MICROWAVE METHODS IN THE SYNTHESIS OF BULK AND PARTICULATE MATERIALS

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“Is there nothing faster than microwaves? ...Doh!”

Homer J. Simpson
Abstract

Microwaves have been used in chemical synthesis for a number of years, primarily as an energy efficient alternative source of heat for organic reactions, and in some cases have been shown to lead to new products compared to those formed during conventional heating. More recently, microwave heating has been applied to solid-state synthesis and materials processing. Further, there have been claims that there is an "athermal microwave effect" in a wide range of microwave-driven reactions, that is, microwave heating appears to accelerate such reactions more than would be anticipated from temperature rise alone. In many cases, careful temperature measurement reveals this effect to arise from superheating; however, cases remain where superheating cannot explain anomalous reaction rates.

This thesis is partly concerned with investigating news ways of applying microwaves in a chemical synthesis; it is also concerned with the mechanism of such processes, including microwave-assisted diffusion, structural changes induced by microwave fields and the effect of pressure on microwave-driven reactions. In some cases we also studied the mechanism of reactions driven by more traditional sources of heat. A novel microwave reactor was designed and constructed to enable us to perform mechanistic studies of the hydrothermal synthesis of iron oxide particles by small angle neutron scattering (SANS); this was performed in parallel with small angle X-ray scattering (SAXS) and EXAFS on samples heated conventionally. SANS measurements showed that after an initial burst of nucleation, particles of 50 Å mean diameter were formed in the first 30 minutes, evolving to a final size of 100 Å after 7.5 hours. The SAXS measurements reported a burst in particle growth as the sample was heated above 50-60°C, producing particles up to 250-300 Å in diameter. However, wide-angle X-ray scattering data showed that the latter samples did not exhibit any Bragg scattering, implying that they had no medium-long range crystalline order when suspended in the growth medium. EXAFS data revealed the presence of very small particles of haematite in solution, which seems to add weight to the hypothesis that haematite particles are produced first through the growth of small particles which then aggregate to larger clusters.

Studies were also performed of the microwave-assisted diffusion of cations into channelled iron and manganese oxides, and showed that the choice of experimental conditions – particularly the nature of the host material - have a significant effect upon the final product. In several cases, microwave heating accelerated diffusion and could also lead to novel routes to insertion compounds.

Further studies on the influence of microwave heating on the structure and dynamics of materials involved the construction of further pieces of apparatus to perform in situ diffraction during microwave irradiation. Neutron diffraction was performed on aspirin to probe proton disorder, and high-resolution powder X-ray diffraction was conducted on the fast-ion conductor beta alumina to look at thermal excitation of the relatively mobile sodium ions during microwave heating. In both cases we demonstrated that the sample could be heated and studied in situ, and structural changes were revealed through changes in the Debye-Waller factors of particular atoms in both materials. The experiments on aspirin indicated that the sample had been subjected to a localised heating effect.

Finally, various organic and inorganic reactions have been performed in a new design of microwave pressure cell. The cell has been tested to a pressure of 250 bar – a record to date for microwave-heated reactions - and applied to chemical reactions at 60 bar.
Acknowledgements

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<tr>
<td>c</td>
<td>Speed of light</td>
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<tr>
<td>g</td>
<td>Grams</td>
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<td>E</td>
<td>Electric field</td>
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<tr>
<td>H</td>
<td>Magnetic field</td>
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<td>m</td>
<td>Metres</td>
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<tr>
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<tr>
<td>ρ</td>
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<td>Conductivity</td>
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<tr>
<td>τ</td>
<td>Relaxation time</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>IR</td>
<td>Infra-red</td>
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<td>MW</td>
<td>Microwave</td>
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<tr>
<td>RF</td>
<td>Radio frequency</td>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>CHN</td>
<td>Carbon, hydrogen and nitrogen</td>
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<tr>
<td>PXRD</td>
<td>Powder X-ray diffraction</td>
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<tr>
<td>EDAX&lt;sup&gt;TM&lt;/sup&gt;</td>
<td>Energy dispersive absorption of X-rays</td>
</tr>
<tr>
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<td>WD</td>
<td>Wavelength dispersive</td>
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<tr>
<td>P.C</td>
<td>Personal computer</td>
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Section 10.1 Conclusions and Next Steps
Chapter 1 - Introduction

The field of nanoparticles and nanostructured materials has been an extremely wide and diverse area of study for many years. The introduction to this thesis can be considered a short review of the current literature of this area. The first Section covers the technological applications of nanoparticles and nanostructured materials. Areas such as quantum dots, high $T_c$ superconductors and magnetic materials will be covered. The synthetic routes to these materials and how the size of particles can be controlled will also be discussed. This will cover a wide range of methodologies including microemulsions, chemical vapour deposition (CVD) and microwave heating. Some of the techniques described have been used as part of experimental work for this thesis carried out at The University of Edinburgh, Daresbury Laboratories and the ISIS Facility. In particular, the application of microwave heating to chemical syntheses has played an integral part of the experimental work and so is covered in greater depth.

1.1 Nanoparticles and Nanostructured Materials

In the past decade there has been increased interest from workers in several disciplines in the area of nanoparticles. The term “nanoparticle” and the related concepts of “nanoscaled” and “nanosized” came into frequent use at the start of the 1990s. Previously the terms submicron and ultrafine had been used. Typically, a nanoparticle or nanostructured material has a length scale of less than 100 nm, consequently uniaxially stacked multilayers and coatings are also included. Of these nanomaterials another subset can be identified, that of nanophase materials with three dimensional structure with a domain size less than 100 nm. Nanophase materials in general are produced by compression of nanoparticles. These materials have a large number of grain boundaries where the local atomic arrangements are different to that of the crystal lattice.\(^2\)

As a consequence of their size, nanoparticles and nanostructured materials exhibit differences in their properties (electronic, optical, electrical, magnetic, chemical and mechanical) compared to the bulk material, making them suitable for new
nanoparticles have hybrid properties, many of which are poorly understood. Such properties include lower melting temperature, increased solid-solid phase transition temperature, lower effective Debye temperature, higher self-diffusion coefficient, changed thermophysical properties and catalytic activity.

Nanoparticles may also be dispersed heterogeneously through a continuous matrix (ceramic or polymer) thus producing a nanocomposite. Two examples of such nanocomposites include supported nanoscale catalysts and pigments, which are of interest due to their large surface area to volume ratio.

1.2 Applications of Nanoparticles and Nanostructured Materials

In the following Section the application of nanoparticles in electronic, optical and magnetic applications is discussed. A variety of materials including insulators, semiconductors, superconductors, metals and alloys, optical and artificially structured materials may be used for such purposes. The majority of applications involve films composed of nanoparticles, supported by a substrate material.

1.2.1 Quantum Dots

There are certain electronics applications where quantum confinement effects may be of use and it has been suggested that these effects may be present in nanoparticles. A zero-dimensional structure, also known as a quantum dot, is a system where electrons are confined to a small domain, for example a nanoparticle. The electrons therefore behave like particles-in-a-box, and their new energy levels are determined by quantum confinement effects. These new energy levels result in a modification of the optoelectronic properties of the dot in comparison with bulk material electronic structure. Discrete energy levels are required to describe electron excitation and transport in quantum dots. Quantum confinement effects result in higher energy level transitions as compared to the bulk material. This effect is observed as a spectral blue-shift.
By changing particle size the band-gap can be tuned to produce quantum dots which emit light of various colours. This is advantageous for two main reasons. Particle size tuning is easier than the current complex techniques of synthesising compound semiconductors. Also the electrons in quantum dots remain in excited states for longer; this is important for laser optical applications.\(^9\)

The processes required to produce quantum dots are technologically demanding. During production the following need to be controlled accurately.\(^{10-11}\)

1. Particle size.
2. Monodispersivity within a few percent.
3. Passivation of the surface.
4. Good control of the particle shape.

The properties of some nanoparticles vary with time. In order to combat the reactivity and instability of the nanoparticles they are frequently embedded in a glass or in a semiconductor with a wider band gap.\(^{12-13}\) These nanocomposite materials are then used in real optical and electro-optical applications. Optical cut-off filters based on \(\text{CdS}_x\text{Se}_{1-x}\) nanoparticles embedded in silicate glass are already commercially available. Other applications such as optical memories, electro-optical switching are also potentially viable through quantum dot technology.

### 1.2.2 Gas Sensors

Gas sensors utilise a material with measurable physical properties (electrical or optical) which can change in the presence of a certain gas. This change in property must be reversible to be commercially viable. A solid state chemical sensor selectively converts microscopic chemical interactions into a measurable electrical signal. Semiconducting oxides, such as \(\text{SnO}_2\), \(\text{ZnO}\) and \(\text{Fe}_2\text{O}_3\) are used extensively as gas sensors.\(^{14}\) The sensor is generally constructed as a porous sintered ceramic body, which is heated between 300 and 700°C. The sensing behaviour is governed by the adsorption of oxygen in the neck region between the grains. A positive space charge, known as the depletion layer, develops in the oxide layer as electrons are transferred
to the adsorbed oxygen. A negative charge develops on the surface. Reducing gases can remove some of the $O^2$ from the surface causing the electrical conductivity to increase.\textsuperscript{15} The use of nanoparticles increases the available surface area, making such sensors very sensitive.

### 1.2.3 Resistors and Varistors

Films made up of small conducting particles embedded in an insulating matrix of either a ceramic or glass exhibit a great variability of the electrical conductivity. By controlling the volume fraction and size of the particle in the matrix it is possible to have a wide range of electrical transport properties. Consequently it is possible for such materials to be used as thick film resistors. An example of such a material is the nanoparticle-glass composite LaB$_6$ which is compatible with copper integrated circuits.\textsuperscript{16}

A varistor is a voltage dependant resistor, which has a very low resistance at high voltage. It is used to protect low power circuits from high voltage transients and is made from doped ZnO and SiC. Control of resistance is presumed to be via grain-boundary contacts or through intergranular insulating layers. Nanoparticles with large grain boundaries are expected to improve varistor properties. Using small (< 100 nm) nanoparticles, the varistor should be more homogenous and so result in better non-linear electrical properties.\textsuperscript{17}

### 1.2.4 Conducting Films

Thin films of wide optical band gap oxides, for example SnO$_2$, In$_2$O$_3$ and indium tin oxide (ITO), which are transparent in the visible spectral region have uses in many applications \textit{e.g.} electrodes and anti-reflective coatings in solar cells as well as transparent electrodes in optoelectronic devices such as photodetectors and charge-coupled imaging devices. Transparent conducting films need to have high transmission in the visible region of the spectrum and a high, if not metallic-like, electrical conductivity.\textsuperscript{18} To obtain such properties, inhomogeneities in the film due to (the presence of) large particles, which cause detrimental light absorption and scattering in the visible region, can be minimised by preparing films made up of
nanoparticles. By controlling the particle size, quantum confinement effects may be produced, as described earlier. This results in the ability to tune the nanomaterials’ absorption characteristics. For example by varying the particle size it is possible to change the IR absorption peaks of a film made of ZnO nanoparticles.\textsuperscript{19}

1.2.5 Capacitive Materials
Nanoscale structures of dielectric materials are of interest due to the reduction in capacitance caused by the scaling down of dynamic random access memories (DRAMs). As materials with high dielectric constants can store more electrical charge than capacitors, materials with even larger dielectric permittivities are sought for the shrinking DRAMs. One method to increase the dielectric permittivity is to disperse conducting particles in a dielectric matrix. However, the dissipation factor then becomes too large.\textsuperscript{20} If 2-8 nm silver nanoparticles are inserted in a lead zirconium titanate matrix the nanomaterial has a high dielectric permittivity with a low dissipation factor. The smaller particles lead to lower dielectric permittivities, but improve the dissipation factor.\textsuperscript{21} It has been calculated using the percolation theory of dielectrics that the optimum topology for high dielectric nanocomposites is that of ellipsoidal metal particles with a small interparticle spacing in the insulating matrix.

