_2$] and Cu(3) [Cu(OH)$_4$Cl$_2$]. The structure can be described as consisting of edge sharing octahedral layers that run along the [101] direction which are linked via edge sharing of the Cu(OH)$_6$ octahedra [34].

The crystal structure of paratacamite is similar to that of clinoatacamite. Offset layers of [Cu(OH)$_4$Cl$_2$] octahedra are linked by a single interlayer octahedron, as in clinoatacamite, however one in every two of the isolated [Cu(OH)$_6$] octahedra exhibits an axial compression. There are two crystallographically unique Cu sites in the paratacamite structure; Cu(1) has the composition [Cu(OH)$_6$] and Cu(2) has the composition [Cu(OH)$_4$Cl$_2$]. The Cu(1) site was found to allow up to 50%
substitution by a non-Jahn Teller distorting cation (such as Zn$^{2+}$, Ni$^{2+}$ and Co$^{2+}$). It was found that when the Cu(1) site had a mixed occupancy of Cu and M$^{2+}$ with between 33 and 50% M$^{2+}$, the mineral phase formed was paratacamite, when the occupancy of M$^{2+}$ was less than 33%, the mineral phase clinoatacamite was stabilised.

More recently, a fourth mineral named anatacamite has been described as a separate Cu$_2$(OH)$_3$Cl polymorph following the collection of a sample at Mina la Vendida, Atacama Desert, in 2003. Initially considered to be clinoatacamite, single crystal X-ray diffraction by Malcherek et al showed a distortion of the clinoatacamite substructure and found that anatacamite crystallises into space group P1, with lattice parameters $a = 9.165$ Å, $b = 9.203$ Å, $c = 9.210$ Å, $\alpha = 95.858^\circ$, $\beta = 96.290^\circ$, $\gamma = 96.507^\circ$ [3]. A summary of the structural information of the Cu$_2$(OH)$_3$Cl polymorphs is presented in Table 6.1

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<td>9.203</td>
<td>9.210</td>
<td>$\alpha = 95.858$ $\beta = 96.290$ $\gamma = 96.507$</td>
</tr>
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</table>

Table 6.1 A summary of the structural information of atacamite, botallackite, clinoatacamite, paratacamite and anatacamite.

6.1.5 Characterisation and stability studies of Cu$_2$(OH)$_3$Cl

The primary methods that have been used to characterise the Cu$_2$(OH)$_3$Cl polymorphs are XRD (both powder and single crystal), spectroscopic techniques (FT-IR and Raman) and thermal analysis (TGA, DSC and DTA). Data obtained from natural samples tends to disagree with data collected from synthetic samples, this is primarily due to natural samples often being multiphase and/or containing small amounts of zinc, magnesium and cobalt (either as oxide impurities or replacing Cu in the structure of Cu(OH)$_3$Cl). Data presented here from the above mentioned characterisation techniques taken from the literature, is either from pure mineral phases or synthetic samples.

6.1.5.1 Diffraction studies

The X-ray diffraction patterns of atacamite, botallackite, clinoatacamite and anatacamite are very similar with only subtle changes in the position of some reflections as a result of similar structures and unit cell parameters. The structure of botallackite is different enough from that of atacamite and clinoatacamite to be easily distinguished. The diffraction patterns of atacamite and clinoatacamite are visually similar. Zincian, cobaltian, magnesian and nickelian modifications of
Cu$_2$(OH)$_3$Cl also have similar diffractions patterns to the Cu$_2$(OH)$_3$Cl polymorphs. Table 6.2 shows the 5 most intense d-spacings and equivalent 2-theta positions (assuming the data were collected using Cu Kα radiation) of natural samples known to contain only copper.

<table>
<thead>
<tr>
<th></th>
<th>d$_1$ (i$_1$)</th>
<th>2θ$_1$</th>
<th>d$_2$ (i$_2$)</th>
<th>2θ$_2$</th>
<th>d$_3$ (i$_3$)</th>
<th>2θ$_3$</th>
<th>d$_4$ (i$_4$)</th>
<th>2θ$_4$</th>
<th>d$_5$ (i$_5$)</th>
<th>2θ$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atacamite [20]</td>
<td>5.48 (100)</td>
<td>16.15</td>
<td>5.03 (70)</td>
<td>17.61</td>
<td>2.27 (69)</td>
<td>39.66</td>
<td>1.61 (57)</td>
<td>57.14</td>
<td>2.75 (55)</td>
<td>32.4</td>
</tr>
<tr>
<td>Botallackite [24]</td>
<td>5.66 (100)</td>
<td>15.64</td>
<td>2.40 (80)</td>
<td>37.42</td>
<td>2.57 (70)</td>
<td>34.87</td>
<td>2.84 (40)</td>
<td>15.73</td>
<td>1.53 (40)</td>
<td>60.43</td>
</tr>
<tr>
<td>Clinoatacamite [33]</td>
<td>5.47 (100)</td>
<td>16.50</td>
<td>2.74 (70)</td>
<td>32.64</td>
<td>2.77 (60)</td>
<td>32.28</td>
<td>2.27 (60)</td>
<td>39.66</td>
<td>2.24 (50)</td>
<td>40.21</td>
</tr>
<tr>
<td>Paratacamite [31]</td>
<td>5.46 (100)</td>
<td>16.22</td>
<td>2.75 (80)</td>
<td>32.52</td>
<td>2.26 (60)</td>
<td>39.84</td>
<td>1.70 (45)</td>
<td>53.87</td>
<td>1.81 (35)</td>
<td>50.35</td>
</tr>
<tr>
<td>Anatacamite [31]</td>
<td>5.43 (100)</td>
<td>16.30</td>
<td>2.75 (94)</td>
<td>32.52</td>
<td>2.26 (56)</td>
<td>39.84</td>
<td>2.90 (31)</td>
<td>30.79</td>
<td>1.70 (29)</td>
<td>53.87</td>
</tr>
</tbody>
</table>

Table 6.2 The d-spacings and 2-theta positions (based on Cu radiation) of the polymorphs of Cu$_2$(OH)$_3$Cl with the relative intensity of reflections shown in brackets.

Figure 6.4 Theoretical PXRD patterns of (a) atacamite, (b) botallackite and (c) clinoatacamite using a wavelength of 1.54056Å [35].
6.1.5.2 Spectroscopic studies

The FT-IR and Raman spectra of all copper hydroxyl analogues are usually complex as a result of the low symmetry due to the distorted octahedral coordination of the copper sites. Two absorption bands in the region 3000-3600cm\(^{-1}\) and 600-1000cm\(^{-1}\) represent the stretching vibration frequencies and the planar deformation frequencies of the hydroxyl group respectively. The absorptions in the region 400-600cm\(^{-1}\) are due to the MO-H stretching vibrations. Table 6.3 shows the FT-IR and Raman absorption bands measured using synthetic samples of the copper hydroxychloride polymorphs.

<table>
<thead>
<tr>
<th>Atacamaite</th>
<th>Botallackite</th>
<th>Clinoatacamite</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR</td>
<td>Raman</td>
<td>IR</td>
</tr>
<tr>
<td>3457</td>
<td>3430</td>
<td>3510</td>
</tr>
<tr>
<td>3328</td>
<td>3347</td>
<td>3412</td>
</tr>
<tr>
<td>3208</td>
<td>3212</td>
<td>3402</td>
</tr>
<tr>
<td>1672</td>
<td></td>
<td></td>
</tr>
<tr>
<td>987</td>
<td>969</td>
<td>870</td>
</tr>
<tr>
<td>974</td>
<td>908</td>
<td>857</td>
</tr>
<tr>
<td>957</td>
<td>817</td>
<td>820</td>
</tr>
<tr>
<td>920</td>
<td>785</td>
<td>791</td>
</tr>
<tr>
<td>912</td>
<td>703</td>
<td>672</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>598</td>
<td>580</td>
<td>510</td>
</tr>
<tr>
<td>515</td>
<td>508</td>
<td>500</td>
</tr>
<tr>
<td>483</td>
<td>449</td>
<td>441</td>
</tr>
<tr>
<td>445</td>
<td></td>
<td></td>
</tr>
<tr>
<td>410</td>
<td>389</td>
<td>402</td>
</tr>
</tbody>
</table>

Table 6.3 The IR and Raman absorption bands of the different polymorphs of Cu\(_2\)(OH)\(_3\)Cl courtesy of the RRUFF website \(^{36}\) (RRUFF ID; atacamite = R050098, botallackite = R070066 and clinoatacamite = R090062).

The OH stretching frequencies show a progressive increase in the strength of hydrogen bonding of botallackite < atacamite < clinoatacamite. It has been shown that order-disorder transitions in crystalline substances are accompanied by characteristic changes of their infrared absorption spectra which stem from the changes taking place in the fields, polarising the ions of the crystal lattice \(^{37}\).

6.1.6 Stability of Cu\(_2\)(OH)\(_3\)Cl polymorphs

Only the chloride analogue, which is part of the Cu\(_2\)(OH)\(_3\)X hydroxide family of materials, exhibits polymorphism. Although atacamite, botallackite, clinoatacamite and anatacamite exist as minerals, attempts to provide reliable synthetic procedures which form stable Cu\(_2\)(OH)\(_3\)Cl polymorphs has been difficult. The stability of the polymorphs was investigated using thermal analysis techniques, which found that weight loss data collected on natural samples of Cu\(_2\)(OH)\(_3\)Cl did not agree with theoretical weight losses, calculated from their proposed decomposition routes \(^{38}\). According to
Sharkey et al in 1971, a progressive increase in the thermal stability of the polymorphs (botallackite < atacamite < clinoatacamite) is observed meaning natural samples tend to be multiphase. This explains the reason for the disagreement in the reported weight losses due to the difficulty in isolating single phase samples, as in most cases, all three polymorphs are present in a single sample. The trend of thermal stability seems to be related to the apparent difficulty in synthesis of the three polymorphs with botallackite proving the most challenging.