1.2.6 High-Temperature Superconductors
It is currently thought that nanoparticles are the answer to flux pinning improvement in high $T_c$ superconductors. The flux pinning problem occurs if the magnetic flux entering the material is not distorted or pinned by suitable defects, thus causing the material to lose its superconducting properties. Nanoparticles can be used as defects when added to the superconducting material, enhancing flux pinning and therefore increasing the critical current density. BaZrO$_3$ has been added to YBa$_2$Cu$_3$O$_7$ to produce an increase of more than one order of magnitude in the critical current density.\textsuperscript{22}

1.2.7 Optical Materials
Scattered light intensity is a function of the wavelength of the incident light and of the particle diameter. In order to attenuate UV light by this mechanism and minimise
attenuation of visible light the particles must be nanosized. Nanoparticles in a suitable dispersion are already used for sunblock and as films for protecting plastics against colour degradation.

Some materials exhibit electrochroism, the phenomenon where the optical properties of the material are altered reversibly through the application of an electric field. Such materials are frequently used for building and aeroplane windows to control the amount and type of light entering. NiO films made up of 5-10 nm sized grains have good electrochromic properties, but as the particle size increases these properties become poorer. The large number of grain boundaries is thought to play a role in the transport of the metal ions into the grains. The greater the number of grain boundaries the greater the rate of metal ion transfer into the grains.\(^{23}\)

### 1.2.8 Magnetic Materials

Ideally magnetic particles used in recording media should have diameters of the order of a single magnetic domain. Nanoparticles of magnetic materials are the size of a single magnetic domain, in which the magnetic spins are aligned to produce a magnetic moment in one direction. The ferromagnetic elements iron, nickel and cobalt have single domains which are of several tens of nanometres in size. Materials which are to be used for high density magnetic recording need to possess high coercivity (resistance to demagnetisation) and high magnetisation. The maximum value for coercivity is obtained for nanocrystals, which have crystal sizes close to the size of a single domain. If the crystal size is larger or smaller than that of a single domain then the coercivity is greatly reduced.

Soft magnetic materials, such as FeSi and FeNi alloys, need to have very low coercivitities. These materials are used in power transformers, magnetic recording heads and microwave applications. It has been shown that the maximum for coercivity against grain size occurs at approximately 100 nm. An alloy with particle size in the range 10-20 nm embedded in an amorphous phase shows very low values for the coercivity. The material also shows very low eddy current losses and high frequency properties.\(^{24-25}\)
The magnetisation of bulk magnetic materials usually decreases as temperature increases and so limits the temperature range in one cooling cycle. Superparamagnetic particles in a non-magnetic host can overcome this limitation through combining the higher magnetisation of ferromagnets with the higher magnetocaloric effect of paramagnets.

Certain nanocomposites exhibit a novel and important property known as giant magnetoresistance (GMR). The electrical resistivity of these materials decreases (up to 80%) when exposed to a magnetic field. The magnetic field aligns the ferromagnetic domains, and reduces the scattering of the conduction electrons and therefore the electrical resistance. These materials may be used for magnetic sensors and storage devices with very high densities. GMR is seen in immiscible metals such as Co-Cu, Fe-Ag, Fe-Cu, Fe-Au and Co-Ag. The smaller the particle size the bigger the GMR effect. The effect is highest near the percolation threshold.

1.3 Synthetic Routes to Nanoparticles and Nanomaterials

1.3.1 Introduction

Traditional methodology for the production of nanoparticles and nanocomposite materials generally fails to produce particles with the specifications required for hi-tech applications. This is due mainly to particles being polydisperse and irregularly shaped. Wide particle size distributions and morphologies affect the desired properties of the particles. It is obviously important to have synthetic routes which usually produce uniformly sized and shaped particles.

Particles and materials have been produced for many years through solid state reactions in furnaces (fondly known as the “shake and bake” method), by hydrothermal precipitation from solution and (even) by grinding bulk materials. Each of these methods has their own specific problems such as polydispersity, poor control of morphology and poor crystallinity. Modifications to the methodology of these techniques has improved the quality of the particles produced, but these techniques can be poor. The shake and bake method has been greatly enhanced through the use of sol-gel routes, and hydrothermal reactions are enhanced by the use of additives such as phosphates.
In order to improve the quality of technologically important materials and particles it is vital to find new chemical routes to monodisperse, uniform particles and materials. To produce such materials would require better understanding of the formation mechanism for particles and new ideas for synthesis.

1.3.2 Microemulsions

The use of microemulsions as micro-reactors has been a recent approach to synthesise monodisperse particles. The droplets in a microemulsion are highly monodisperse and so the microemulsion should favour monodisperse particles. There are two types of emulsion: emulsions that are thermodynamically stable are known as microemulsions; those that are unstable are known as macroemulsions. Both have characteristics in common, although microemulsion droplets tend to be smaller in size. In microemulsions, for the dispersed phase to remain stable then the water-oil interface must contain an additional component known as an amphiphilic surfactant.

1.3.2.1 Self-assembly of Amphiphiles

Amphiphilic molecules spontaneously self-organise, forming structures of various kinds. One such structure is the micelle, a pocket of a dispersed phase surrounded by a bulk dispersion medium, for example water in oil. A compromise needs to be made between complete phase separation and a molecularly dispersed solution. In the case of a micelle the amphiphilic surfactant molecules self-assemble to produce a microphase in which the hydrocarbon chains of the surfactant solubilise in the oil phase, and the polar head groups of the surfactant orient themselves towards the aqueous phase (Figure 1.1).

![Figure 1.1 - Structure of a water-in-oil micelle.](image-url)
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The stage at which we can determine the micellisation process is known as the critical micelle concentration (cmc), the concentration that needs to be surmounted before micelles may form. Self-assembly is a physicochemical process and so amphiphilic molecules associate physically, not chemically; the size and shape of microstructures formed will be controlled by small changes in concentration, salt content, temperature, pH and pressure.

An example of an amphiphilic molecule is sodium bis(2-ethylhexyl)sulfosuccinate (AOT). AOT has non-polar branched hydrocarbon tails and a polar sulphate head (Figure 1.2). AOT when mixed with water and an organic solvent may form monodisperse micelles which may be used to grow particles.

![Figure 1.2 - Structure of AOT.](image)

1.3.2.2 Prediction of Surfactant Aggregate Structures

Emulsion droplets are not necessarily spherical in shape. By changing the surfactant and its concentration it is possible to form a variety of aggregate structures in which to grow particles. Possible aggregate structures depend upon the properties of the amphiphile in question. In order to make structural predictions such as size and shape then molecular parameters (hydrophobic volume, chain length and head group area) and intensive variables (temperature and ionic strength) need to be linked with microstructure. Most theories try to predict the optimal aggregate through free energy minimisation arguments. The free energy of surfactant self-assembly in dilute solutions consists of three terms.
1. A favourable hydrophobic contribution due to the hydrocarbon chains solubilising in the oil phase.

2. A surface term reflecting the tendency of the polar head to minimise hydrocarbon-water interactions.

3. A packing term, which requires the hydrophobic exterior of the micelle to exclude water and the polar head groups of the surfactant. Hence, the hydrophobic exterior should only contain oil and surfactant hydrocarbon tails.

The surface and packing terms take on different functional forms for each aggregate geometry; the optimal aggregate form is that with the minimum free energy. In the case of dilute solutions where interactions between aggregates are minimal then these terms can be described as the surfactant number $N_s$.

$$N_s = \frac{v}{l a_o} \quad 1.1$$

where $v$ is the volume of hydrophobic part of the surfactant molecule (nm$^3$), $l$ is the length of hydrocarbon chains (nm) and $a_o$ is the effective area per head group (nm$^2$).

Surfactant numbers relate the properties of the molecule to the preferred curvature of the aggregate. When $N_s$ is small then highly curved aggregates are expected and vice versa. The varying shapes of aggregates are summarised in Table 1.1.

<table>
<thead>
<tr>
<th>Shape of Aggregate</th>
<th>Surfactant Number ($N_s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical micelles</td>
<td>0.33</td>
</tr>
<tr>
<td>Infinite cylinders</td>
<td>0.50</td>
</tr>
<tr>
<td>Planar bilayers</td>
<td>1.00</td>
</tr>
<tr>
<td>Inverted cylinders and micelles</td>
<td>&gt;1.00</td>
</tr>
</tbody>
</table>

Table 1.1 - Relationship between shape and surfactant number.
Surfactant numbers only give an approximate suggestion for an aggregate structure, but show how changes in solution condition and molecular structure will change an aggregate’s size and shape.  

By controlling the properties of the water-in-oil microemulsion it is possible to produce spherical droplets of known size. If the droplet contained a precursor mixture to be reacted, then the size and shape of the final particle should be constricted to the size and shape of the micelle. These micelles may be considered to be “mini-reactors” and it is hoped that by controlling the form of the micelle it would be possible to control the particles formed. Microemulsions tend to be monodisperse systems and the micelles tend to be spherical as this geometry is usually thermodynamically the most stable. Nanoarticles of CdS, CdSe, \(^{32-33}\) various iron oxides as particles and magnetic fluids have all been produced using microemulsion methods. \(^{34-37}\)

### 1.3.3 Chemical Vapour Deposition

Chemical vapour deposition (CVD) is a method where a volatile molecular species (frequently metal containing) is transported into a reactor that contains a substrate where the molecular species is adsorbed and reacts to produce a film of a particular material. CVD is a broad technique, which can be broken down into more specific techniques; CVD will only be discussed here in general terms. \(^{38}\) Various precursors are used including organometallics and metal-organic compounds. The properties of these precursors are important as their volatility and reactivity are vital for the preparation of the final material. CVD involves the transport of a metal-containing precursor into a reactor. The reactor contains a substrate to which the precursor first physisorbs then chemisorbs. The precursor then reacts on the substrate, releasing the unnecessary ligands, which are then lost from the reactor (Figure 1.3).
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Figure 1.3 – Diagram of a typical CVD reactor.

As with any process, CVD has advantages and disadvantages. The precursor may dissociate before coming in contact with the substrate; similarly the precursor may pass over the substrate without reacting. Such problems can in most cases be removed through engineering new CVD ligands for specific metals.

Good precursors should have the following properties:
1. Good vapour pressure at a specified temperature.
2. Undergo thermal decomposition in a controlled manner.
3. Produce a film with the desired composition, morphology and purity.

In practice, a vapour pressure of approximately 10 torr is required to ensure that the precursor reaches the reactor. This feature is particularly important when the precursor is delivered using bubblers, which are heated at raised temperatures to ensure delivery. Partial decomposition of the precursor can drastically affect the delivery rates and so vary the film properties and cause irreproducibility in the films produced. There is usually a narrow temperature window for substrate reactivity. At the low-temperature end of the window the precursor should be inert, whereas at the high-temperature end the precursor should react at high rates to deposit films. Metal hydrides, metal alkyls, metal halides and mixed-ligand systems are most frequently used industrially as CVD precursors.
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The metal-containing precursor falls into three groups, depending on the metal-ligand bonding involved.

1. Inorganic compounds, which do not contain carbon.
2. Metal-organic compounds, which contain carbon but not metal-carbon bonds.
3. Organometallic compounds, which possess carbon-containing ligands with metal-carbon bonds.