Equation 6.1 details the thermal decomposition of Cu$_2$(OH)$_3$Cl to CuO, which occurs in two well defined steps. With the absence of any adsorbed surface moisture and in an air atmosphere, dehydroxylation of the copper hydroxysalt occurs first leading to the formation of copper oxide, a copper oxychloride phase and water, with a 12.65% loss in weight. In the second step, loss of chloride gas via the reaction of copper oxychloride with oxygen leads to the formation of Cu(II)O with a loss of 12.83% weight. The decomposition route and weight loss is the same regardless of the starting polymorph of Cu$_2$(OH)$_3$Cl. Differences are observed in the temperatures at which each of the steps takes place for the different polymorphs as reported by Sharkey and Lewin. Equation 6.1 shows the calculated decomposition route and the temperature ranges as reported using a heating rate of 20ºC min$^{-1}$ in air.

\[
\text{Step 1} \quad 2\text{Cu}^{II}_2\text{(OH)}_3\text{Cl(s)} \rightarrow \text{Cu}^{II}\text{O} \cdot \text{Cu}^{2+}\text{Cl}_2(s) + 2\text{Cu}^{II}\text{O(s)} + 3\text{H}_2\text{O(g)} \quad 12.65\%
\]

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>atacamite</td>
<td>265-301°C</td>
</tr>
<tr>
<td>botallackite</td>
<td>251-281°C</td>
</tr>
<tr>
<td>clinoatacamite</td>
<td>254-295°C</td>
</tr>
</tbody>
</table>

\[
\text{Step 2} \quad \text{Cu}^{II}\text{O} \cdot \text{Cu}^{2+}\text{Cl}_2(s) + 2\text{Cu}^{II}\text{O(s)} + \frac{1}{2}\text{O}_2(g) \rightarrow 4\text{Cu}^{II}\text{O(s)} + \text{Cl}_2(g) \quad 12.83\%
\]

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>atacamite</td>
<td>399-442°C</td>
</tr>
<tr>
<td>botallackite</td>
<td>413-437°C</td>
</tr>
<tr>
<td>clinoatacamite</td>
<td>407-443°C</td>
</tr>
</tbody>
</table>

Equation 6.1 The thermal decomposition route of Cu$_2$(OH)$_3$Cl in air.

Inter-conversion of polymorphic Cu$_2$(OH)$_3$Cl has been of interest due to uniqueness amongst the basic copper halide series, with the effects of water, Cu$^{2+}$ and Cl$^-$ concentrations, and temperature playing a large role in conversion rates. Sharkey and Lewin as well as Oswald and Feitknecht performed extensive work on the inter-conversion of Cu$_2$(OH)$_3$Cl in sealed tubes using temperature, time and the presence of water as variables. Table 6.4 shows a summary of this work. From these sealed tube experiments it was observed that botallackite in a moist atmosphere converts to pure clinoatacamite after heating at 50°C for 20 hours and atacamite in a moist atmosphere converts to clinoatacamite when heated in a sealed tube at 200°C for 48 hours. From these observations it was concluded that clinoatacamite is the most stable polymorph, at least above 200°C. This observation is not confirmed when analysing the frequency of occurrence of the polymorphs in nature, whereby atacamite is the most commonly occurring Cu$_2$(OH)$_3$Cl mineral.
Studies into the formation of atacamite were carried out to investigate possible formation pathways in nature. One study of magnesite crystals submerged in a solution containing CuCl₂ for several months showed the natural formation of atacamite with a slow reaction rate and therefore concluded that at room temperature, atacamite is most stable. Subsequent synthesis of atacamite in the laboratory has shown that the reaction rate does not affect the formation of atacamite as it can be rapidly synthesised by the suspension of powdered CaCO₃ in dilute CuCl₂ solution.

From stability studies, it was also noted that at no temperature was clinoatacamite observed to thermally convert into atacamite or botallackite. A number of studies [40] have observed a recrystallisation phenomenon amongst the polymorphs of Cu₂(OH)₃Cl and have suggested that OH⁻:Cl⁻ ratios, concentrations of [CuCl]⁺(aq) and higher chloride complexes contribute to the phase formed. Under all experimental procedures, botallackite has been found to form first with its subsequent recrystallisation into either atacamite or clinoatacamite promoted by the presence of Ca²⁺ cations and inhibited by Cl⁻ anions. An experiment involving a suspension of copper metal in a copper chloride solution found that the pH rises initially as oxygen is reduced until botallackite begins to precipitate out of solution. The pH of the solution then falls and remains stable after approximately 48 hours. It was also noted that the presence of Ca²⁺ cations promotes the formation of atacamite and conversely inhibit the formation of clinoatacamite. The exact role of Ca²⁺ and its mechanism in promoting the formation of atacamite is not well understood with further investigations needed.

<table>
<thead>
<tr>
<th>Starting polymorph</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Completion (%)</th>
<th>Condition</th>
<th>Resulting Polymorph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atacamite</td>
<td>280</td>
<td>12</td>
<td>100</td>
<td>Dry</td>
<td>Clinoatacamite</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>100</td>
<td>18</td>
<td>Dry</td>
<td>Atacamite / clinoatacamite</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>200</td>
<td>0</td>
<td>Dry</td>
<td>Atacamite</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>9</td>
<td>21</td>
<td>Moist</td>
<td>Atacamite / clinoatacamite</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>30</td>
<td>40</td>
<td>Moist</td>
<td>Atacamite / clinoatacamite</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>48</td>
<td>100</td>
<td>Moist</td>
<td>Clinoatacamite</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>840</td>
<td>0</td>
<td>Moist</td>
<td>Atacamite</td>
</tr>
<tr>
<td>Botallackite</td>
<td>80</td>
<td>20</td>
<td>100</td>
<td>Moist</td>
<td>Clinoatacamite</td>
</tr>
<tr>
<td>Atacamite / clinoatacamite (1:1)</td>
<td>150</td>
<td>63</td>
<td>100</td>
<td>Moist</td>
<td>Clinoatacamite</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>282</td>
<td>50</td>
<td>Moist</td>
<td>Clinoatacamite / atacamite</td>
</tr>
<tr>
<td>Clinoatacamite</td>
<td>500</td>
<td>7</td>
<td>0</td>
<td>Dry</td>
<td>Clinoatacamite</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>192</td>
<td>0</td>
<td>Dry</td>
<td>Clinoatacamite</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>840</td>
<td>0</td>
<td>Moist</td>
<td>Clinoatacamite</td>
</tr>
</tbody>
</table>

Table 6.4 A summary of the conversion data obtained during experiments performed by Sharkey and Lewin in sealed tubes under various conditions.
6.1.7 Reported routes of synthesis for Cu₂(OH)₃Cl

There have been several methods reported for the synthesis of the various polymorphs of Cu₂(OH)₃Cl. Synthetic procedures for clinoatacamite are well known and relatively straightforward, whereas synthetic procedures for atacamite and botallackite are more complex and their mechanisms less well understood. Solid solutions of botallackite and atacamite have been reported [40, 41, 42, 43] however they often form initially as unstable intermediates that recrystallise over a wide range of concentrations into clinoatacamite. This recrystallisation seems to be dependent on pH, temperature and the presence of other cations. Recrystallisation to the more thermodynamically stable clinoatacamite is usually observed, however the presence of Ca²⁺ cations favours the formation of atacamite. The objective of this study is to find simple synthetic procedures that produce stable, pure and crystalline polymorphs of Cu₂(OH)₃Cl. The stability of the materials synthesised and conversion of botallackite into clinoatacamite will also be explored.

6.1.7.1 Atacamite

A method for producing synthetic atacamite was first proposed by Sharkey et al (1971) based on its natural occurrence in high Ca²⁺ environments. It was reported that pure synthetic atacamite was obtained by addition of finely ground CaCO₃ to a CuCl₂ solution. The solution was left for 4-5 hours until the chalk had completely dissolved with the formation of a blue-green suspension observed. Pure atacamite was recovered and reported to be stable with no conversion into clinoatacamite. A method reported by Pollard et al found that titration of NaOH into CuCl₂ solution produces stable atacamite, however the concentration of CuCl₂ must be strictly kept to 0.1M. CuCl₂ concentrations of 0.150 to 0.095 M produced a mixture of atacamite and clinoatacamite, however after a few days only clinoatacamite was present in all samples.

6.1.7.2 Botallackite

Botallackite is described as the least thermodynamically stable Cu₂(OH)₃Cl polymorph and often reported as an unstable intermediate when suspended in solution that readily converts into clinoatacamite [44]. However earlier in this study (chapter 4), stable and very crystalline botallackite was synthesised via a “one pot” anion exchange reaction of copper hydroxyacetate with sodium chloride. An anion exchange type reaction was used by Oswald et al (1964) to form botallackite whereby synthetic brochantite ((Cu₄(OH)₆(SO₄)) is left to stand in a saturated solution of potassium chloride for 48h with no stirring. It is claimed that any sort of mechanical stirring results in the formation of clinoatacamite. A completely different approach has recently been reported whereby potassium chloride is added to a solution of copper formate at room temperature with stirring [45]. Another synthetic procedure involving the laser ablation of CuO powder and formation of gold/copper nanospheres to assist the formation of botallackite has also been reported, however this method would not be practical for the large scale material synthesis needed for radiochemical applications. The synthesis of botallackite was attempted here using the methods, or variations of the methods, shown above.

6.1.7.3 Clinoatacamite

The most commonly used synthetic procedure for clinoatacamite involves the titration of CuCl₂ solution with NaOH solution. This method was shown to be appropriate over a range of CuCl₂.
concentrations however at of 0.1M CuCl₂, atacamite is formed \[^{[46]}\]. It was suggested by Oswald et al (1964) that a synthetic anion exchange material such as brochantite (Cu₄(OH)₆(SO₄)) added to a saturated NaCl solution forms botallackite, however upon stirring, conversion to clinoatacamite is observed. A third method that mimics the natural conditions needed to form clinoatacamite has been reported that involves the suspension of copper foil in CuCl₂ solution under stirring \[^{[46]}\]. Synthesis of clinoatacamite using variations of the methods explained above was carried out.

6.2 Comparison of reported synthetic procedures and inter-conversion of phases

6.2.1 Experimental

Several synthetic procedures were attempted to produce atacamite, botallackite, clinoatacamite and paratacamite phases. Some procedures are based on previous studies in the literature and some are novel based on previous observations in this thesis. In each case, a resulting suspension was filtered under suction washed twice with deionised water (50ml), one with acetone (10ml) to remove any impurities, and oven dried at 50°C. In some cases, the suspension was so fine that a centrifuge was needed to separate the powder from liquid.

6.2.1.1 Preparation of atacamite

Table 6.5 shows a summary of synthetic procedures used to synthesize atacamite with two procedures based on the literature and one novel procedure performed in an attempt to synthesize atacamite;

<table>
<thead>
<tr>
<th>Method</th>
<th>Summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Calcite</td>
<td>CuCl₂ (1g) + CaCO₃ (0.1M in 100ml)</td>
</tr>
<tr>
<td>2 Titration</td>
<td>CuCl₂ (0.1M) + NaOH (0.1M)</td>
</tr>
<tr>
<td>3 Combination</td>
<td>CaCO₃ (1g) + (CuCl₂ (0.1M) + NaOH (0.1M))</td>
</tr>
</tbody>
</table>

Table 6.5 A summary of synthetic procedures for atacamite.

6.2.1.2 Preparation of botallackite

Table 6.6 shows a summary of three procedures based on literature and one novel procedure performed in an attempt to synthesize botallackite;
1. In a novel one pot exchange method, a solution of NaOH (0.1M) and NaCl (0.1M) was added drop wise under stirring to a solution of Cu(OAc)$_2$ (0.1M, 1000ml) until a Cu$^{2+}$:OH$^-$ ratio of 1 was achieved. A blue suspension formed during the addition and was stirred for a further 24h. A light blue fine powder was recovered.

2. In a literature exchange method, a solution of NaCl (0.1M) was added drop wise and under stirring to a suspension of Cu$_2$(OH)$_3$(OAc)$_2$.H$_2$O (0.3g in 50ml) until a OAc$^-$:Cl$^-$ ratio of 1 was reached. A blue suspension was then stirred vigorously for 10mins. A light blue fine powder was recovered.

3. In a literature formate method, a solution of KCl (0.1M) was added drop wise and under stirring to a solution of Cu(OFm)$_2$ (0.1M, 1000ml) until a Cl$^-$:OFm$^-$ ratio of 1 was achieved. The solution was stirred for a further 24hr during which a blue suspension formed. A light blue fine powder was recovered.

4. In a modified literature brochantite exchange method, Cu$_2$(OH)$_3$(OAc)$_2$.H$_2$O (0.3g) was carefully added to saturated solution of NaCl (50ml) and a light blue suspension left to stand for 48h. A light blue fine powder was recovered.

<table>
<thead>
<tr>
<th>Method</th>
<th>Summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 One pot exchange</td>
<td>Cu(OAc)$_2$ (0.1M) + (NaOH + NaCl) (0.1M)</td>
</tr>
<tr>
<td>2 Exchange</td>
<td>Cu$_2$(OH)$_3$(OAc)$_2$.H$_2$O + NaCl (1:1)</td>
</tr>
<tr>
<td>3 Formate</td>
<td>Cu(OFm)$_2$ (0.1M) + CuCl$_2$ (0.1M)</td>
</tr>
<tr>
<td>4 Bronchantite</td>
<td>CuHA (0.3g) + NaCl (saturated solution, no stirring)</td>
</tr>
</tbody>
</table>

Table 6.6 A summary of synthetic procedures for botallackite.

6.2.1.3 Preparation of clinoatacamite

Table 6.7 shows the two procedures based on literature and one novel procedure performed in an attempt to synthesise clinoatacamite;

1. In a literature titration method, a solution of NaOH (0.08M) was added drop wise and under stirring to a solution of CuCl$_2$ (0.08 M, 1000ml) until a Cu$^{2+}$:OH$^-$ ratio of 1 was reached. The solution was stirred for a further 24h during which a blue/green suspension was formed. A blue-green fine powder was recovered.

2. In a literature copper suspension method, a small metal strip of copper (~ 50x10x3mm) was suspended in a solution of CuCl$_2$ (1M, 250ml). The strip was left stationary for 1 week during which a blue deposit formed on the metal surface. A blue deposit was scrapped off the metal strip and a fine powder recovered.

3. In a novel autoclave method used previously in this study in the synthesis of Cu$_2$(OH)$_3$NO$_3$, Cu dust (0.1g) was added to a saturated solution of CuCl$_2$ (10ml) contained within a Teflon-lined autoclave. The autoclave was then heated to 150$^\circ$C (just above the decomposition temperature of clinoatacamite) in an oven for 48 hours. An off white fine powder was recovered.
6.2.1.4 Inter-conversion of Cu₂(OH)₃Cl

Samples of atacamite, botallackite and clinoatacamite were exposed to several conditions in an attempt to promote inter-conversion of the polymorphs. Previous studies have utilised sealed tubes and high temperatures. These methods are expensive and time consuming, therefore new, more inexpensive and rapid methods of investigating the inter-conversion of Cu₂(OH)₃Cl were investigated. Table 6.8 shows a summary of the conditions used. It has been demonstrated that the presence of a reaction medium (water) is essential in controlling the rate of conversion along with the input of energy. Samples were exposed to 4 conditions under each of these conditions the temperature and the mechanism for mixing were also varied.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Procedure</th>
<th>Temperature(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Suspension in de-ionised water</td>
<td>Stirring</td>
<td>50°C, 80°C</td>
</tr>
<tr>
<td></td>
<td>Sonication</td>
<td></td>
</tr>
<tr>
<td>2 Suspension in NaCl solution (0.1M)</td>
<td>Stirring</td>
<td>50°C, 80°C</td>
</tr>
<tr>
<td></td>
<td>Sonication</td>
<td></td>
</tr>
<tr>
<td>3 Suspension in Cu(OAc)₂ solution (0.1M)</td>
<td>Stirring</td>
<td>50°C, 80°C</td>
</tr>
<tr>
<td></td>
<td>Sonication</td>
<td></td>
</tr>
<tr>
<td>4 Suspension in CaCO₃ solution (0.1M)</td>
<td>Stirring</td>
<td>50°C, 80°C</td>
</tr>
<tr>
<td></td>
<td>Sonication</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.8 Conditions used in the attempted inter-conversion of polymorphic copper hydroxychloride

Previous reports suggested that the presence of an excess amount of Cu²⁺, Cl⁻ and Ca²⁺ ions have a large impact on recrystallisation, therefore samples of atacamite, botallackite and clinoatacamite were exposed to the appropriate ions in solutions of NaCl, Cu(OAc)₂ and CaCO₃. Samples were then mixed either by conventional stirring with a magnetic flea or in an ultrasonic bath, at both 50°C and 80°C. The experiments which were stirred were carried out over 24 hours, whereas those that were carried out in an ultrasonic bath lasted 30 minutes. Once completed, the suspension was filtered under suction, washed twice with deionised water (50ml) and one with acetone (10 ml) to remove any impurities, and oven dried at 50°C.

6.2.1.5 Characterisation

All the samples were then characterised using PXRD, FT-IR, TGA and elemental analysis as previously described in chapter 2. PXRD was primarily used for phase identification and patterns collected from 10 - 60° 2θ with a step size of 0.014°. FT-IR data were used to compare with
previously reported data, and to confirm the phase present, as PXRD patterns of atacamite and clinoatacamite are very similar. Data was collected as an average of 16 runs from 4000-300 cm\(^{-1}\) wave numbers. TGA data were collected to establish the thermal decomposition route of the Cu\(_2\)(OH)\(_3\)Cl polymorphs and data were collected from 30°C to 900°C with a heating rate of 1.5°C min\(^{-1}\). All samples were dried in an oven at 50°C for 1 week to remove any surface water. Elemental analysis and gravimetric data were collected under conditions stated in chapter 2.

6.3 Results and discussion

6.3.1 PXRD

PXRD was primarily used for phase identification. PXRD data collected on samples in this study were compared to calculated patterns based on crystallographic information proposed by Wells (1949) for atacamite, Zheng (2006) for botallackite and Grice (1996) for clinoatacamite.

6.3.1.1 Atacamite

![Figure 6.5](image.png)

Figure 6.5 PXRD patterns collected on atacamite samples produced from methods in table 6.5 expected observed reflections marked (* = reflection indicative of atacamite (17.62° and 31.53° 2θ to highlight).

Figure 6.5 shows the PXRD patterns for the attempted syntheses of atacamite. The quality of the diffraction data is very poor and given that the patterns for atacamite and clinoatacamite are very similar, phase identification is difficult. Two clear reflections at 17.62° and 31.53° 2θ unique to atacamite are present when using the calcite method. There are no intense reflections unique to clinoatacamite that can be used to identify it over atacamite, however due to the broadness of the reflections observed; it is difficult to say for sure whether the sample is single phase with no clinoatacamite impurity. Using the combination method, small broad reflections indicative of atacamite are also present, however the intensity of these reflection is much reduced indicating the presence of clinoatacamite in the majority. Pollard et al reported that titration of exactly 0.1M NaOH against 0.1M
CuCl₂ formed atacamite; however in these studies only broad reflections indicating the presence of clinoatacamite are observed. Given the broadness of the reflections observed, the presence of atacamite cannot be discounted. Table 6.9 gives a summary of the products formed.

<table>
<thead>
<tr>
<th>Method</th>
<th>Material(s) formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Calcite</td>
<td>Atacamite (confirmed) / clinoatacamite (possible)</td>
</tr>
<tr>
<td>2 Titration</td>
<td>Clinoatacamite (confirmed) / atacamite (possible)</td>
</tr>
<tr>
<td>3 Combination</td>
<td>clinoatacamite (major) / atacamite (minor)</td>
</tr>
</tbody>
</table>

Table 6.9 A summary of products recovered in the synthesis of atacamite.

6.3.1.2 Botallackite

Figure 6.6 PXRD patterns collected on samples produced via methods in table 6.6. The expected reflections for botallackite are marked (* = reflection indicative of atacamite (17.62° and 31.53° 2θ to highlight).

Figure 6.6 shows the PXRD patterns for the attempted syntheses of botallackite. The reflection observed at ~15.6° can be used to identify the presence of botallackite, which was shown to be formed using the exchange, bronchantite no stir and one pot methods. Zheng et al (2004) reported the combination of Cu(OFm)₂ and KCl formed botallackite, however in this study reflections at ~17.8° and ~22.5° indicate the presence of atacamite (and possibly clinoatacamite as previously discussed). The intensity and sharpness of reflections observed in stirred exchange and non-stirred bronchantite methods are very similar indicating that mechanical stirring has little effect on the formation of botallackite. Using the one pot method, the intensity and sharpness of reflections observed indicate a
very crystalline phase has formed. Table 6.10 gives a summary of the products recovered during the synthesis of botallackite.

<table>
<thead>
<tr>
<th>Method</th>
<th>Material(s) formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 One Pot</td>
<td>Botallackite</td>
</tr>
<tr>
<td>2 Exchange</td>
<td>Botallackite</td>
</tr>
<tr>
<td>3 Formate</td>
<td>Atacamite (confirmed) / clinoatacamite (possible)</td>
</tr>
<tr>
<td>4 Bronchantite (No Stir)</td>
<td>Botallackite</td>
</tr>
</tbody>
</table>

Table 6.10  A summary of products recovered in the synthesis of botallackite.

### 6.3.1.3 Clinoatacamite

![Hydrothermal bomb](image)

![Suspension](image)

![Titration](image)

Figure 6.7  PXRD patterns collected on samples produced via methods in table 6.7. The expected reflections for clinoatacamite are marked.

Figure 6.7 shows the PXRD patterns for the attempted syntheses of clinoatacamite. Clinoatacamite is formed using both the titration and suspension methods. The products formed, however, exhibit poor crystallinity with a characteristic broad reflection observed at ~13° along with general broadening and reduction in intensity of reflections observed. It is difficult to determine the presence of any atacamite, as the reflections at 17.8° and 22.5° 2θ may be obscured by the broad reflections attributed to clinoatacamite. The hydrothermal method was not successful at forming any
Cu$_2$HCl phase. Sharpe and intense reflections indicate the presence of Cu(I)Cl. Products recovered are summarised in Table 6.11.