These precursor compounds may react through many pathways to produce the desired products. Such mechanisms include: reductive elimination, bond homolysis, ligand dissociation, reduction, redox, metathesis, and ligand elimination. The pathway that the precursor takes to form the desired product is complex and often poorly understood. This makes it difficult to design new precursor compounds.

1.3.4 Modified Hydrothermal Reactions

Hydrothermal reactions generally produce particles through precipitation from aqueous solutions. Typically, pressures range from ambient to several atmospheres and the temperature is often close to or at the boiling point of the solvent. The particles formed are generally polydisperse crystallites with varying morphologies. It would be advantageous to modify such reactions to produce monodisperse particles with controlled morphology. Certain additives may be introduced to the reaction in order to facilitate the control of particle size and shape.

The forced hydrolysis of aqueous trivalent iron solutions has been extensively used to produce relatively monodisperse iron oxide colloids and exemplifies this kind of process; typically the iron oxide haematite (α-Fe₂O₃) is the final product. The formation of such colloids is facilitated by the addition of various inorganic anions as precipitation agents. The additive can act by chelating the metal ions in solution, forming soluble precursors with high reactivity towards hydrolysis, thus causing a single nucleation event. Other additives bind preferentially to a particular crystal face, preventing growth of the crystal in that direction. There have been many studies into additives for the iron system. Such additives are based on various oxoanions of inorganic phosphates, sulphates, perchlorates and amines. The additive is only
present in a very low amount (iron: additive mole ratio of approximately 50:1). Infrared analysis of the surface of the haematite crystals formed shows that the additives remain bound to the surface of the crystals. This is observed as P-O, S-O and Cl-O stretches in the IR spectra. The additives can be removed through treatment with strongly alkaline solutions.

When NaH$_2$PO$_4$ was used as a morphological agent, monodisperse, spindle-shaped particles of haematite were formed. Electron diffraction studies of the crystals showed that the phosphate binds preferentially to the crystal faces parallel to the c-axis of haematite and so stabilises these faces allowing the crystal growth observed. When NaSO$_4$.10H$_2$O was used, oval particles were formed. Compared with the phosphate case the particles had a wider size distribution and smaller aspect ratio. Electron diffraction studies again showed that binding of the morphological agent was parallel to the c-axis of the haematite. Use of NaClO$_4$.H$_2$O as an additive produced no effect on size distribution or particle morphology. The addition of phosphate esters, phosphonates and diphosphonates resulted in the incomplete hydrolysis of the iron (III) solution. In particular 1,2-ethylenediphosphonic acid gave akaganeite (β-FeOOH) as the product. However, n-butyl phosphate, naphthyl phosphate, methyl phosphonate and phenyl phosphonate produced lepidocrocite (γ-FeOOH) as the final product. Again infrared studies showed that the additive remain bound to the surface of the crystallites.

As many of the additives studied have been found to remain bound to the crystals after reaction, it has been realised that certain additives may be suitable as corrosion inhibitors. Currently, various hydroxybenzenes e.g. catechol are being studied for this application. It is hoped to find an additive that can bind to the surface of the crystal, blocking the approach of various oxidising species, for example atmospheric oxygen, water etc.

1.3.5 Sol-Gel Process Route
The sol-gel process (SGP) has been used successfully to produce numerous types of particles and materials, a particularly notable use being the high T$_c$ superconductor.
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YBa$_2$Cu$_3$O$_{7-\delta}$. SGP has been defined as when a molecular solution is converted into a molecular solution to a sol which reacts further to form a gel and on firing becomes a polymeric inorganic solid. The SGP provides improved homogeneity at lower temperatures and often at less expense. The improved homogeneity is due to manipulation of inorganic species at a molecular level, resulting in mixing on a nanometre scale. Lower firing temperatures may be achieved, due to smaller particle sizes and greater homogeneity.

The starting materials for the SGP should be soluble in organic solvents and be readily convertible to the corresponding oxides on firing. Metal alkoxides (M(OR)$_n$) are the most commonly used, where M is the metal atom and OR is the alkoxide group. The solution is then converted into the gel by reaction with water followed by heat treatment to produce the metal oxide powder. The solidification reaction occurs stepwise with water and organic materials being removed by vaporisation/decomposition. The sol then becomes a viscous gel of metal oxide containing trapped solvent molecules. Through further heating these molecules are lost by evaporation and decomposition to produce a crystalline solid. The dry gel is frequently very porous, allowing lower firing temperatures. The main advantage of this is that it often prevents unfavourable phase changes and volatilisation of the components. However, during the drying process cracks often appear. This is obviously bad where monolithic and thin film materials are required. The transformation from solution to gel is a dynamic, time dependant process by virtue of the number and kinds of species present, which are changing continuously.

A typical synthetic route to a mixed oxide would be as follows. The nitrate salt of the metal would be dissolved in water and citric acid would be added in a 1:3 ratio of metal:citrate. The pH would be set at approximately seven by the addition of ammonia. Metal nitrates are used as they are thermally unstable, decomposing to give NO$_2$ plus the metal oxide. Ethylene glycol is then added to increase the viscosity of the matrix. The mixture is stirred in order that the components are thoroughly mixed, and then the mixture is heated. This route produces a well mixed solution which gives a high purity precursor to the final product.$^{45}$
1.4 Application of Microwave Heating to Chemical Systems

1.4.1 Introduction

Another method that is being increasingly used in material synthesis is microwave heating. Microwaves exhibit properties that make them attractive in a variety of chemical syntheses. The electromagnetic spectrum is made up of various regions, for example X-rays, ultraviolet and infra-red regions. The region found between the infra-red and radio wave region is known as the microwave region. These waves have wavelengths between 0.01 and 1 metre, and frequencies between 30 and 0.3 GHz respectively (Figure 1.4).

![Figure 1.4 - The electromagnetic spectrum.](image)

Much of the microwave region is used for telecommunications, in particular for mobile telephones and RADAR. To avoid interference with such activities, industrial and domestic microwave systems operate within an internationally regulated region. Commonly, the frequency used for heating apparatus is 2.45 GHz. In the UK the frequencies 0.896 and 22 GHz are also used. Microwave equipment operating outside these frequencies needs to be shielded in order to prevent interference with other microwave sources.

Electromagnetic waves are made up of two components, the magnetic and the electric fields, which are orthogonal. Materials can be heated with high frequency electromagnetic waves. Such heating is almost entirely due to the electric field component of the electromagnetic wave (Figure 1.5) coupling with charged or polar particles contained in the material.
This interaction causes two principal effects, which in turn are responsible for the heating observed in the material.

1. If the charged particles are mobile then a current will be induced which will move in phase with the electric field. Consequently, the material exhibits conductive heating.

2. If the molecules are polar and mobile, the electric field component will force them to move until the opposing internal forces in the material equals the electric force. Consequently, the material exhibits dipolar polarisation.

These effects will be discussed more fully later in this chapter.

### 1.4.2 Dielectric Polarisation

Charged particles that are partially bound in the material, are unable to follow the rapidly changing high frequency electric field and so the material heats. The total polarisation (\(\alpha_t\)) of the material can be expressed as follows.

\[
\alpha_t = \alpha_e + \alpha_g + \alpha_d + \alpha_i
\]

1.2
where $\alpha_e$ is the electron charge displacement in relation to the material’s nuclei, and $\alpha_d$ is the displacement of nuclei relative to each other in materials with unequal charge distribution.

The time-scale for polarisation of $\alpha_e$ and $\alpha_d$ is smaller than the timescale for reversals in a microwave field. Therefore, the charged particles follow the phase of the microwave field and so do not contribute to microwave heating unless through conductive heating. $\alpha_d$ results from the reorientation of polar molecules or other permanent dipoles in the material. The timescale for this reorientation is similar to that of microwaves, thus making it the most important form of polarisation with respect to microwave heating. $\alpha_n$, the Maxwell-Wagner interfacial polarisation in inhomogeneous materials, has only limited contribution at microwave frequencies.

The dielectric properties of homogenous materials can be described using the complex dielectric constant $\varepsilon^*$, and is the sum of real and imaginary dielectric constants.

$$\varepsilon^* = \varepsilon' + i\varepsilon'' \quad 1.3$$

$\varepsilon'$ is representative of the material’s ability to be polarised by an external electric field. When the frequency is very high or very low, in the presence of a static field then $\varepsilon'$ is equivalent to the total dielectric constant of the material. When electromagnetic energy is converted to heat in the material, then $\varepsilon'$ is non-zero and is a measure of the heating efficiency. The tangent of the loss angle is used frequently in the literature. This quantity is related to the complex dielectric constant:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad 1.4$$

The angle $\delta$ is the phase difference between the polarisation of the material and the electric field (Figure 1.6).
1.4.3 Dipolar Polarisation

In solvent systems microwave heating mainly results from dipolar polarisation. Many solvents possess a permanent electric dipole due to the difference in the electronegativities of the molecule’s atoms. This dipole is susceptible to external electric fields and so will attempt to align with the electric field by rotating. The field provides the energy for this rotation. For free molecules this rotation occurs quickly, but for molecules in a liquid, rotation is restricted due to collisions with other molecules. As a result the ability of a dipole to respond to the field is limited; this affects the molecules’ behaviour at different electric field frequencies.

In the presence of electric fields of high frequency, dipoles are unable to align with the field due to the short timescale involved and so do not rotate. This lack of rotation results in no energy being transferred, so no heating occurs. In the presence of electric fields of low frequency, dipoles are able to align in phase with the field. The molecule gains energy during rotation, but some energy is also lost due to collisions with other molecules. This results in a small heating effect overall.
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The frequency of microwaves lies between these two cases, meaning that dipoles have time to align with the electric field. However, this rotation is still slightly out of phase with the field and this phase difference allows the dipole to lose energy through collisions and this gives rise to dielectric heating.

Debye’s theoretical expressions for $\varepsilon'$ and $\varepsilon''$ form the basis for understanding the frequency dependant properties of dielectric materials. The dielectric constant and the dielectric loss factor, ($\varepsilon'$ and $\varepsilon''$ respectively) are dependant upon both frequency and temperature. Frequency dependency is expressed explicitly in the Debye equations, whereas temperature is introduced indirectly through other variables:

\[
\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + \omega^2 \tau^2} \quad 1.5
\]
\[
\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + \omega^2 \tau^2} \quad 1.6
\]

where $\varepsilon_\infty$ and $\varepsilon_s$ are the dielectric constants under high frequency and static fields respectively. $\varepsilon_\infty$ results from atomic and electronic polarisations (as infra-red frequencies are considered to be infinite relative to microwaves) and $\varepsilon_s$ results from the sum of all the polarisation mechanisms described in this Section. Stoke’s theorem is used to derive the relaxation time $\tau$.

\[
\tau = \frac{4\pi \eta r^3}{kT} \quad 1.7
\]

where $r$ is the molecular radius, $\eta$ the viscosity, $k$ is Boltzmann’s constant and $T$ is the temperature.

The molecular dipoles in solid materials are unable to rotate without significant input of energy, but are restricted to a number of equilibrium positions, which are separated by potential barriers which we will assume to have a value $W$. This model
represents two of the (many) possible alignments for the dipole. The dipole relaxation time is related to the barrier by:

\[ \tau = A e^{\frac{W}{kT}} \]  \hspace{1cm} 1.8

where \( A \) is a temperature dependant constant. Dipolar solids tend to show very small dielectric losses since \( W \) tends to be very large. An example of this is water-free ice, which does not heat when irradiated with microwaves.

1.4.4 Maxwell-Wagner Interfacial Polarisation

For inhomogeneous dielectric samples made up of one dielectric within another dielectric, it is possible to derive expressions for the overall dielectric properties if the individual geometry and dielectric properties of each dielectric are known.