<table>
<thead>
<tr>
<th>Method</th>
<th>Material(s) formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Titration (Cu)</td>
<td>Clinoatacamite</td>
</tr>
<tr>
<td>2 Copper suspension</td>
<td>Clinoatacamite</td>
</tr>
<tr>
<td>3 Hydrothermal bomb</td>
<td>CuCl</td>
</tr>
</tbody>
</table>

Table 6.11 A summary of products recovered in the synthesis of clinoatacamite.

6.3.1.4 Inter-conversion of the Cu$_2$(OH)$_3$Cl polymorphs

Investigations into whether phase transformation behaviour between the known polymorphs of Cu$_2$(OH)$_3$Cl was carried out. Results from the analysis of PXRD data collected on the samples after they had undergone various treatments, as detailed in table 6.8, are presented in table 6.12. It was found that in the case of both atacamite and clinoatacamite, no phase transitions occurs under any of the experimental conditions used. Botallackite, however, always transformed to clinoatacamite when sonicated at 50ºC under any of the conditions used. Whereas at 80ºC it either partially decomposed to produce a mixture of botallackite and CuO, when the reaction mixtures were stirred under all the conditions tried, or decomposed to CuO completely when the reactions mixtures were sonicated (table 6.12).

<table>
<thead>
<tr>
<th></th>
<th>Atacamite 50ºC</th>
<th>Atacamite 80ºC</th>
<th>Botallackite 50ºC</th>
<th>Botallackite 80ºC</th>
<th>Clinoatacamite 50ºC</th>
<th>Clinoatacamite 80ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Stir</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>Bot (Major)</td>
<td>CuO (Minor)</td>
<td>No change</td>
</tr>
<tr>
<td>Sonic</td>
<td>No change</td>
<td>No change</td>
<td>Clino (Full)</td>
<td>CuO (Full)</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td>2 Stir</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>Bot (Major)</td>
<td>CuO (Minor)</td>
<td>No change</td>
</tr>
<tr>
<td>Sonic</td>
<td>No change</td>
<td>No change</td>
<td>Clino (Full)</td>
<td>CuO (Full)</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td>3 Stir</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>Bot (Major)</td>
<td>CuO (Minor)</td>
<td>No change</td>
</tr>
<tr>
<td>Sonic</td>
<td>No change</td>
<td>No change</td>
<td>Clino (Full)</td>
<td>CuO (Full)</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td>4 Stir</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>Bot (Major)</td>
<td>CuO (Minor)</td>
<td>No change</td>
</tr>
<tr>
<td>Sonic</td>
<td>No change</td>
<td>No change</td>
<td>Clino (Full)</td>
<td>CuO (Full)</td>
<td>No change</td>
<td>No change</td>
</tr>
</tbody>
</table>

Table 6.12 A summary of products recovered when samples of atacamite, botallackite, clinoatacamite and paratacamite are exposed to conditions given in table 6.8.

Figure 6.8 compares the PXRD patterns when clinoatacamite is prepared via the titration method and formed by sonication of botallackite at 50ºC. The intensity and sharpness of reflection
observed in the sample of clinoatacamite formed by sonication are comparable to its botallackite precursor. Comparison of the PXRD patterns of clinoatacamite prepared by the titration method and by sonication of botallackite, shows the reflections of the transformed clinoatacamite to be much sharper than those of the clinoatacamite synthesized via the titration method, suggesting the transformed clinoatacamite is a much more crystalline sample. The quality of data collected is comparable to that of natural samples and exceeds that of any previously reported synthetic data. There was no evidence that any of the conditions used formed atacamite.

6.3.2 FT-IR and Raman spectroscopy data

Samples of each of the polymorphs of Cu$_2$(OH)$_3$Cl that were the most pure and crystalline (determined through the sharpness of the reflections on the PXRD patterns): atacamite synthesised via addition of CaCO$_3$ to CuCl$_2$, clinoatacamite formed from sonication of botallackite and botallackite made by the “one pot” method were then analysed using FT-IR and Raman (Figure 6.9). The data collected were compared to that of literature values for natural samples (Table 6.13 and table 6.14).

Comparison of the FT-IR data collected for the Cu$_2$(OH)$_3$Cl polymorphs are presented in figure 6.9 and table 6.13. FT-IR data collected for atacamite compares well to literature values, apart from absorption bands reported in literature at 974 cm$^{-1}$, which is not present in the data collected here. Two strong absorption bands located either side at 987 cm$^{-1}$ and 951 cm$^{-1}$ may obscure this reported
absorption band at 974 cm$^{-1}$. Two absorption bands at 893 cm$^{-1}$ and 848 cm$^{-1}$ are not reported in literature datasets. These absorption bands do not correspond to any bands observed in reported data for botallackite, clinoatacamite, CaCO$_3$ or Cu(OH)$_2$. Raman data collected for atacamite correlates well to literature data aside from an absorption band reported in literature at 580 cm$^{-1}$ (table 6.14). This band is reported to be of low intensity and in close proximity to a highly intense band located at 508 cm$^{-1}$, giving a possible explaining for its omission in this study.

The FT-IR data collected on the botallackite sample corresponds very well to literature data with no traces of an acetate analogue present. The only small discrepancy is a broadening of reflections located at 3424 cm$^{-1}$ and 3406 cm$^{-1}$. Raman data collected on this sample also compare well to that reported in the literature (Table 6.14).

Data collected on the clinoatacamite sample shows a good correlation with literature values (table 6.13). There is a band located at 702 cm$^{-1}$ in laboratory data which doesn't correspond to literature data for clinoatacamite, but may correspond to an absorption band in botallackite. There are no other bands indicating the presence of botallackite so it can be assumed that full conversion from botallackite to clinoatacamite has been achieved (table 6.13). Raman data shows a general correlation between data sets, however 5 bands located at 868 cm$^{-1}$, 798 cm$^{-1}$, 576 cm$^{-1}$ and 445 cm$^{-1}$ present in the literature values are not present in the clinoatacamite sample prepared in this study. A possible reason for the inability to locate these peaks is due to the signal to noise ratio in the spectra obtained for clinoatacamite in this study being relatively poor in respect to that of literature values.
The background noise and lack of focussing made peaks at low wave numbers particularly difficult to identify (Table 6.14).

<table>
<thead>
<tr>
<th>Atacamite</th>
<th>Botallackite</th>
<th>Clinoatacamite</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR</td>
<td>IR</td>
<td>IR</td>
</tr>
<tr>
<td>3457</td>
<td>3510</td>
<td>3457</td>
</tr>
<tr>
<td>3328</td>
<td>3412</td>
<td>3361</td>
</tr>
<tr>
<td>3208</td>
<td>3402</td>
<td>3301</td>
</tr>
<tr>
<td>1672</td>
<td>1680</td>
<td>1671</td>
</tr>
<tr>
<td>987</td>
<td>870</td>
<td>987</td>
</tr>
<tr>
<td>974</td>
<td>857</td>
<td>926</td>
</tr>
<tr>
<td>957</td>
<td>820</td>
<td>915</td>
</tr>
<tr>
<td>920</td>
<td>785</td>
<td>900</td>
</tr>
<tr>
<td>912</td>
<td>703</td>
<td>865</td>
</tr>
<tr>
<td></td>
<td>893</td>
<td>830</td>
</tr>
<tr>
<td>598</td>
<td>510</td>
<td>568</td>
</tr>
<tr>
<td>515</td>
<td>500</td>
<td>513</td>
</tr>
<tr>
<td>483</td>
<td>441</td>
<td>460</td>
</tr>
<tr>
<td>410</td>
<td>402</td>
<td>395</td>
</tr>
</tbody>
</table>

Table 6.13  Observed infrared absorption bands (cm\(^{-1}\)) of polymorphic Cu\(_2\)(OH)\(_3\)Cl with a comparison to literature data obtained via the RRUFF database \(^{[36]}\).

<table>
<thead>
<tr>
<th>Atacamite</th>
<th>Botallackite</th>
<th>Clinoatacamite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman</td>
<td>Raman</td>
<td>Raman</td>
</tr>
<tr>
<td>3430</td>
<td>3405</td>
<td>3443</td>
</tr>
<tr>
<td>3347</td>
<td>3424</td>
<td>3358</td>
</tr>
<tr>
<td>3212</td>
<td>3204</td>
<td>3314</td>
</tr>
<tr>
<td>969</td>
<td>927</td>
<td>971</td>
</tr>
<tr>
<td>908</td>
<td>892</td>
<td>928</td>
</tr>
<tr>
<td>817</td>
<td>855</td>
<td>893</td>
</tr>
<tr>
<td></td>
<td>791</td>
<td>868</td>
</tr>
<tr>
<td></td>
<td>672</td>
<td>897b</td>
</tr>
<tr>
<td>580</td>
<td>499</td>
<td>576</td>
</tr>
<tr>
<td>508</td>
<td>449</td>
<td>513</td>
</tr>
<tr>
<td>449</td>
<td>445</td>
<td>512b</td>
</tr>
<tr>
<td>389</td>
<td>367</td>
<td>364</td>
</tr>
</tbody>
</table>

Table 6.14  The observed Raman data (cm\(^{-1}\)) of polymorphic Cu\(_2\)(OH)\(_3\)Cl with a comparison to literature data obtained via the RRUFF database \(^{[36]}\).
6.3.3 Thermal analysis

The thermal decomposition routes of atacamite (calcite), botallackite (one pot) and clinoatacamite (sonicated) were studied using TGA over the temperature range 30°C to 900°C in an air atmosphere with a heating rate of 1.5°C min⁻¹. Heating rates of 0.5º and 5ºC min⁻¹ were also employed, however the data collected differed only slightly, therefore are not presented. A summary of TGA data collected is shown below (Table 6.15). Samples were dried in an oven at 50°C for 1 week to remove any surface water (Equation 6.1).

**Step 1**

\[ 2\text{Cu}_2(\text{OH})_3\text{Cl(s)} \rightarrow \text{CuO.CuCl}_2(s) + 2\text{CuO(s)} + 3\text{H}_2\text{O(g)} \] 12.65%

**Step 2**

\[ \text{CuO.CuCl}_2(s) + 2\text{CuO(s)} + \frac{1}{2}\text{O}_2(g) \rightarrow 4\text{CuO(s)} + \text{Cl}_2(g) \] 12.83%

Equation 6.1 The thermal decomposition route of Cu₂(OH)₃Cl in air.