Maxwell \(^{47}\) considered the case of a plate capacitor of \( n \) dielectric sheets of dielectric properties \((\varepsilon)\) and conductivities \((\gamma)\) \(\varepsilon_1\gamma_1, \ldots, \varepsilon_n\gamma_n\). Differential equations relating the field across the dielectric as a function of current through the layers were derived. This model correlated well with the observed data. Wagner \(^{48}\) then considered small spheres with material properties \(\varepsilon_2\gamma_2\) dispersed so as to preclude electrostatic interaction with one another through a medium with properties \(\varepsilon_1\gamma_1\).

Sillars simplified matters further by assuming that the matrix behaved as a perfect dielectric \(\gamma_1 = 0\). Again the inclusions were spherical with the \(a\)-axis in line with the field and \(b\) equal to \(c\). The geometry was described with two variables, \(q\), the volume fraction of dielectric two, and the axial ratio \(a/b\). The conducting inclusions behave as point dipoles in the dielectric matrix and hence forms relations similar to Debye’s equations.

\[ \varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_1 N}{1 + \omega^2 \tau^2} \]  \hspace{1cm} 1.9
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\[ \varepsilon'' = \frac{\varepsilon'_i N \sigma \tau}{1 + \omega^2 \tau^2} \]  \hspace{1cm} 1.10

where \( \varepsilon_\infty, N \) and \( \tau \) are given by-

\[ \tau = \frac{\varepsilon'_i (\lambda - 1) + \varepsilon'_2}{\gamma_2} \]  \hspace{1cm} 1.11

\[ N = \frac{q \varepsilon'_i \lambda^2}{\varepsilon'_i (\lambda - 1) + \varepsilon'_2} \]  \hspace{1cm} 1.12

\[ \varepsilon_\infty = \varepsilon'_i \left( 1 + \frac{q (\varepsilon'_2 - \varepsilon'_i)}{\varepsilon'_i (\lambda - 1) + \varepsilon'_2} \right) \]  \hspace{1cm} 1.13

The non-linear variation of \( q \) with the axial ratio suggests that little can be ascertained about the dielectric properties of a heterogeneous material unless the shapes of the inclusions are known. These theories are backed up experimentally, but at high concentration interparticle interactions must also be taken into consideration.

1.4.5 Conduction Effects

When materials are irradiated they may lose heat through dielectric losses or by conduction. Such conduction losses can be accounted for by a separate term in the complex dielectric constant:

\[ \varepsilon^* = \varepsilon'_i + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + i \omega \tau} - \frac{i \sigma}{\varepsilon'_s} \]  \hspace{1cm} 1.14

Addition of dissolved salts in water greatly affects the dielectric properties as conduction increases and may eventually swamp dielectric losses. Conversely, the dielectric losses of many solids are due mainly to these conduction terms. Dielectric properties (\( \varepsilon \)) of solids increase with temperature and so thermal runaway may be observed. As the temperature increases the dielectric loss factor also increases making heating more effective. If irradiation is not monitored closely, then the temperature may rise to dangerous levels.\(^{15-16}\)
1.4.6 Use of Microwaves in Chemical Syntheses

The literature shows that microwaves have been used for the curing of polymers since 1967 \(^{46}\) and also for organic syntheses since 1980. \(^{57}\) Since that time microwaves have been applied to synthesis in almost every branch of chemistry. Such applications will be discussed in terms of liquid, solid and gas phase reaction.

1.4.6.1 Microwave Synthesis in Liquids

Any low molecular weight, dipolar solvent may be heated or even superheated using microwave irradiation (Table 1.2). Such superheating may be explained mechanistically by nucleate bubble formation, which is required for boiling.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling Point with microwaves/°C</th>
<th>Boiling Point (literature)/°C</th>
<th>ΔBP/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>104</td>
<td>100</td>
<td>4</td>
</tr>
<tr>
<td>Ethanol</td>
<td>103</td>
<td>79</td>
<td>24</td>
</tr>
<tr>
<td>Methanol</td>
<td>84</td>
<td>65</td>
<td>19</td>
</tr>
<tr>
<td>DCM</td>
<td>55</td>
<td>40</td>
<td>15</td>
</tr>
<tr>
<td>THF</td>
<td>81</td>
<td>66</td>
<td>15</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>107</td>
<td>81</td>
<td>26</td>
</tr>
<tr>
<td>Propan-2-ol</td>
<td>100</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td>Acetone</td>
<td>81</td>
<td>56</td>
<td>25</td>
</tr>
<tr>
<td>Butanol</td>
<td>132</td>
<td>118</td>
<td>14</td>
</tr>
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<td>1,2-Dimethoxyethane</td>
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<td>Diglyme</td>
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<td>13</td>
</tr>
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<td>Ethyl Acetate</td>
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<td>17</td>
</tr>
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<td>Acetic anhydride</td>
<td>155</td>
<td>140</td>
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<td>Butan-2-one</td>
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<td>153</td>
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</tr>
</tbody>
</table>

Table 1.2 – Properties of organic solvents heated by 2.45 GHz microwaves.\(^{51}\)

The effect whereby some organic solvents have boiling points raised by up to 20°C is known as superheating. It is this effect that is thought to produce many of the reported rate and yield enhancements in many organic liquid phase reactions. A
variety of heterocyclic and organometallic reactions may be driven by microwaves, in most cases with higher rates and yields. They are also of importance in polymer chemistry. The use of polar starting materials and final products allow rapid, specific and controllable syntheses. These reactions may be monitored by measuring the changes in the dielectric properties as the reaction progresses. The advantage of microwave production of polymers is in their efficiency and so the energy savings may be huge.

1.4.6.2 Microwave Syntheses Involving Solids
Some oxide and sulfide materials have layered structures, which are able to incorporate other organic and organometallic compounds between these layers a process known as intercalation. Some intercalation reactions have a small activation barrier and so occur readily, but those with a significant barrier may require thermal activation or sonication to overcome the barrier. However, these methods may disrupt the final material crystallinity and so make characterisation difficult.

Ceramic materials may also be produced using microwaves as many (when dry) are capable of effective dielectric heating. The major application of microwaves for ceramic processing is sintering. At lower frequencies inhomogeneous heating may occur (as microwaves do not penetrate the sample completely) which is clearly undesirable. To overcome this, so-called “caskets” are employed. If the sample is contained in a tight-fitting, microwave transparent and chemically inert material then high temperatures can be reached quickly and can be maintained. Also the quality of the final sintered product is vastly improved and tends to be denser than the thermal equivalent. The sintered products can be obtained at temperatures as much as 400°C lower than by using conventional thermal methods.

1.4.6.3 Microwave Synthesis Involving Gases
The synthesis of powder materials is difficult, particularly for complex materials. The usual methods of mechanical blending and grinding, and even chemical precipitation will often not produce a homogenous product. However, this problem may be overcome by using pyrolytic processes, such as microwave plasmas. Using
microwave plasmas as the source of thermal energy minimises the major drawbacks of pyrolytic synthesis, in particular high energy demands. For a reaction occurring in a flame process the need to take into account the chemistry and safety of the reaction is vital. A microwave plasma has the advantage that these criteria are not important as the direct coupling of microwaves to an aerosol of a salt solution does not produce the final product, as the coupling of 2.45GHz microwaves with the droplets is not strong enough.

![Figure 1.7 - Formation of a particle from an aerosol droplet.](image)

A microwave plasma is heated through the transfer of energy to a charged particle in the presence of an oscillating electric field. This energy transfer is inversely proportional to both the mass of the charged particle and the square of the frequency of the electric field. Microwaves have high frequency therefore the transfer of energy is small. A much greater proportion of the energy is transferred to the electrons as their mass is so small in comparison with the ions. Therefore, energy transfer to the ions is due to elastic and inelastic collisions with the electrons. The free electron “temperature” is higher than the “temperature” of the free ions. The energy of the electrons can be controlled by the strength of the electric field and by the frequency of collision. The temperature of a gas passing through a microwave plasma can be regulated by adjustment of the field strength, gas pressure and gas species. Typically, plasmas can be obtained between 50-900°C (Figure 1.8).
Figure 1.8 – Photograph of a microwave generated plasma produced in a stream of $N_2$ gas passed through a silica tube running vertically in the Figure. The waveguide cavity aperture shows the location of the plasma which fills the choke regions and up into the silica tubing.

A variety of ceramic and metallic powders have been synthesised using microwave and radio frequency plasmas. The particles are usually spherical due to the spherical nature of the precursor droplets. Particle sizes are typically in the nanoscale region depending upon their residency time in the plasma.$^{55-56}$
1.5 Aims of this Thesis

The main aim of this work was to produce a study of the interaction of microwaves with matter and their application in certain areas of materials synthesis, in order to provide a comprehensive understanding of the differences between microwave synthesis and traditional synthetic techniques. There has been much in the way of speculation as to a specific microwave effect, that is enhanced rates or yields when compared with conventional methods with respect to a variety of chemical syntheses. In many cases, such differences have been explained in terms of inaccurate temperature measurement or superheating of the solvent. Very little has actually been done to study the actual effect of microwaves through direct structural probes that reveal the evolution of microwave-driven reactions in situ. This project has examined specific fundamental properties such as particle size, thermal parameters of atoms, and ion diffusion in order to identify, if not quantify, the effect of microwaves.

Chapters Three, Four and Five are concerned with the mechanism for the formation of particles during the forced hydrolysis of iron salt solutions, in the presence and absence of a microwave field. Chapter Six examines how microwaves can influence diffusion in porous materials. Chapters Seven and Eight involved the use of single crystal and power diffraction in the study of the effect of microwaves on hydrogen bonding and fast ion conductors respectively. Finally, Chapter Nine discusses the development and application of a new design for a microwave pressure vessel.
1.7 Bibliography


46. N. H. Williams, *J. Microwave Power*, 2, 123 (1967)
Chapter 2 – Microwave Generation and Application

2.1 Introduction
The aim of this chapter is to provide an overview of the theoretical and practical considerations behind microwave generation and their application. Chapter one provided an account of the mechanisms involved in the heating of chemical systems; this chapter will describe how microwaves are generated and subsequently transmitted to a load. The function of common types of microwave applicators are described, as are the different types of microwave generator.

2.2 Microwave transmission
2.2.1 Forward and reflected waves
Consider a parallel wire transmission line that is much longer than the wavelength of the microwave generator feeding it, terminated with a resistive load $L$ (Figure 2.1).

![Figure 2.1 - Generator (G) connected to a resistive load (L) via a transmission line.](image)

The input of the generator to the transmission line is a sinusoidal voltage $V_{\text{Forward}}$ which travels at a velocity $C$ towards the load. The transmission line has a characteristic impedance $Z_0$ that is “seen” by the wavefront as it moves along the line away from the generator. If at any point along the line a discontinuity should appear then the impedance changes locally because the capacitance and/or the inductance will change at that point. Energy can be propagated with equal ease in both directions along the line. Since the condition for maximum power transfer is now broken at the discontinuity, less power will be transmitted forward from that point. The balance of
power at the discontinuity is a balance of three components: power absorbed at the discontinuity, power reflected back to the generator and power transmitted to the load. If the discontinuity comprises a simple localised change in capacitance or inductance there will be no power absorbed, since perfect capacitors and inductors absorb no power. However, should the discontinuity have resistance then power will be dissipated as a reflection.