<table>
<thead>
<tr>
<th>Cu₂(OH)₃Cl Polymorph</th>
<th>Step Number</th>
<th>Temperature Range (°C)</th>
<th>% loss Calculated</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atacamite</td>
<td>1</td>
<td>210</td>
<td>12.65</td>
<td>12.79 (0.56)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>355</td>
<td>12.83</td>
<td>12.50 (0.45)</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>201</td>
<td>25.48</td>
<td>25.29 (0.87)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>163</td>
<td>12.65</td>
<td>12.40 (0.51)</td>
</tr>
<tr>
<td>Botallackite</td>
<td>2</td>
<td>339</td>
<td>12.83</td>
<td>12.67 (0.66)</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>163</td>
<td>25.48</td>
<td>25.07 (1.01)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>161</td>
<td>12.65</td>
<td>12.20 (0.64)</td>
</tr>
<tr>
<td>Clinoatacamite</td>
<td>2</td>
<td>340</td>
<td>12.83</td>
<td>12.65 (0.61)</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>161</td>
<td>25.48</td>
<td>24.84 (0.98)</td>
</tr>
</tbody>
</table>

Table 6.15 TGA data collected on samples of atacamite, botallackite and clinoatacamite.

The TGA data collected for atacamite showed two clear weight losses of 12.79% and 12.50% which agree well with the calculated values. De-hydroxylation occurs at 210º, which is 55º C lower than previously reported, however an end point of 306º C agrees well. The loss of the halide is initiated at 355 ºC, which is again slightly lower than reported but, as with the de-hydroxylation step, the end point agrees well.
The TGA trace for botallackite shows two weight losses and an overall weight loss of 25.07% is 0.31% less than what would be expected. As with botallackite, the two weight losses are initiated at slightly lower temperatures (163 °C and 339 °C) than reported, but the end point agrees well with previously reported data.

The TGA data collected on the clinoatacamite sample also have two weight loss steps. In the first step, 12.20% mass is lost which is 0.45% less than what is to be expected. In the second step, a mass loss of 12.65% is 0.18% less than what is to be expected. As with the samples of atacamite and botallackite, de-hydroxylation and loss of halide steps start at a lower temperature than previously quoted. This amounts to a larger disparity than losses observed in samples of atacamite and botallackite. The significance in the difference between observed and reported temperature ranges of the weight loss steps is very little due to the large disparity in the heating rates used. A heating rate of
1.5 °C min is more sensitive to changes is mass and the most probable cause for the difference in temperature ranges.

Figure 6.12 TGA trace of clinoatacamite.

6.3.4 Quantitative analysis

Gravimetric analysis was carried out on samples of atacamite (calcite), botallackite (one pot), and clinoatacamite (sonicated). Synthesis of the samples was performed in an inert \( \text{N}_2 \) atmosphere to eliminate the presence of \( \text{CO}_3^- \) (Table 6.16).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Attempt</th>
<th>Ideal mass of AgCl (g)</th>
<th>Mass of AgCl (g)</th>
<th>% of ideal Cl content</th>
<th>Average %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atacamite</td>
<td>1.0233</td>
<td>0.6867</td>
<td>0.6659</td>
<td>96.97</td>
<td>97.56</td>
</tr>
<tr>
<td>Calcite</td>
<td>1.0089</td>
<td>0.6770</td>
<td>0.6612</td>
<td>97.66</td>
<td>97.66</td>
</tr>
<tr>
<td></td>
<td>1.0120</td>
<td>0.6791</td>
<td>0.6661</td>
<td>98.04</td>
<td></td>
</tr>
<tr>
<td>Botallackite</td>
<td>1.1113</td>
<td>0.7457</td>
<td>0.7098</td>
<td>95.19</td>
<td>95.18</td>
</tr>
<tr>
<td>One pot</td>
<td>1.2352</td>
<td>0.8289</td>
<td>0.7836</td>
<td>94.53</td>
<td>95.18</td>
</tr>
<tr>
<td></td>
<td>1.0085</td>
<td>0.6768</td>
<td>0.6484</td>
<td>95.80</td>
<td></td>
</tr>
<tr>
<td>Clinoatacamite</td>
<td>1.0111</td>
<td>0.6785</td>
<td>0.6455</td>
<td>95.13</td>
<td>95.05</td>
</tr>
<tr>
<td>Sonicated</td>
<td>1.0102</td>
<td>0.6779</td>
<td>0.6399</td>
<td>94.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.9987</td>
<td>0.6702</td>
<td>0.6410</td>
<td>95.64</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.16 Gravimetric analysis of \( \text{Cu}_2(\text{OH})_3\text{Cl} \) (\( M_a \text{Cu}_2(\text{OH})_3\text{Cl} = 213.57 \), \( M_a \text{AgCl} = 143.32 \), solubility \( \text{AgCl} = 1.26 \times 10^{-3} \text{M} \)).

Atacamite displays an average chloride content of 97.56%, which over 2% greater than that observed in botallackite and clinoatacamite. However, the sample of clinoatacamite was formed via sonication from botallackite and perhaps this is the reason these samples have similar chloride contents. All products were analysed using PXRD with reflections observed suggesting the presence of only \( \text{AgCl}_2 \).
6.4 Conclusion

The main aim of this study was to investigate and propose synthetic procedures for the different polymorphs of Cu₂(OH)₃Cl. A summary of the successful synthetic or transformation methods for each of the studied Cu₂(OH)₃Cl polymorphs is presented in (Table 6.17).

### Atacamite

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>2 CuCl₂ + CaCO₃ + 3 H₂O → Cu₂(OH)₃Cl</td>
</tr>
<tr>
<td>Formate</td>
<td>CuCl₂ + 3 Cu(Fm)₂ + 3H₂O → 2Cu₂(OH)₃Cl</td>
</tr>
</tbody>
</table>

### Botallackite

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>One pot</td>
<td>Cu(OH)₃(OAc) + NaCl → Cu₂(OH)₃Cl</td>
</tr>
<tr>
<td>Exchange</td>
<td>Cu(OAc)₂ + (3 NaOH + NaCl) → Cu₂(OH)₃Cl + 4 Na(OAc)</td>
</tr>
</tbody>
</table>

### Clinoatacamite

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration</td>
<td>2 CuCl₂ + NaOH + 2H₂O → Cu₂(OH)₃Cl + NaCl + 2HCl</td>
</tr>
<tr>
<td>Copper suspension</td>
<td>CuCl₂ + 3Cu + 3H₂O→ Cu₂(OH)₃Cl</td>
</tr>
<tr>
<td>Sonication</td>
<td>botallackite in ultrasonic bath at 50°C → clinoatacamite</td>
</tr>
</tbody>
</table>

Table 6.17 A summary of the successful synthetic procedures for polymorphous Cu₂(OH)₃Cl.

Of the three methods used to form atacamite, it was difficult to be conclusive in whether the sample was single phase or multiphase containing a clinoatacamite impurity, as the observed reflections were broad and may mask the presence of trace amounts of clinoatacamite. FT-IR bands indicate that no clinoatacamite is present in the sample prepared by the calcite method and the TGA data perhaps also indicate the sample is single phase. Controlled mixtures of atacamite and clinoatacamite studied using XRPD, IR and TGA may indicate the levels of effect that an impurity may have, thus helping to resolve this matter. However, although the decomposition pathway for clinoatacamite is different to atacamite, trace amounts of clinoatacamite would not be resolved from the TGA data collected. The presence of Ca²⁺ (or other soft divalent metal cations) is reported to have a major effect of the preferential formation of atacamite. This is further demonstrated in the other synthetic methods (apart from the formate method) whereby no Ca²⁺ cations are present thus no atacamite is formed. Zheng et al (2004) claimed that mixing potassium chloride and copper formate produced stable botallackite, however in this study, stable atacamite is formed. Poor crystallinity is observed in natural samples of atacamite due to poor stacking of the layers. This was also observed in the samples synthesised during this study. The presence of carbonate or formate ions in the system also seems to effect the phase formed. It is thought that the presence of carbonate in a basic solution may form malachite, which could then ion exchange to form the copper hydroxyl chloride. Atacamite is not formed during any of the studies into the phase transformation behaviour between polymorphs. The atacamite sample itself also does not undergo any polymorphic phase transition.

Botallackite is described as the least thermodynamically stable polymorph with conversion into
clinoatacamite readily observed, especially when the sample is suspended in solution. In this study, stable and crystalline botallackite is obtained via the addition of sodium hydroxide and sodium chloride solution into a solution of Cu₂(OAc)₂. This method effectively forms the copper hydroxyacetate exchange material and allows the migration of chloride anions into the newly formed exchange material as it is formed in situ. As a result, the PXRD data collected on this botallackite sample displayed sharper reflections compared to PXRD data collected on a botallackite sample formed in a standard anion exchange reaction. Phase purity of the botallackite sample was confirmed by FT-IR and TGA data. Botallackite is not formed during any of the studies into the phase transformation behaviour between polymorphs, when either atacamite or clinoatacamite is the starting polymorph. Sonicating botallackite at 50°C, shows full conversion into clinoatacamite. This is consistent with previous studies, however the reports that botallackite is unstable in solution have been disproved here.

As previously discussed, clinoatacamite is the most thermodynamically stable polymorph and is easily produced via titration of sodium hydroxide against copper(II) chloride until a Cu:OH ratio of 1 is achieved. In this study, clinoatacamite is formed across a wide range of concentrations of CuCl₂, despite Pollard et al claiming that 0.1M CuCl₂ produces stable atacamite. Oswald et al (1961) proposed that adding an anion exchange material such as synthetic brochantite (Cu₄(OH)₆(SO₄)) to a saturated solution of a chloride salt under vigorous stirring results in the formation of clinoatacamite with botallackite formed as an intermediate if the solution is not stirred. In this study, copper hydroxyacetate was used as the anion exchange material instead of brochantite. The structure of the two materials differs slightly as a result of the charge on the exchangeable anion. Copper hydroxyacetate contains a monovalent exchangeable acetate anion whereas brochantite contains a divalent sulphate anion. When chloride migrates into the layers of brochantite, it replaces the sulphate anion however the framework of the material is different to that of botallackite so the material is unstable. This is reflected when the solution undergoes a small amount of mechanical stirring, initiating a phase transition into clinoatacamite. When a chloride anion replaces the acetate anion in Cu₂(OH)₃(OAc).H₂O, the framework of the structure is much more stable and so the botallackite formed does not undergo a phase transition into clinoatacamite when stirred. The third and fourth method used to synthesise clinoatacamite in this study involved the addition of copper metal to a solution of CuCl₂. Suspension of a copper strip in copper chloride solution yields pure clinoatacamite. A blue crust formed after 1 week was less than 1 mm thick which did not increase if left for more than 1 week. Copper dust exposed to a saturated solution of CuCl₂ in a Teflon-lined autoclave heated to 150°C forms copper(II) chloride. As reported in a precious section, addition of copper dust and Cu(NO₃)₂ solution in a high temperature and pressure environment was successful in producing very crystalline Cu₂(OH)₃(NO₃). However, the product recovered was copper(I) chloride formed via the reduction of copper(II) chloride with copper metal. A novel “sonicating” method has shown that clinoatacamite can easily be synthesised using “one pot” botallackite as a template, when botallackite suspended in water is heated at 50°C for 30 minutes. The PXRD data of clinoatacamite produced in this way shows reflections that are much sharper compared to clinoatacamite synthesised via other routes. When considering the mechanism for which this conversion occurs, it is clear that the phase pure and very crystalline nature of the botallackite template is vital in producing a crystalline sample of clinoatacamite. This suggests that complete dissolution and re-crystallisation is an unlikely
mechanism as it is unlikely that the crystalline characteristics of botallackite would not be transferred to that of the subsequent clinoatacamite. A more likely mechanism is partial dissolution of the botallackite and/or atomic rearrangement.