2.2.2 Twin open-wire, coaxial and parallel-plate transmission lines

Twin open-wire, coaxial and parallel-plate transmission lines are different to a hollow waveguide because D.C. cannot be passed in the latter. Forward and backward paths exist in the open wires and their ability to transmit D.C. makes them a special case solution to Maxwell’s equations.\(^3\)

In hollow waveguide transmission lines (in the fundamental mode) energy propagates with the associated electric and magnetic fields transverse to the axis of the line. The axial components of both the electric and magnetic fields are zero. This mode is known as the transverse electromagnetic (TEM) mode. The characteristic impedance \(Z_0\) for a TEM transmission line is \(\sqrt{L/C}\). Table 2.1 shows values for \(Z_0\) for air dielectric, where the lines are filled with material of dielectric constant \(\varepsilon_d = \varepsilon' - i\varepsilon''\). The velocity of propagation for the plane wave is \(\frac{1}{\sqrt{\mu_0\varepsilon_0}}\) in each of the three cases.

<table>
<thead>
<tr>
<th>Line type</th>
<th>(L/(H/m))</th>
<th>(C/(F/M))</th>
<th>(Z_0/\Omega)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel plate spacing (a, b)</td>
<td>(\mu_0 a / b)</td>
<td>(\varepsilon_0 b / a)</td>
<td>(\frac{a}{b} \sqrt{\frac{\mu_0}{\varepsilon_0}})</td>
</tr>
<tr>
<td>Coaxial line</td>
<td>(\mu_0 \log_\varepsilon (b / a) / 2\pi)</td>
<td>(\frac{2\pi \varepsilon_0}{\log_\varepsilon (b / a)})</td>
<td>(\frac{1}{2\pi} \sqrt{\frac{\mu_0}{\varepsilon_0}} \log_\varepsilon (b / a))</td>
</tr>
<tr>
<td>Parallel wire conductors</td>
<td>(\mu_0 / \pi \log_\varepsilon (d / r))</td>
<td>(\frac{\pi \varepsilon_0}{\log_\varepsilon (d / r)})</td>
<td>(\frac{1}{\pi} \log_\varepsilon (d / r) \sqrt{\frac{\mu_0}{\varepsilon_0}})</td>
</tr>
</tbody>
</table>

Table 2.1 – Characteristics defining \(L, C\) and \(Z_0\) for twin open-wire, coaxial and parallel plate transmission lines.
The parallel plate line is used for microwave ovens with wide conveyer bands; parallel conductor lines are not used at microwave frequencies as they are very long and radiate heavily; instead they are used for radio frequency applications. Coaxial lines are often used as the output line for magnetrons and are also convenient for low power (<1 kW) use but have high attenuation compared with the waveguide. Their main advantage is that they are compact compared with waveguides and are capable of handling high power on a voltage breakdown basis. However, this is not possible under continuous wave operation because of high power dissipation which results in cooling problems; these problems are negligible for low power applications.

2.2.3 Rectangular waveguide

Waveguides play an essential role in the transfer of microwave power from the generator to the load. In many cases the sample chamber is also based on waveguide technology. It is possible to derive the field equations from Maxwell’s equations, but in practice it is the results that are of greater importance. Such results include the forms of the $E$ and $H$-field distribution, the wall-current patterns, waveguide wavelength and cutoff wavelength, attenuation and power handling.

Maxwell’s equations are derived in rectangular coordinates $O_x, O_y, O_z$. $E$ and $H$ have the subscripts $x, y, z$ representing, respectively, the components of the fields in the directions of those axes (Figure 2.2). The variation of the field with respect to time is assumed to be sinusoidal, with an angular frequency $\omega = 2\pi f$. Two differential equations can then be obtained (2.1 and 2.2) both of which correspond to two classes of wave propagated along the axis $O_z$ of the waveguide.

\[
\frac{\partial^2 H_z}{\partial x^2} + \frac{\partial^2 H_z}{\partial y^2} + k^2 H_z = 0 \quad 2.1
\]

\[
\frac{\partial^2 E_z}{\partial x^2} + \frac{\partial^2 E_z}{\partial y^2} + k^2 E_z = 0 \quad 2.2
\]
where

\[ k^2 = \frac{f^2}{c^2} + \gamma^2 = \frac{1}{\lambda^2} + \gamma^2 \quad 2.3 \]

and

\[ c = \frac{1}{\sqrt{\mu_o e_o}} \quad 2.4 \]

\( \gamma \) is the complex propagation constant, \( \alpha \) is the attenuation and \( \beta \) is the phase constant.

Propagating waves based on equation 2.1 are designated \( H \) modes or \( TE \) (transverse-electric) modes: they have an axial component of magnetic field \( H_z \) and no axial electric field \( (E_z = 0) \). Only the transverse electric fields \( E_x \) and \( E_y \) are possible for solutions based on equation 2.1, hence the label \( TE \) mode. Examination of equation 2.2 shows that the solution has an axial component \( E_z \) to the solution, with \( H_z = 0 \). Its modes are called \( E \) modes or \( TM \) (transverse-magnetic) modes. A double-subscript notation is used to designate the various \( TE \) and \( TM \) waves, leading to \( TE_{01}, TE_{11} \) etc waves (Figures 2.2 and 2.3). In the case of rectangular waveguides these subscripts denote the number of half-period variations of the fields along the \( x \) and \( y \) axes respectively. When \( k = 0 \) then \( E_z \) and \( H_z \) are also zero then the solutions of equations 2.1 and 2.2 are then degenerate.\(^{1,3,4}\)
Figure 2.2 — Rectangular waveguide, and field distributions inside the waveguide corresponding to the fundamental forms of wave-guide transmission.

Figure 2.3 — Higher order modes of transmission in a rectangular waveguide.
2.2.4 Circular waveguide

Circular waveguides are used as transmission lines for specialised ovens. They have a serious problem; the plane of polarisation for the fundamental mode analogous to the $TE_{10}$ mode in a rectangular waveguide can twist, resulting in power loss and mismatch. This cannot happen in rectangular waveguide because the orthogonal mode ($TE_{01}$) is cut off by the waveguide having an aspect ratio of 2:1.

Maxwell's equations in the case of circular waveguides involve the use of the circular cylindrical coordinates $r, \theta, z$. The derivation of the field equations follows the same pattern as for rectangular waveguide, results in a pair of wave equations like 2.1, 2.2, 2.3 and 2.4, but expressed in $r, \theta, z$ coordinates, and can easily be converted into Bessel's equations.

A circular waveguide, like a rectangular waveguide, can support both $TE$ and $TM$ waves (Figure 2.4). There is a family of modes for each type of wave, that have their own cut-off wavelengths. A double-subscript notation is used to designate the various modes in a circular waveguide. The first subscript denotes the number of full cycles in the radial field pattern that is traversed when the angle $\phi$ passes through $360^\circ$, while the second subscript denotes the number of half cycles of field variation along a radial component between the centre and the walls.
Figure 2.4 – Field distribution corresponding to the fundamental modes of transmission possible in a circular waveguide.
2.2.5 Waveguide practice

Waveguide practice varies depending upon its use. In RADAR (radio detection and ranging) and communications, waveguide transmission lines need to convey power at low loss and to meet accurate specifications for impedance matching in order to prevent signal distortion. However, in a heating system the waveguide must be able to convey power with minimum loss. Impedance matching is of less importance as it affects power transmission. Consequently, the price of communications waveguide is considerably higher than that of heating waveguide as the specifications are higher. Heating waveguide does however have some specific requirements.

2.2.5.1 Waveguide size

Rectangular waveguide is most commonly designed to operate in the $TE_{10}$ mode. However, the size of the waveguide for a certain frequency is a compromise between minimising the power loss and avoiding possible excitation of higher-order modes, which can cause resonance and impedance matching problems. To avoid these problems there needs to be a significant margin between operating and cutoff wavelengths as the presence of waveguide bends and junctions tend to excite higher order modes. The $TE_{10}$ mode is usually operated at 25% less than cutoff as the waveguide wavelength changes very rapidly close to cutoff thus making impedance matching very sensitive to frequency; further $f^2R$ losses increase rapidly.

There exists an international standard for waveguide sizing. This standard specifies the optimum waveguide size for operation at specified frequencies throughout the microwave region. The standard ensures an aspect ratio of 2:1, which satisfies the conditions described above.

2.2.5.2 Materials and fabrication

Waveguide can be made from a wide range of metals and alloys including aluminium, brass, gold plate, lead, steel and nickel/chromium. The choice of the materials used is generally a compromise between high conductivity to minimise losses, corrosion and ease of fabrication (welding, machining etc). Aluminium is a popular choice due to low cost and high thermal and electrical conductivity. Copper
and brass are not commonly used in industrial applications but are used for low-power laboratory apparatus. The cost of these materials is high and their performance low relative to that of aluminium.

Experience has shown that flanges should be cast as part of the waveguide because welded flanges can often distort the waveguide resulting in matching problems. Flanges are generally bolted, plain-faced with a metal gasket. The waveguide should also be assembled without stress i.e. long sections of waveguide should be supported, as this can also lead to distortion.

Microwave currents flow over the internal surface of the waveguide, but any defect on the surface (such as a joint or a seam) will disrupt this current flow possibly causing leakage of energy. Any seams should be continuously welded and flawless; spot welding or rivets are clearly unsatisfactory in this situation, as they will disrupt current flow significantly. Therefore, the only safe approach is to have secure joints in all cases.

### 2.2.5.3 Multistub tuners

A multistub tuner is a simple but effective way to modify microwaves at low power. The tuner consists of a set of adjustable stubs (usually four) set in a block forming the broad face of the waveguide. Each stub provides a variable, capacitive susceptance whose amplitude is a function of the degree to which it is inserted into the waveguide. Therefore, it is possible to generate a reflection of any amplitude and phase simply by setting the stubs for minimum net reflected power from the load/tuner combination. As the screw is inserted, its capacitive susceptance increases, as does its inductance due to currents flowing in the stub. Once the stub is inserted more than halfway the stub becomes resonant resulting in its electrical properties changing completely. The stub may be prevented from doing this by means of a bolt.
2.3 Microwave heating applicators

2.3.1 Multimode ovens
Multimode ovens are by far the most commonly used type of microwave heating applicator. They are in essence a closed metal box, therefore they are simple to make. This is where the simplicity ends, as they support a large number of resonant high-order modes simultaneously, which add vectorally in space and time to give a resultant field pattern. A rectangular multimode oven can be considered a waveguide, with a large cross-section compared with the excitation wavelength and short-circuited at both ends by metal walls. A domestic microwave oven is an example of a multimode oven.

2.3.2 Aperiodic structures
Microwave generators exhibit a broadband, non-resonant frequency response. Termination occurs by using an absorbing load, which dissipates the residual power that is not dissipated by the actual load. In a well-designed system the power absorbed in the terminator is less than 10%. The main feature of this type of applicator is a transmission line (TE_{10} mode) in which the microwave energy propagates along the same axis as the workload motion (either in the same direction or counterflow). Waveguides are used extensively with this type of applicator.

2.3.3 Resonant structures
In some cases the tangent of the load is so low that the heat-dissipation density using the applicators described in 2.3.1 and 2.3.2 is too low at the electric-field intensities they create. Resonance allows the field intensity to be raised, thus giving satisfactory heat dissipation. In other situations it may be necessary to have a high rate of temperature increase in high loss factor materials; again resonance may be used. The form of the load is very important when using resonance cavities. Materials made up of filaments, i.e. a small cross-section of material with respect to wavelength, are easy to heat using a resonance cavity. However, problems arise due to standing waves should a sheet of material be used. Resonant systems are difficult to control and so are only commonly used for plasma generation.
2.4 Microwave generators

2.4.1 The magnetron

Magnetrons were first made during the Second World War during the development of accurate RADAR equipment. Today they are used extensively in domestic microwave ovens and for industrial applications. They are made up of seven essential components.

I. A cylindrical heated cathode, emitting electrons.

II. A circular anode concentric with and surrounding the cathode and having an array of radial slots forming resonators tuned to the desired operating frequency.

III. A high strength magnetic field aligned axially to the anode-cathode assembly. This may be provided by a permanent magnet in small magnetrons, or an electromagnet for higher power magnetrons.

IV. A high value D.C. EHT (extra high tension) voltage (2-20 kV) applied between the anode and cathode. The anode is earthed and the cathode is at negative potential.

V. The entire magnetron is enclosed in a high (10⁻⁶ mmHg) vacuum.

VI. A probe antenna coupled to the resonator and sealed by an output window of microwave transparent material.

VII. The assembly must be easy to rebuild/replace after damage or failure.

Electrons are drawn from the heated cathode by the electric field. Due to the magnetic field the electrons travel a spiral path in the space between the cathode and the anode, therefore the centrifugal velocity can be controlled by using the EHT and the applied D.C. magnetic field. As the magnetic-field strength is reduced the radius of the trajectory of the outermost electrons increases and there is a critical point at which it equals the radius of the anode bore, it is at this point when anode current begins to flow.

The anode is made up of a ring of cavities, which are in principle $\lambda/4$ ($\lambda_0$=free space wavelength) width transmission lines short-circuited at the outer end and open at the
inner end where the microwave electric field is high and the electrons are at grazing incidence. Those electrons that enter a positive microwave-electric field gradient will accelerate and *vice versa*. Therefore the electron cloud becomes bunched and appears as a rotating spoked wheel. If the speed of this “wheel” is increased by raising the applied EHT voltage then the number of electrons at grazing incidence tries to exceed that of the microwave field, but it cannot due to synchronism between the two. The microwave field slows the high-energy electrons and their kinetic energy is dissipated in it. The microwave power generated is proportional to the change in kinetic energy and the rate of arrival at the anode, which also determines the anode current. A small number of electrons are deflected back to the cathode where they lose their kinetic energy as heat. To overcome overheating, the filament heater current is reduced as the anode current rises.

The transfer of power is very efficient, typically greater than 88% at 0.9 GHz and 70% at 2.45 GHz. The lost power is dissipated as heat and so the anode is cooled by air or a suitable liquid.\(^7\)

Figure 2.3 – (Left) Plan view of a magnetron and (right) electron motion in a magnetron
2.4.2 The klystron

Klystron generators were the principal source for microwaves industrially for over 20 years. They are able to generate 50 kW of output at 2.45 GHz. It is for this reason that they are used for high power heating at 2.45 GHz. A klystron generates microwaves in this fashion:

Electrons generated, and accelerated by a high D.C. voltage at the cathode, are first passed through a circular resonant cavity. An applied axial D.C. magnetic field (0.15 T) collimates the electron, beam and ensures that no electrons hit the cavity structure. As the electrons exit the first cavity there is a speed distribution, as the beam travels thought the drift tubes (Figure 2.2) the faster electrons catch up with the slower electrons and bunches are formed at intervals along the beam resulting in alternating high and low electron densities. Subsequent cavities are designed to be located at these bunches and microwaves are induced in them. The resultant $E$ field further intensifies the electron bunching, and the frequency field patterns of bunching is repeated through to the final cavity, where the bunching is at its most intense and the power is coupled to the output waveguide.\(^9\)

![Figure 2.2 – A PPM focussed klystron generator.](image-url)
2.4.3 The gyrotron

A gyrotron consists of an electron gun, an acceleration chamber, and a resonance chamber immersed in a strong magnetic field and a collector. An electron beam is accelerated and introduced to a strong magnetic field generated by superconducting magnets. These electrons gyrate at high speed and start to emit an electromagnetic wave. The frequency of this wave is the gyration frequency of the electrons around the magnetic field lines. This frequency is matched to the resonance chamber where relativistic electrons interact further with the electromagnetic field. The wave is therefore strongly amplified and is coupled out of the cavity to mirror systems where the wave is guided to the target. The decelerated electron beam reaches the collector where the rest of the energy is dissipated.\textsuperscript{10} Gyrotrons are used when microwaves of very high frequency are required \textit{e.g.} plasma heating.
2.5 Bibliography

10. [http://www.thetubeguy.com](http://www.thetubeguy.com)
Chapter 3 - Small Angle Neutron Scattering From Iron Oxide Colloids

3.1 Introduction

As outlined in Chapter One, the growth of fine particles of controlled size and shape is important for both applications in a wide range of industries and in fundamental sciences. However, the control of the growth of such materials still proves to be difficult. Many of the most successful methodologies have been found through trial and error. One of the most extensively studied systems is that of iron oxides. Various iron oxides occur naturally (e.g. haematite $\alpha$-Fe$_2$O$_3$), but they can also be synthesised in the laboratory through the forced hydrolysis of aqueous ferric and ferrous ($\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ respectively) salt solutions.$^{1-3}$ Many of the products and their derivatives are used in the magnetic recording industry today and commercial companies are interested in improving the properties of the particles produced as this would improve the quality of their products, namely video and audio tapes and also computer storage media.$^4$

In order to produce particles of some desired size and shape it is desirable to understand the mechanisms behind their formation. It is not ideal to sample, dry and perform post mortem analysis as the drying process may alter the morphology and size of the particles due to dehydration of the particles. Instead it is desirable to perform such mechanistic studies in situ. In order to be able to collect data relating to the formation of a particle a probe is required which can collect data in real time and does not rely on post mortem analysis such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM), which may structurally change the sample during the preparation of the sample. Small angle scattering neutron (SANS) was to be used in situ to reveal features of the structure necessary to be able to probe the stages of particle formation. It should be possible to follow the nucleation and coagulation events at the beginning of the reaction that eventually leads to the formation of particles suspended in a medium.
3.2 Experimental background

Microwaves have been used to produce a variety of iron oxide particles by heating aqueous solutions containing iron ions. Some of these materials are not produced when heated conventionally. If an aqueous solution containing ferric and ferrous ions is heated at 80°C for several hours, acicular magnetite (Fe₃O₄) is formed instead of the predicted haematite (α-Fe₂O₃). This is unusual for two reasons. Firstly, a different product is formed. Secondly, this is the first known direct synthesis of acicular magnetite from solution. Other routes tend to produce other iron oxides or magnetite with cubic or irregular morphology, see Figure 3.1.

![Synthetic routes to various iron oxides.](image)

This diagram shows how the morphology of these iron oxides depends on the reaction conditions. It has been suggested that the haematite particle formation proceeds via the acicular goethite (β-FeOOH) intermediate, which is then followed by the microwave-assisted diffusion of ferrous ions into the lattice of the oxyhydroxide thus producing Fe₃O₄.
One of the key questions in this field is how particles of controlled shape grow. There are two schools of thought. One is that needle shaped particles form when the systems passes through a phase (e.g. goethite) for which a combination of lattice and interfacial energy favours needles. As long as this transforms isostructurally to products, the needle shape remains. The other school of thought holds that much smaller, primary particles form (e.g. 30 Å spheres) and these then aggregate to form needles, though the driving force for this shape is unclear. The evidence for this is TEM data which appear to reveal needles built of these primary particles.

In order to further elucidate the mechanism involved it is vital to follow the reaction in real time. Microwaves were chosen as the source of heat because they provided a means of heating the solution uniformly and may under some circumstances lead to different products. Small angle neutron scattering provides the necessary requirements to be able to probe the size of particles in this system.

The strength of neutron scattering, quantified as the scattering length from different elements, has a complex dependency with the atomic number (Z). It is possible to choose a reaction medium that shows good contrast with the growing particles. H₂O and D₂O have scattering lengths of opposite sign (+6.38 x 10⁻¹⁰ and −0.56 x 10⁻¹⁰ cm respectively); if the ratio of D₂O/H₂O is varied it is possible to produce an aqueous medium that scatters neutrons in a very different way to particles suspended in that medium. However, there are associated problems. Reagents and products for the growth of well-defined particles are at low concentrations. This means that the rate at which data are collected will be low. However, the rate of particle growth in this system is relatively slow (typically 18-24 hours for complete reaction); this suggested that a low rate for data collection would not necessarily be detrimental in this case. In order to prevent bubble formation within the sample chamber, which would lead to anomalous scattering, it was necessary to keep the temperature significantly below the solvent’s boiling point. Typically, the temperature was set to 95°C for the duration of the experiment.
3.3 The LOQ instrument

The small angle neutron scattering experiment was performed on the experimental station LOQ at the ISIS Facility located at the Rutherford-Appleton Laboratory, UK.

ISIS is a spallation neutron source in which a 50 Hz pulsed proton beam impacts on a tantalum target to produce short pulses of neutrons which are then slowed down by moderators to the desired energy range. The arrival time of the neutrons at a detector 10-15 m away from the moderator establishes their wavelengths.

LOQ may be used to investigate the shape and size of large molecules, small particles or porous materials with dimensions in the range 1 to 100 nm. Length scales of up to 400 nm can be probed in highly anisotropic systems. This instrument has been used to study colloids, polymers, biomolecules, alloys, composites or porous systems. The principal benefit of conducting SANS experiments at ISIS is that a "white" incident beam is combined with time-of-flight detection techniques to give LOQ a very large dynamic range in scattering vector, $Q$ (0.008 to 1.6 $\AA^{-1}$). The entire range of $Q$ is accessible during a single measurement, without any need to reconFigure the instrument, in contrast with SANS techniques using fixed wavelengths.6

![Figure 3.2 - Photograph of the LOQ pit.](image)

As can be seen from Figure 3.2 the constricted geometry of the pit in which the sample and sample environment apparatus is located restricted the size and
orientation of any equipment. This necessitated the design and construction of a custom microwave applicator. This is described in detail in the next Section.

3.4 Apparatus

A commercial 0-1 kW variable power microwave source (Microwave Heating Type GU14) was used to generate microwaves of frequency 2.45 GHz, which were delivered to the sample chamber via a compact waveguide arrangement using waveguide 9a (312) sections (Figure 3.3). The apparatus had been modified to provide optimum temperature control and also reduced background scattering from unwanted material in the beam.

![Arrangement of the apparatus for in situ SANS experiment.](image)

**Figure 3.3** – Arrangement of the apparatus for *in situ* SANS experiment.
Due to space limitation within the LOQ pit at ISIS the waveguide was arranged in a particular fashion (Figure 3.4).

The microwaves are initially turned downwards through 90° using an E-bend into an isolator and four-stub tuner. To have waveguide cross section transitions between the source and the isolator is undesirable. However, the geometry of the pit makes this situation unavoidable. After the four-stub tuner, the waves are turned back through a 180° E-bend to provide an upright position for the rectangular to circular waveguide transition and the cylindrical sample cavity. For a low-angle neutron diffraction instrument, the relatively small angular range of the incident and diffracted beams allows the use of two $17.5 \text{ mm} \phi$ holes, placed with axial symmetry. These holes were 17 cm from the waveguide termination, and acted as neutron windows that were large enough to accommodate the 12 mm $\phi$ neutron beam without causing any unwanted scattering. Their small diameter also means that chokes or aluminium windows are not required in order to keep microwave leakage within safe legal limits. The port for the reflux attachment at the top of the microwave cavity includes a 6 cm choke to prevent excess leakage resulting from the presence of a glass/water dielectric core.

A 100 cm³, pyrex round-bottomed laboratory flask held the bulk of the 50 cm³ sample aligned axially within the cylindrical cavity. This reservoir was then connected directly to a fused silica sample cell via a short 3 mm i.d. tube. The cell
was designed to be as close as possible to the dimensions and transmission properties of typical SANS cells. This made the compensation for background scattering during the data analysis straightforward. In order to maintain a representative sample in the sample cell, the solution is circulated via 0.5 mm i.d. PTFE tubing at a rate of approximately 1 cm³ min⁻¹ using a peristaltic pump.