The increased thermal stability of clinoatacamite may increase stability in a high pH environment; however this has not been explored in this study. As explained in chapter 5, the use of LHSs may be limited to use in the separation of waste streams and not necessarily in the long term immobilisation of active anions such $^{35}\text{Cl}$. 
6.5 References

4. S. Church, *J. Chem. Soc.*, 18, 212
30. C. Frondel, *Mineralogical Magazine*, 29, 34
Chapter 7

Summary and Future Work
Several factors must be taken into account in order for an exchange material to be seriously considered for use in the separation and long term storage of anionic nuclear waste. Recent developments have shown that LHSs represent a family of materials that are relatively cheap to synthesise and are able to host exchange anions. Some selectivity studies suggest that small monovalent anions are preferentially held in the interlayer spacing of LHSs, however the stability of these materials in a chemically diverse environment, such as that found in an underground repository, has not been investigated fully. The studies presented in this thesis, shows a progression from the synthesis, anion exchange capabilities and stability of a family of LHS materials.

7.1 Synthesis and Characterisation of Anion Exchange Materials

The synthesis of nitrate and acetate analogues of copper, zinc, nickel and lanthanum layered hydroxysalts has been investigated. Single phases of the LHSs Cu$_2$HN (monoclinic), Cu$_2$HA, Zn$_3$HN$_2$, Zn$_5$HA$_2$, LaHA and Ni$_2$HN were all easily prepared. Oxide impurities were always found to be present in samples of Zn$_5$HN and LaHN regardless of the synthetic method used. A mixture of the orthorhombic and monoclinic polymorphs of Cu$_2$HN is formed using hydrolysis and titration methods, although the ratio seems to increase in the favour of the monoclinic modification when using the titration method. The suggestion that a monoclinic modification is a meta-stable high temperature phase has not been confirmed during these studies. The work presented in this thesis seems to suggest that formation of the orthorhombic phase is promoted by increased acidity and the conversion from a monoclinic to an orthorhombic phase, is extremely slow, if possible at all. In the case of Ni$_2$HA, analysis of the XRPD pattern was inconclusive, however subsequent elemental and FTIR analysis suggests the presence of a LHS. XRPD and FTIR analysis of the products recovered generally agreed with previously reported data. The only notable discrepancy between data collected in this study and that previously reported is a reduction in the difference between the asymmetric and symmetric NO$_3^-$ absorption band observed in a sample of Ni$_2$HN. This reduction suggests the nitrate anion is less strongly bound to the brucite like layers. Of the synthetic procedures used, no single method was able to produce a phase pure sample for every composition targeted. The titration method was able to produce a LHS with no oxide or hydroxide impurity in all samples except the lanthanum material, LaHA. Given the ease at which this method can be employed at room temperature (expect for Ni modifications to increase crystallinity) and the purity of samples produced, it is clear that this method could be targeted for the synthesis of LHSs on a larger scale.

7.2 Anion Exchange Capabilities of LHSs

The second part of this study concentrated on the exchange capabilities of LHSs synthesis in part one. One of the primary anions of interest, iodide, was chosen as a standard to assess selectivity, capacity and exchange rate over occupying nitrate and acetate anions. It was found that Cu$_2$HA is the best precursor for anion exchange reactions with iodide over all other LHS materials studied here. XRPD and FTIR data indicate full iodide exchange occurs only with a copper based LHS with acetate as the occupying anion. The relative sizes of the nitrate and iodide anions results in only partial exchange with respect to both orthorhombic and monoclinic modifications of a Cu$_2$HN LHS. Nitrate analogues of Ni$_2$ and Zn$_5$ LHSs are also able to partially exchange with iodide, albeit with a metal oxide formed as a byproduct either in the synthesised or exchange phase. The acetate analogues of Zn, Ni and La based LHSs exhibited no exchange capabilities with respect to iodide.
The success of an anion exchange is monitored by analysis of the PXRD data, through changes in the relative basal spacing reflections.

Quantitative analysis in this study has shown iodide content post exchange to be ~92-93% of the ideal stoichiometric value. This is contrary to the results obtained from XRPD and FTIR analysis, which indicate 100% exchange. Either an impure Cu₂-HA starting material or an incomplete exchange must be responsible for this lower than expected value and shows the shortcomings of using XRPD or FTIR for use in quantitative analysis. This study has shown that only monovalent anions are hosted by Cu-based LHSs. A linear trend between the size of an anion and the interlayer spacing required to host it was found which allows the effective anionic radius of an anion to be predicted using Cu LHSs. The only monovalent anions that are not hosted by Cu LHSs are trigonal pyramidal that cause steric hindrance with the host brucite like layers. Exposure of ReO₄⁻ (used as a surrogate for TcO₄⁻) to CuHA resulted in complete loss of the layered structure with only reflections indicative of the sodium perrehenate salt present. The primary advantage of Cu LHSs over LDHs is poor selectivity towards di- and trivalent anions especially carbonate.

7.3 Stability and Applications of Copper Hydroxyacetate to the Nuclear Industry

Active iodide and pertechnetate have been hosted by a Cu LHS as confirmed by quantitative radioactivity counting analysis. Subsequent XRPD analysis does not show the presence of a TcO₄⁻ containing phase, as observed using the surrogate ReO₄⁻ anion. Radioactive counting agreed with other quantitative methods whereby 92-93% exchange occurs. This study has used 3 methods of quantifying the amount of iodide actually migrating into the layers of a Cu LHS. It was important to gain as much evidence as possible to show uptake is consistent across multiple collection methods. It may be important to easily quantify the amount of an anion separated and immobilised by an exchange material. When selecting a quantitative method that can be employed in the nuclear industry, radioactivity counting seems like the most logical choice. A potential problem with this method may be interference from other active species. Using an ion specific probe is more selective than activity counting, although both can only show how much activity is taken out of solution. This is unless an exchanged sample is dissolved with acid (in the case of LHS), thus allowing quantification of the anion actually contained within exchange material. Gravimetric analysis is method that can easily quantify the amount of an anion contained within an exchange material, however like activity counting, may be prone to inference particularly from halide and carbonate analogue.

Exposure of Cu₂HI to various pH conditions resulted in loss of iodide. Quantitative analysis of CuHI exposed to increasing pH solution indicates that even at pH7, some iodide is lost. Activity counting provided more precise information than other techniques such as XRPD and FTIR which were unable to detect a change in the crystal structure until a significant loss of iodide (50%) occurs. Exposure of iodide, chloride and nitrate analogues of a Cu LHS to a saturated carbonated solution gave some interesting results. Exposure of the acetate analogue to an equimolar solution of carbonate resulted in no interaction. When the concentration of carbonate is increased, the acetate and iodide analogues are replaced by the basic copper carbonate malachite; this is not a true exchange reaction. The lost acetate anions remains free in solution, however the iodide anion precipitates out of solution forming Cu²⁺. The degradation of the chloride analogue is less, this is
proposed to be due to a smaller interlayer spacing, allowing less malachite to form than in the acetate analogue. Unsurprisingly, exposure of iodide to a chloride solution results in almost complete migration of chloride into layers, even at low concentrations. A larger anion such as nitrate is less prone to replace iodide with a molar ration of 1:5 iodide to nitrate required for full exchange.

With the development of low pH cements by García Calvo et al. (2009) for use in the nuclear industry, it was hoped that LHSs may be stable enough to be used. These cements have a significant resilience to ground water aggression; therefore the lack of stability of LHSs to smaller anions may not be significant. However, the lack of stability of LHSs under even low pH conditions mean they may not be seriously considered for use in the long term storage of active waste in a cementitious environment. The use of LHSs to temporarily separate anionic waste is possible as LHSs selectively exchange with small monovalent anions. To confirm this, studies of anion release may be carried out in samples of cement rather than in simulated conditions used in this study. The use of Cu LHS to selectively immobilise and separate active monovalent anions present in complex sludges is more applicable. Other uses of these materials may include the reduction in nitrate content from sewage, wetlands, nitrate rich ground water as a result of high fertiliser use, re-circulatory systems in aquariums and removal of anions such as Cl\(^-\), I\(^-\) and TcO\(_4\)\(^-\) present in legacy waste of military origin.

7.4 Future work

In this study, only Cu, Ni, Zn and La based LHSs were investigated in depth. The use of a copper X-ray tube made XRPD characterisation of Mn and Co based LHSs difficult. The use of another X-ray tube (such as Co) that reduces fluorescence with respect to these metals would aid characterisation. There are a wide variety of other cations such as Mg\(^{2+}\), Ca\(^{2+}\), Sc\(^{3+}\), Y\(^{3+}\), Ln\(^{3+}\) and An\(^{3+}\), as well as mixed cations that may exhibit a greater anion exchange capacity than those investigated in this study. The primary reason for not investigating other cations was a lack of time and to allow a more focussed study of the Cu-based materials. This study utilised nitrate and acetate as the occupying anion. There are other larger organic anions that may be investigated (Figure 8.1). As the size of the organic anion increases in size, it is expected that the interlayer spacing will also increase. Newman and Jones (1999) reported the synthesis of a copper hydroxybenzoate compound with an interlayer spacing of \(~ 15.7\text{Å}, ~ 6.3\text{Å}\) larger than that observed in the acetate analogue.

![Increasing interlayer spacing](image)

Figure 8.1 The structure of some organic anions that may be used in an anion exchange material.
The exchange mechanism has not been established with any amount of certainty. In the case of exchanges using Cu-based LHS materials, no intermediate phase is observed indicating a topotactic exchange mechanism. This is contrary to Ni and Zn LHS based exchanges whereby an oxide impurity found after exchange may indicate the presence of an intermediate phase, and thus a dissolution re-precipitation exchange mechanism. Monitoring the real time anion exchange of LHSs using time resolved synchrotron powder diffraction data would offer invaluable information regarding the kinetics and mechanism of an exchange. Data were collected on the high resolution powder diffraction beamline I11 at the Diamond Light Source using a flow cell originally designed to obtain time resolved PD data on gas-solid interactions (Figure 8.2). An equimolar solution of the required anion was passed through a Kapton capillary tube containing the LHS mixed with glass beads. PXRD data were collected at 10 s intervals with the object to fully model the structural subtleties of these materials.

![Figure 8.2](image.png)

**Figure 8.2** The flow cell used in time resolved exchange studies.

It was hoped that the gas-solid flow cell would be transferrable to use in liquid-solid interactions, however several problems limited the data that were collected. The capillary design of the flow cell was not robust enough to give reproducible measurements or maintain the appropriate flow rates. The metal seals around the Kapton capillary tube were not strong enough to prevent leakage of the solution. Reversing the flow so that the liquid was pulled through the tube and adding plastic sleeves did reduce the frequency and severity of leaks significantly. Furthermore the geometry of the I11 beam line was not versatile enough to allow replacement of the capillary cell with a more robust cell design. Figure 8.3 shows a sample of the quality of data collected with a gap in the data as a result of stopping the experiment to amend a leak.
XRPD data indicates loss of acetate and formation of a bromide phase occurs within 60s of exposure. After 180s, the acetate basal spacing reflection has reduced by ~80% and continues to reduce in intensity as the reaction progresses. A broad basal spacing reflection for a bromide analogue is observed that does not increase in intensity, however the broadness of this reflection significantly reduces as the reaction progresses. During the time in which data were not collected, this reflection does increase significantly in intensity. After restarting the experiment, only one more data set was collected as a result of another leak. Interestingly, there are no traces of an intermediate present. The slow and progressing growth of the bromide basal spacing reflection does indicate a topotactic exchange mechanism. The data presented indicates that time resolved data are obtainable on anion exchange reactions, however the flow cell design requires some significant improvements. Additional beam time was applied for to carry out further experiments using the I12 - JEEP beam line at diamond that contains a larger and more versatile experimental hutch that would allow space to build a more fit for purpose experiment. Modifying a published cell design (Figure 8.4) to work in transmission geometry with powdered samples was discussed, however the proposal was not accepted [8].
From the studies presented in this thesis, it is clear that quantitative analysis would provide a greater insight into the loss of anions when exposed to carbonate and chloride/nitrate solutions. The lack of time was the main reason these further studies were not carried out, however particularly the amount of iodide precipitated out as Cu\textsuperscript{II} and the amount of iodide that remains in solution when exposed to a carbonate is of particular interest.

Figure 8.4  The flow cell used for \textit{in situ} time resolved synchrotron diffractions studies by Webster et al (2009).
7.5 References

Appendix

List of Conferences attended, Selected Abstracts and Future Publications
### List of selected conferences attended and selected abstracts.

<table>
<thead>
<tr>
<th>Meeting location and details</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. WP2 annual meeting (Leeds University)</td>
<td>07/07/2009</td>
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<tr>
<td>Abstract and presentation submitted.</td>
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<td>2. DIAMOND’09 Conference (York)</td>
<td>9-10/09/2009</td>
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<td>3. WP2 annual meeting (Imperial London)</td>
<td>25/03/2010</td>
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<tr>
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<td>4. NNL and Sellafield ltd visit to Loughborough University</td>
<td>08/04/2010</td>
</tr>
<tr>
<td>Presentation.</td>
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<td>5. BCA annual spring meeting (Kegworth)</td>
<td>13/05/2010</td>
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<td>6. DIAMOND’10 Conference (Manchester)</td>
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<td>8. DIAMOND’11 Conference (Coventry)</td>
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<td>9. RSC Solid State Christmas meeting</td>
<td>19/12/2011</td>
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Anion Exchange Behaviour of Layered Copper Hydroxides Under Batch and Flow Conditions

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ABSTRACT
Layered copper hydroxides of the formula Cu₂(OH)₃XₙH₂O have been synthesised and their anion exchange properties examined. Exchanged products have been investigated by powder x-ray diffraction, volumetric analysis and gamma spectroscopy to determine the extent of ion exchange. Under static conditions, where X = OAc⁻, complete exchange for ions such as I⁻, Cl⁻, Br⁻ and IO₄⁻ has been shown to occur after a period of 10 minutes and partial exchange with SbO₃⁻ after 1 hour. Competing anion experiments have implied that when X is small, the product is more stable than the starting material and does not undergo further exchange. Ion exchange experiments with solutions containing ¹²⁵I⁻ suggest that the layered structure is not strongly affected by incorporation of radioactive iodide. A prototype capillary flow cell for monitoring in-situ ion exchange experiments has been developed in collaboration with colleagues at the DIAMOND light source. Preliminary experiments under flow conditions suggest that time resolved exchange experiments to measure anion exchange properties will be possible.

INTRODUCTION
A long term solution for the immobilisation and storage of iodine-129 and technetium-99 is urgently required. Both are formed as a by-product as part of the nuclear fission process and are able to form anionic species. Iodine-129 is produced with a fission yield close to 1% and has a half life of 1.29x10⁶ years. As an anionic species, ¹²⁵I⁻ has a considerable risk associated with it due to the number of physical properties such as volatility, ability to form corrosive salts and ease of displacement of iodide by other anionic species in ground waters¹. In addition, iodide has the potential to accumulate in the thyroid of humans and animals as it is assimilated in the functioning of the gland². Technetium-99 is produced with a fission yield of approximately 6% with a half life of 2.12x10⁵ years. In its elemental form, technetium-99 is relatively immobile and safe, however upon oxidisation the ⁹⁹TcO₄⁻ anion is formed. The pertechnetate anion is extremely mobile in the environment and if ingested, concentrates in the gastrointestinal tract and thyroid gland, and so, like iodide, can be considered a biohazard³. Due to the high mobility of ¹²⁵I⁻ and ⁹⁹TcO₄⁻, the most likely route of human exposure is via ingestion of food and water.

At present, the common route for disposal of iodine-129 is via discharge into the ocean. This dilution and dispersion approach is used to ensure minimal exposure to humans. However, this method of disposal is no longer deemed acceptable and ever-tighter regulations to reduce the amount of nuclear waste discharged into the marine environment are certain to be passed⁴. Technetium-99 is currently treated with a concentrate and containment method using tetraphenylphosphonium bromide (TPPB). The waste is then incorporated in solid waste streams for possible future disposal in underground repositories using cement as a backfill. However, research has shown that in an alkaline cementitious environment, TPPB can degrade, thus releasing the TcO₄⁻⁵. Therefore, a new inexpensive approach for the sustainable and safe long-term immobilisation of iodine-129 and technetium-99 is needed.

Layered hydroxyl salts (LHS) are classified as anionic clays, which have a structure closely related to both brucite (Mg(OH)₂) and Layered Double Hydroxides⁶. The positive charge on the layers of a LHS is generated by the loss of one quarter of the hydroxides in the brucite-like structure⁷. This positive charge is then balanced by an anion located in the gallery spacing, either chemically bonded or electrostatically held giving the general formula of M⁺²(2)(OH)⁻(4-x)Y⁻(x)·nH₂O (Figure 1)⁸.
The structure of LHS leads to strong intralayer bonding and therefore increasing physical and chemical stability e.g. Cu₂(OH)₃NO₃ is both stable at pH 11-12 and has good thermal stability to 200°C. The size of the interlayer spacing can dramatically change depending on the occupying anion and can lead to compounds with facile exchange properties. Figure 2.

Previous studies by the authors on these compounds have shown that many different anions can be incorporated into the interlayer spacing by free movement of the layers to allow anions of varying size and shape to be incorporated between the layers of edge sharing octahedra.

While absolute exchange capacity is important, a number of other factors must be considered in preparing new anion exchange materials for the radiochemical industry. Firstly, the ion exchanged product must be stable in a high pH environment and to further ion exchange so the host does not change over time in the environment. In addition, for radiochemical applications, the host must not break down in the presence of the highly energetic emissions generated by the trapped radioactive anion. Another important factor is the rate of ion incorporation and whether the species can be incorporated under flowing effluent conditions or whether vat storage will be necessary. Previous work in this area by the authors has centred on identifying materials which undergo complete anion exchange, here studies relate to the speed as well as the efficacy of the ion-exchanger in addition to the stability of the products under active conditions.

EXPERIMENTAL

Previous ion exchange experiments have indicated that the most promising materials for undertaking rapid and efficient ion exchange are layered copper hydroxsalts with nitrate or acetate within the layers and the following experiments focus on using these materials.

SYNTHESIS OF EXCHANGE MATERIALS

Synthesis of Cu₂(OH)₃(NO₃) was carried out using a method of digestion developed in house. Metal oxide or metal dust was added to a concentrated solution of metal nitrate salt, contained within a Teflon-lined autoclave and heated to 250°C. Due to the instability of layered acetate materials above 100°C, this method could not be used for synthesis of copper hydroxyacetate. Cu₂(OH)₃(OAc).H₂O was therefore prepared via titration of 2M copper acetate solution with 2M NaOH solution (Cu:OH = 1:1).

SUITABILITY AND RELIABILITY

The rate of exchange of copper hydroxynitrate and copper hydroxyacetate was explored using iodide as a standard target anion. Cu₂(OH)₃(X).YH₂O (Y=NO₃⁻,OAc⁻) (0.1M) was added to a solution of sodium iodide (20 ml) in a molar ratio of 1:1. The solution was then stirred for 1 day at room temperature and the resulting solid recovered through filtration.
that iodide exchange with the nitrate is incomplete with the $d_{001}$ reflections for both the anion analogues, $\text{Cu}_2(\text{OH})_3(X)$, $X=\text{NO}_3^-$, $\Gamma^-$ are present. The relative intensities of the two 001 reflections indicate that nitrate is still the majority anion occupying the interlayer spacing and complete exchange was only observed after 10 days. This reaction was much slower than anticipated based on previous studies. The reason for this may be that due to a large particle size of the copper hydroxynitrate as a result of the high temperature needed for synthesis. The increased particle size decreases the surface area for an exchange reaction to occur. In the case of copper hydroxyacetate, complete exchange occurs within 1 day with only the 001 reflection for copper hydroxyiodide present. This confirms that the larger gallery spacing of the acetate analogue plays a large role in the efficiency of an exchange reaction. The next step is to determine the amount of time needed for a complete exchange of iodide for acetate. Copper hydroxyacetate is added to a sodium iodide solution as explained above and the reaction observed. It was noted that within 30 seconds of addition of the exchange material, a colour change from blue to yellow-green was observed indicating a reaction had already taken place. After just 10 mins exposure to the sodium iodide solution, the XRD pattern indicated a complete exchange.