The reaction vessel was held vertically, with markers to ensure the correct axial orientation and positioning with respect to the beam. It was held centrally with microwave-transparent plastic spacers. The temperature was monitored using a calibrated gas pressure thermometer. This was capable of measuring the temperature with an accuracy of greater than 0.1 K. The control software (written by Dr. Gavin Whittaker in Visual Basic 5.0) controlled the microwave output power to hold the temperature of the sample to within ±0.5 K for the duration of the experiment. This was an important feature, since the presence of air or vapour bubbles in a refluxing sample may lead to anomalous neutron scattering, so making any data analysis difficult.

3.5 Experimental procedure

Due to the space limitations near the instrument the apparatus had to be assembled in the pit with respect to the neutron beam at the start of the experiment (Figure 3.5). Fine-tuning of the height of the entire apparatus was achieved by the use of adjustable supports. Through the use of a laser the windows were aligned centrally in the waveguide. After the successful alignment of the microwave applicator, the sample chamber was fitted into position, the alignment was rechecked and adjusted using the laser. Markers on the vessel and PTFE spacers allowed repeatable alignment of the apparatus on each set of measurements (Figure 3.5).
After sample alignment, the peripheral instrumentation was installed. This included the peristaltic pump and temperature controller. To allow remote control of the microwave output, the P.C. controlling the microwave generator was located outside the pit; this was also due to space limitations.

Upon complete assembly the reactants (50 cm$^3$ of 0.03 M FeCl$_3$ in D$_2$O) were added to the sample chamber. The peristaltic pump was started in order to remove any air pockets from the measurement cell. The sample was then heated at 95°C (±0.5°C) for 8 hours and scattering data collected in consecutive 30 minute runs.

3.6 Data Refinement

The data obtained for this experiment were analysed using the data fitting program FISH. There are currently 45 models in FISH that relate to specific types of scattering from discrete structures in solution. These models are least-squares fitted to small angle diffraction data.

The data obtained from this experiment were analysed using three models: spheres, discs of negligible thickness and radius $R_p$, and rods of negligible cross-section of length $L$. Synthetic iron oxides particles are generally spherical or acicular in shape.
and so these models were chosen as they are the closest to known geometries of iron oxide particles in aqueous solutions. Such particle morphologies have been observed using techniques such as SEM and TEM. The form factors $P(Q)$ for each model are shown below.\(^9\)\(^-\)\(^10\)

\[
P(Q) = \left[\frac{3\sin(QR_p) - QR_p \cos(QR_p)}{(QR_p)^3}\right]^2 \tag{3.1}
\]

\[
P(Q) = \frac{2}{(QR_p)^2} \left[1 - \frac{J_1(2QR_p)}{QR_p}\right] \tag{3.2}
\]

\[
P(Q) = \frac{2S_i(QL)}{QL} - \frac{\sin^2(QL/2)}{(QL/2)} \tag{3.3}
\]

Where $J_1$ is a first-order Bessel function and $S_i$ is the sine integral function.

### 3.7 Results and discussion

Standard SANS data corrections for the wavelength dependencies of the incident spectrum, sample transmission and detector efficiencies, were made to combine the SANS patterns from the different wavelengths recorded by time-of-flight. This gives the differential scattering cross-section, $(d\Sigma/d\Omega)(Q)$, which for a dilute system of particles of size $R$ and volume $V_p$ is:

\[
\frac{d\Sigma}{d\Omega}(Q) = N_p V_p^2 (\Delta\rho)^2 P(Q, R) + B(\lambda) \tag{3.4}
\]

where $N_p$ is the number concentration, $\Delta\rho$ is the neutron scattering length density difference between the particles and solvent, and $B(\lambda)$ is the wavelength-dependent background signal. The particle form factor, $P(Q)$, describes interference between radiation scattered by different parts of the same particle and is sensitive to the shape of the particle.
Model fits to the SANS signal may incorporate an integration over a suitable particle size distribution function $N_p(R)$. Three types of particle shape were modelled to the data obtained. The models were: a disc of negligible thickness and radius; a rod of negligible cross-section; and length and polydisperse spheres as these were the most chemically realistic. It was shown that the model representing polydisperse spheres fitted the data best. A Schultz function (this function is similar to a log-normal) was used to describe polydispersity:

$$N_p(R) = \left[\frac{(Z + 1)}{R}\right]^{Z+1} R^Z \exp\left\{-(Z + 1)\frac{r}{\bar{R}}\right\} / \Gamma(Z + 1) \quad 3.5$$

where $\bar{R}$ is the average particle radius, the polydispersity index, $\frac{\sigma}{R} = (Z + 1)^{-\frac{1}{2}}$, is a measure of the width of the distribution, and $\Gamma$ is the Gamma function. The least squares fits to the data are illustrated in Figure 3.6.9-10

Data obtained from heating the sample of FeCl$_3$ in D$_2$O at 95°C indicated that particle formation had already begun within the first 30 minute time frame. The SANS signal was lower than expected, possibly indicating that the scattering particles were rather diffuse. The data did not allow the polydispersity to be precisely.
determined and so this was fixed at 20% as this was a reasonable value for this system based on the author’s experience. The apparent mean particle size, $\bar{R}$, remained at 105(±3) Å for the second run and all of the subsequent runs, although the intensity of the SANS signal increased about 35% from 0.5 to 2.5 hours, and by a further 20% before the end of the 7.5 hour run. Detailed analysis of the data revealed that, after 30 minutes, particles with a modal radius of approximately 50 Å are formed (Figure 3.7).

![Graph showing particle size distribution curves](image)

**Figure 3.7 - Particle size distribution curves for the microwave-induced hydrolysis of FeCl$_3$ after 30 and 400 minutes at 95°C.**

Longer reaction times change this radius very little, and after 400 minutes, the modal radius has only doubled to 100 Å. However, over this period the formation of macroscopic particles becomes evident in the visible appearance of the solution. Small angle X-ray scattering (SAXS) measurements (Chapter Four) on this system under conventional heating are consistent with these observations, and suggest that rapid initial particle growth to sizes of approximately 100 Å takes place, which subsequently agglomerate to produce macroscopic particles. This process is also known as Ostwald ripening. The intensity of the scattered beam in the SANS experiment displays some complex behaviour during the early stages of the reaction, and complementary X-ray experimental data would be required for a fuller understanding of the mechanism of particle formation. This experiment was carried out and the results are described in Chapter Four.
3.8 Conclusions

We have successfully built a microwave applicator, which is suitable for use in SANS experiments on chemical systems. For the first time, in situ SANS measurements on the hydrothermal preparation of iron oxide particles have been carried out, and have yielded new results. The principal limitation of the apparatus described here is the time-scale of the measurement required for reasonable signal to noise ratio in the data, and confines the systems that may be studied to those that generate particles over relatively long periods. This problem may be circumvented with the advent of new, higher flux instruments, or brighter neutron sources. The apparatus may also be adapted for wide-angle X-ray diffraction (WAXS) measurements to probe structure on atomic length scales and determine the chemical character of the species that are formed. This would also require much higher flux, or far more concentrated samples than were used in the experiments described here.

The basic principles that have been employed in the design of this apparatus also lend themselves to other in situ measurements on chemical systems. In particular, we are currently planning complementary experiments using a microwave applicator, which has been designed for use with synchrotron radiation sources. Once again, more rapid data collection and the possibility of in situ WAXS and extended X-ray absorption fine structure (EXAFS) measurements to complement the existing data make such apparatus an attractive and worthwhile goal.
3.9 Bibliography

Chapter 4 – Small and Wide Angle X-ray Scattering From Iron Oxide Colloids

4.1 Introduction

The experiment described in this chapter is complementary to that in the previous chapter, describing the SANS experiment on the iron oxide system. The motives for looking at this system are the same as described previously. The results obtained from the SANS experiment showed that there was an initial burst of (microscopic) particle growth within 30 minutes of heating. However, there was no information as to the structure and composition of the particles formed. It was hoped that by using in situ SAXS in combination with WAXS techniques, that particle growth in this system could be understood more fully.

4.2 Experimental background

The hydrolysis of ferric and ferrous salts is very sensitive to reaction conditions such as pH, concentration, temperature and the nature of any anions. The hydrolysis of certain concentrations of Fe (III) in the presence of certain anions produces needle-shaped haematite particles typically of 0.1 μm in length, with an aspect ratio of 10:1.3-5 As discussed in Chapter three there are two proposed mechanisms for this crystal growth. The SANS results suggested that particle growth mainly occurs within the first 30 minutes when the solution is heated from room temperature. Due to the nature of neutron experiments, i.e. long data collection timescales and the need for deuterated samples, it was obvious that a different technique was required to probe the initial stages of nucleation and particle growth in this system. A SAXS experiment provides the necessary requirements, i.e. short time scale for data collection and no expensive requirement for deuteration. Station 8.2 at the synchrotron source at the SRS, Daresbury laboratories also has the ability to measure WAXS simultaneously, so it should be possible to detect diffraction from any particles formed and hence their structure and perhaps even composition could be determined.6
4.3 The instrument on experiment station 8.2 at the SRS

This experiment was performed on station 8.2 at the Synchrotron Radiation Source (SRS) located at the Daresbury Laboratories, UK.

Daresbury contains a synchrotron X-ray radiation source at whose heart is a large, evacuated ring containing fast moving electrons. When a charged particle is accelerated it emits radiation. If an electron has circular motion then the acceleration is perpendicular to the direction of motion and so radiation is emitted by the electron in the synchrotron. The presence of bending magnets and wigglers in the ring causes the production of the synchrotron radiation by deflection of the electron beam. In the bending magnets, uniform circular motion causes the production of the synchrotron radiation whilst the wiggler uses a periodic field to produce radiation with no deflection and in turn can be used to control the synchrotron radiation. Pumping is required to ensure that the ring is under a vacuum of typically $10^{-9}$-$10^{-10}$ Torr.

Figure 4.1 – Generation of synchrotron radiation.