**EXCHANGE CAPABILITIES OF Cu$_2$(OH)$_3$(OAc).H$_2$O**

The experiments described above have shown that copper hydroxyacetate is a suitable material for the immobilization of iodide. There are however, other anionic species such as $\text{IO}_3^-$, $\text{IO}_4^-$, $\text{TCO}_4^-$, $\text{Cl}^-$, $\text{SbO}_3^-$ and $\text{Cr}_2\text{O}_7^{2-}$ that are also of particular concern. Exchange reactions involving the relevant sodium salts ($\text{ReO}_4^-$ used as a surrogate for $\text{TCO}_4^-$) and copper hydroxyacetate were carried out as previously described. The powder XRD data collected on the materials after the anion exchange experiments are presented in (Figure 4).

The results presented in figure 4 show the products after 1 hour of mixing of the copper hydroxyacetate with the sodium salt. A shift in the 001 reflection occurs after reactions with $\text{IO}_4^-$ (Fig. 4e), $\text{Cl}^-$ (Fig. 4b), $\text{SbO}_3^-$ (Fig. 4f) and $\text{ReO}_4^-$ (Fig. 4g) indicating an exchange has taken place. The shift of the $d_{001}$ reflection to a higher $2\theta$ angle in all exchanged products represents a reduction in the interlayer spacing. Interestingly the positions of the 001 reflection for periodate and antimonite are at similar $2\theta$ angles indicating both anions are of similar size. The starting material was still present after exchange with $\text{SbO}_3^-$, however this may be due to the poor solubility of sodium antimonate. Despite the occurrence of $\text{Cu}_2(\text{OH})_3(\text{IO}_3)$ in nature, exchanges with iodate have proved unsuccessful. A possible reason for this inhibited migration of the iodate anion into the gallery spacing is the stereoactive lone pair of electrons present in the pyramidal shape. The lone pair may inhibit the ability of the iodate anion to enter the negatively charged interlayer spacing. Exchange reactions with $\text{Cr}_2\text{O}_7^{2-}$ degraded the starting acetate material. The divalent dichromate anion causes decomposition of the structure and the formation of copper(II) oxide. It should be noted however that in the presence of other divalent anions, no degradation takes place and the dichromate anion takes no part in a reaction.

**STABILITY OF COPPER HYDROXY SALTS IN HIGH pH**

The most probable disposal route for solid waste is via encapsulation in a cementitious environment and subsequent storage in an underground repository.
Therefore, the stability of any material used to encapsulate mobile active species in high pH (11-13.5 depending on the cement used) is vital. Exchanged Cu$_2$(OH)$_3$I was added to solutions of basic Na$_2$CO$_3$ with pH controlled with the addition of NaOH (Figure 5).

The results of this study show that Cu$_2$(OH)$_3$I remains intact up to pH 11. However, from pH 11-11.5, the structure breaks down forming CuO. This shows that the exchanged Cu$_2$(OH)$_3$I material is stable up to pH 11 and stable in a high CO$_3$$^{2-}$ environment. Past pH 11.5, Cu$_2$(OH)$_3$I exchanges I$^-$ for OH$^-$ rather than forming either a copper carbonate or copper hydroxyl carbonate species.

**EXCHANGES WITH RADIOISOTOPES OF IODIDE**

It has been shown that Cu$_2$(OH)$_3$(OAc).H$_2$O is able to exchange with I$^-$ efficiently and the subsequent Cu$_2$(OH)$_3$I material is stable up to a pH of ~11. It is assumed that the chemical properties of the stable $^{127}$I anion will be identical to those of radioactive $^{125}$I anion. However, the emission of $\beta$ and $\gamma$ radiation by the species may disrupt the crystal structure of the exchange material. Therefore, a standard exchange reaction of Cu$_2$(OH)$_3$(OAc).H$_2$O with stable $^{127}$I was performed for 10 mins, however a small amount (10%) of radioactive $^{125}$I was introduced into solution. $^{125}$I was used as a surrogate for $^{129}$I ($t^{1/2}$=$^{129}$I = ~60 days) in order to determine the effect on the crystallinity of the sample and also to obtain a quantitative amount of $^{125}$I present in the exchanged material (Figure 6).

![Figure 5 - Powder XRD pattern of (a) Cu$_2$(OH)$_3$I post exposure to a variety of pH solutions (* = Cu$_2$(OH)$_3$I, +=CuO, -=Cu(OH)$_2$)](image)

After 6 months exposure to radiation, the crystal structure of Cu$_2$(OH)$_3$I (Fig 6b) remains intact. There is some preferred orientation and loss in crystallinity, however this is most likely due to the degradation of $^{125}$I and the formation of a species containing $^{125}$Te. It is difficult to determine the presence of $^{125}$Te in the sample, due to the low concentration of radioactive exchange material used. Further work is needed to determine where the $^{125}$Te is located and if further reactions occur.

To determine the uptake of iodide, quantitative measurements can also be obtained using a spiked iodide solution. Samples of the pre and post exposed 10% $^{125}$I solutions were placed in a radiation detector and the counts per minute (cpm) obtained for comparison (Table 1).

<table>
<thead>
<tr>
<th></th>
<th>Cpm of spiked iodide solutions</th>
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<tbody>
<tr>
<td>Pre exposure</td>
<td>775 cpm</td>
</tr>
<tr>
<td>Post exposure</td>
<td>140 cpm</td>
</tr>
<tr>
<td>Difference</td>
<td>635 cpm</td>
</tr>
<tr>
<td>Blank</td>
<td>33 cpm</td>
</tr>
<tr>
<td>Adjusted difference</td>
<td>632 cpm</td>
</tr>
<tr>
<td>% loss of $^{125}$I</td>
<td>82%</td>
</tr>
</tbody>
</table>

**Table 1 – Cpm of spiked iodide solutions**

Quantitatively, 82% of the activity observed in the initial solution is lost post exposure to the exchange material. This indicates that a large amount of the $^{125}$I anion has been captured after 10 mins and, when the exposure time is increased to 1 hour, 92% is shown to have been captured.

**REAL TIME IN-SITU EXCHANGE REACTIONS**

It has been shown that in static conditions, Cu$_2$(OH)$_3$(OAc).H$_2$O is able to capture a variety of anions efficiently and the subsequent exchanged material is then stable. The behavior of these materials under flow conditions has never previously been determined. Time resolved studies using environmental cells with synchrotron radiation sources have been carried out over the last 3...
Appendix – List of Conferences attended, Selected Abstracts and Future Publications

A.D. Butterworth

decades to study a variety of reactions, such as catalysis, hydrothermal reactions, cation exchange and mineral-fluid interactions. The ability to monitor the progression of reactions real time through studying structural changes as a function of temperature, pressure, pH, humidity using synchrotron radiation has allowed kinetic parameters to be quantified as well as reaction mechanisms to be determined at the atomic scale. A time resolved study of the interaction of Cu$_2$(OH)$_3$(OAc).H$_2$O was carried out using the high resolution powder diffraction beamline I11 at the Diamond Light Source. A flow cell was used to introduce a salt solution of known concentration and flow rate into a Kapton® capillary containing Cu$_2$(OH)$_3$(OAc).H$_2$O. (Figure 7).

Figure 7 – The flow cell used to introduce a salt solution into a Kapton capillary containing Cu$_2$(OH)$_3$(OAc).H$_2$O

The flow cell was mounted on the diffractometer back plate. A syringe pump was used to control the flow rate of the salt solution and the diffraction data collected using a “Mythen 2” position sensitive detector (Figure 8).

Figure 8 - The flow cell mounted on the I11 diffractometer backplate

Powder XRD data were collected at 30 second intervals with an exposure time of 10 seconds during an exchange experiment of Cu$_2$(OH)$_3$(OAc).H$_2$O with a solution of NaCl, with an intended flow rate of 1ml/min The data are presented in (Figure 9).

Figure 9 – Selected powder XRD patterns at 40s intervals of the anion exchange process Cu$_2$(OH)$_3$(OAc).H$_2$O with NaCl

As a function of time, the 001 reflection of Cu$_2$(OH)$_3$(OAc).H$_2$O (*) was observed to initially reduce dramatically in intensity upon exposure to NaCl solution. Concomitantly the intensity of the 001 reflection (*) then remains stable and the 001 reflection of the Cu$_2$(OH)$_3$Cl exchange material (+) increases in intensity rapidly. The flow cell used in these experiments was not ideal as a substantial the salt solutions permeated the seals between the kapon capillary and the flow tubes This in turn meant the flow rate could not be controlled. The reactions then could not go to completion due to issues with reliability. The width of the Cl exchanged 001 reflection (+) indicated the exchanged material is relatively less crystalline that that of the starting material. The initial rapid loss of the Cu$_2$(OH)$_3$(OAc).H$_2$O reflection (*) indicates that the exchange material is broken down in solution. It is proposed that the OAc anion is removed rapidly from the interlayer spacing when placed in solution. The disrupted Cu(OH)$_3$+ sheets will the reform a layered material when in the presence of a suitable anion, such as Cl-. Initially the formation of the chloride phase is slow, but with time the rate increases. No intermediate phases were indentified during the exchange process.

CONCLUSION

Layered hydroxyosalts have potential as exchange materials for anions containing radioactive species such as iodine. This study has shown that using large exchangeable anions such as acetate allows reactions with iodide to occur in less than 10 mins and results are reproducible. The exchange material is not stable above 100˚C as previous studies have shown however this study indicates that copper hydroxyacetate and its exchanged analogues are stable in solutions of high carbonate and basic conditions. Exchanges under static conditions with other anions likely to be of interest to the radiochemical industry
include periodate, chloride, antimonite and perrhenate (Rh used as a surrogate for Tc) have been successful. XRD analysis of the products formed by exchange reactions give a qualitative result to determine whether an exchange has occurred. Radioactive $^{125}\text{I}$ has been shown to be incorporated into the structure of copper hydroxyl salt and the crystal structure of the exchanged material remains intact. Quantitative measurement to determine uptake of $^{125}\text{I}$ by copper hydroxyacetate has shown a high efficiency of 92% uptake after 1 hour. Flow experiments have shown that time resolved data collection is possible to observe structural changes in the anion exchanger in situ. However the capillary design of the flow cell was not robust enough to give reproducible measurements or maintain the desired flow rates. Furthermore the geometry of the I11 beamline places constraints on the cell design and means replacement of the capillary cell with a more robust cell is not possible. Beamtime has been requested on the multipurpose beamline I12-JEEP as its large experimental hutch has more flexibility to build and manipulate equipment. Discussions with beamline scientists on beamlines I11 and I12 on our proposed re-design of a flow cell, modifying a published cell design to work in transmission geometry with powdered samples, have taken place and we are confident the new design of the cell will allow us to carry out mass balance experiments successfully.