Various experimental stations are located at strategic points around the synchrotron ring. Station 8.2 is a simultaneous time resolved small and wide angle scattering/fibre station operating at a fixed wavelength of 1.54 Å. X-rays are focused horizontally and vertically. Horizontal focussing is achieved by means of a bent triangular Ge (III) monochromator, asymmetrically cut for beam compression located 20 m from the tangent point, and vertically by a bent, uncoated quartz plane mirror situated 22 m from the tangent point. Background scatter can be minimised by means of four horizontal and vertical sets of slits, giving excellent resolution in the scattering vector, $Q$ (0.0068 - 2.0 Å$^{-1}$). Scattered X-rays are detected with a camera.
whose position is variable, providing spatial resolutions ranging from 0.1 to 100 nm in the SAXS/WAXS configuration. Measurements in the subsecond time regime are performed routinely. The data acquisition and detector systems allow data collection in one and two-dimensional modes. Station 8.2 has been used to investigate a variety of systems including time resolved polymer studies, protein assembly/disassembly, liquid crystalline phase transitions and glass formation.²

![Figure 4.2 – Photograph of the 8.2 experimental hutch and sample stage in the foreground.](image)

### 4.4 Apparatus for sample heating

This experiment did not involve the use of microwaves or the apparatus described previously. Instead, a customised heating stage was used to heat capillaries containing various iron solutions. The heating stage was supplied by Linkam Scientific Instruments Ltd. (model HFS 91, Figure 4.3). This approach was taken because X-rays are not as penetrating as neutrons, and so the sample and reaction vessel needed to be as transparent as possible to optimise penetration and will have better defined optics to consequently allow X-ray scattering to be measured directly. The small scale of the experiment prohibited the use of the microwave apparatus, as the sample chamber in our microwave equipment was too large to fit on the sample stage.
Samples were placed inside X-ray transparent quartz glass capillaries (glass number 14) supplied by Hilgenberg. These had very thin walls and so scatter a very small fraction of the X-ray beams. The capillaries were 2 mm in diameter and 80 mm in length, with a wall thickness of 0.01 mm. Only one end of the capillary was open; once filled with solution the open end was then sealed using two-part epoxy resin. The sealed capillary was then inserted into the silver heating block of the Linkam stage, perpendicular to the 3 mm-diameter X-ray aperture. The block had been modified to contain a 2 mm diameter hole through the centre of the silver heating block to allow the insertion of the capillary. The heating stage was programmed using a Linkam controller. This allowed ramp rates, dwell times and temperatures to be pre-set so that the apparatus did not have to be altered as data were being collected (Figure 4.4).
4.5 Experimental procedure

The Linkam heating stage was mounted on the goniometer arm. There were several calibrations that had to be performed before data could be collected. When the camera length was set at 3.5 in, a capillary was filled with silicon powder and a powder pattern was obtained. When the camera length was set at 0.8 in, a second capillary was filled with silver behenate \([\text{CH}_3(\text{CH}_2)_2\text{OOCOOAg}]\) and a powder pattern was obtained. Finally, a pattern was measured for wet rat tail collagen; this was performed for both camera lengths. These standard calibrations were all required for the data refinement. We also measured the scattering for a capillary containing water; this was our background measurement. The detector response was determined using a calibrated radioactive Fe\(^{55}\) source as this was also required for the data refinement. These calibrations also ensured that the X-ray beam was passing directly through the aperture and not clipping the edges of the silver block. An I.R. laser was also used to double-check the alignment of the apparatus with respect to the beam.

A set of solutions were made up as described in Table 4.1 and loaded into the glass capillaries using a pasteur pipette. All of the chemicals and acids were used without further purification and the water used was deionised. The solutions were made up in volumetric flasks before being transferred to the capillary. The capillary was then sealed using two-part epoxy resin, and was left for approximately 20 minutes to allow the resin to set. The capillary was then inserted into the silver block. The temperature program was started and data collection began once the various interlocks on the experimental hutch had been set. A typical temperature program was heating from room temperature \((22\, ^\circ\text{C})\) to 95\(^\circ\text{C}\) over the course of 15 minutes, remaining at 95\(^\circ\text{C}\) for 15 minutes after which heating and data collection ceased. Data collection involved multiple 60 second timeslices over 514 channels. A channel is an interpolation from the wires on one of the detectors. There are some 200 wires, but 512 channels. Channel number was later converted to Q as part of the data refinement process.

Table 4.1 shows the various samples that were prepared and measured over the course of the experiment. Column 1 is the experiment run number, columns 2-4...
shows the concentrations of the iron salt, acid and NaHPO$_4$ used for the run, column 5 shows the ramp and dwell time for the run, and column 6 shows the temperature range measured during the run. It should be noted that the acid used corresponds to the counterion of the iron salt used.

<table>
<thead>
<tr>
<th>Run number</th>
<th>[Iron Salt] /M</th>
<th>[Acid] /M</th>
<th>[NaHPO$_4$] /M</th>
<th>Time/mins (Ramp+dwell)</th>
<th>Temperature range/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>B01</td>
<td>FeCl$_3$/0.03</td>
<td>0</td>
<td>5 x 10$^{-3}$</td>
<td>15 + 15</td>
<td>22-95</td>
</tr>
<tr>
<td>B02</td>
<td>FeCl$_3$/0.03</td>
<td>0</td>
<td>0</td>
<td>15 + 15</td>
<td>22-95</td>
</tr>
<tr>
<td>B03</td>
<td>FeCl$_3$/0.03</td>
<td>HCl 0.001</td>
<td>0</td>
<td>15 + 15</td>
<td>22-95</td>
</tr>
<tr>
<td>B04</td>
<td>FeCl$_3$/0.03</td>
<td>HCl 0.01</td>
<td>0</td>
<td>15 + 15</td>
<td>22-95</td>
</tr>
<tr>
<td>B05</td>
<td>FeCl$_3$/0.03</td>
<td>HCl 0.1</td>
<td>0</td>
<td>15 + 15</td>
<td>30.5-95</td>
</tr>
<tr>
<td>B07</td>
<td>Fe$_2$(NO$_3$)$_3$/0.03</td>
<td>HNO$_3$ 0.001</td>
<td>0</td>
<td>15 + 15</td>
<td>25.4-95</td>
</tr>
<tr>
<td>B08</td>
<td>Fe$_2$(NO$_3$)$_3$/0.03</td>
<td>HNO$_3$ 0.01</td>
<td>0</td>
<td>15 + 15</td>
<td>31.2-95</td>
</tr>
<tr>
<td>B09</td>
<td>Fe$_2$(NO$_3$)$_3$/0.03</td>
<td>HNO$_3$ 0.1</td>
<td>0</td>
<td>15 + 15</td>
<td>31.5-95</td>
</tr>
<tr>
<td>B10</td>
<td>FeCl$_3$/0.15</td>
<td>HCl 0.001</td>
<td>0</td>
<td>15 + 15</td>
<td>32.5-95</td>
</tr>
<tr>
<td>B11</td>
<td>FeCl$_3$/0.15</td>
<td>HCl 0.01</td>
<td>0</td>
<td>15 + 15</td>
<td>32-95</td>
</tr>
<tr>
<td>B12</td>
<td>FeCl$_3$/0.15</td>
<td>HCl 0.1</td>
<td>0</td>
<td>15 + 15</td>
<td>30-95</td>
</tr>
<tr>
<td>B13</td>
<td>FeCl$_3$/0.15</td>
<td>0</td>
<td>0</td>
<td>15 + 15</td>
<td>26.6-95</td>
</tr>
<tr>
<td>B14</td>
<td>Fe$_2$(NO$_3$)$_3$/0.15</td>
<td>HNO$_3$ 0.001</td>
<td>0</td>
<td>15 + 15</td>
<td>32.5-95</td>
</tr>
<tr>
<td>B15</td>
<td>Fe$_2$(NO$_3$)$_3$/0.15</td>
<td>HNO$_3$ 0.01</td>
<td>0</td>
<td>15 + 15</td>
<td>32.5-95</td>
</tr>
<tr>
<td>B16</td>
<td>Fe$_2$(NO$_3$)$_3$/0.15</td>
<td>HNO$_3$ 0.1</td>
<td>0</td>
<td>15 + 15</td>
<td>31-95</td>
</tr>
<tr>
<td>B17</td>
<td>Fe$_2$(NO$_3$)$_3$/0.15</td>
<td>0</td>
<td>0</td>
<td>15 + 15</td>
<td>31-95</td>
</tr>
<tr>
<td>B18</td>
<td>FeCl$_3$/0.15</td>
<td>0</td>
<td>0</td>
<td>Run time Dried 3h</td>
<td></td>
</tr>
<tr>
<td>B19</td>
<td>FeCl$_3$/0.15</td>
<td>0</td>
<td>0</td>
<td>Run time Heated 104 for 3h</td>
<td></td>
</tr>
<tr>
<td>B20</td>
<td>FeCl$_3$/0.15</td>
<td>0</td>
<td>0</td>
<td>5 min runs Heated 200 over 15 min</td>
<td></td>
</tr>
<tr>
<td>B21</td>
<td>FeCl$_3$/0.15</td>
<td>HCl 0.1</td>
<td>0</td>
<td>15 + 15</td>
<td>33-95</td>
</tr>
<tr>
<td>B24</td>
<td>FeCl$_3$/0.006</td>
<td>0</td>
<td>0</td>
<td>15 + 2.5</td>
<td>24-95</td>
</tr>
<tr>
<td>B25</td>
<td>FeCl$_3$/0.03</td>
<td>As B20, dried at 200°C</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>B26</td>
<td>FeCl$_3$/0.03</td>
<td>Dried sample</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 – Summary of the solution compositions and reaction conditions for all experimental runs for the hydrolysis of Fe(III).

4.6 Data refinement

Before refinement, the data had to be manipulated in order for it to be in the correct format. The data were processed using the program XOTOKO to correct and normalise the data. The scattering data were divided by the detector response and background subtraction removed any scattering due to the capillary and water. The data for the oriented rat tail collagen and silver behenate was used to produce a conversion to change channel number into Q. Silver behenate exhibits 13 well
defined (00l) peaks at values of 2θ less than or equal to 20° when irradiated with 1.54 Å synchrotron radiation. These peaks begin at 1.5° and continue at intervals of approximately 1.5° and end at 19.7°. It should be noted that the peaks are not equally spaced in 2θ, but rather in \( \frac{1}{d} \). All of these peaks, except the (0, 0, 13) peak at 19.7°, are free from overlaps. The first five peaks show the strongest intensity, particularly the (00l) peak (Figure 4.5).\(^7\)

![Figure 4.5](image)

**Figure 4.5** – Silver behenate calibration pattern for \( I = 1-7 \).

A similar condition exists for wet rat-tail collagen (Figure 4.6).

![Figure 4.6](image)

**Figure 4.6** – Wet rat-tail collagen calibration pattern.

The calibration using the rat-tail collagen was used to provide the conversion from channel number to \( Q \) for the long camera setting.\(^8\) The channel correlating to the
maximum intensity for each of the first nine orders of diffraction in the rat tail data were determined. A plot of channel number against order was then produced (Figure 4.7). A linear regression through these points could then be used to determine the channel where the order was zero and the gradient of this line provided the channel number-Q conversion required. Table 4.2 shows how rat-tail order is related to $Q$ and $d$-spacing.

<table>
<thead>
<tr>
<th>Order</th>
<th>Q-value</th>
<th>$d$-spacing (d)/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0093770</td>
<td>670.0</td>
</tr>
<tr>
<td>2</td>
<td>0.018754</td>
<td>335.0</td>
</tr>
<tr>
<td>3</td>
<td>0.028131</td>
<td>223.3</td>
</tr>
<tr>
<td>4</td>
<td>0.037508</td>
<td>167.5</td>
</tr>
<tr>
<td>5</td>
<td>0.046885</td>
<td>134.0</td>
</tr>
<tr>
<td>6</td>
<td>0.056262</td>
<td>111.7</td>
</tr>
<tr>
<td>7</td>
<td>0.065639</td>
<td>95.71</td>
</tr>
<tr>
<td>8</td>
<td>0.075016</td>
<td>83.75</td>
</tr>
<tr>
<td>9</td>
<td>0.084393</td>
<td>74.44</td>
</tr>
<tr>
<td>10</td>
<td>0.093770</td>
<td>67.00</td>
</tr>
<tr>
<td>11</td>
<td>0.10315</td>
<td>60.91</td>
</tr>
<tr>
<td>12</td>
<td>0.11252</td>
<td>55.83</td>
</tr>
<tr>
<td>13</td>
<td>0.12190</td>
<td>51.54</td>
</tr>
<tr>
<td>14</td>
<td>0.13128</td>
<td>47.86</td>
</tr>
<tr>
<td>15</td>
<td>0.14065</td>
<td>44.67</td>
</tr>
<tr>
<td>16</td>
<td>0.15003</td>
<td>41.88</td>
</tr>
<tr>
<td>17</td>
<td>0.15941</td>
<td>39.41</td>
</tr>
<tr>
<td>18</td>
<td>0.16879</td>
<td>37.22</td>
</tr>
<tr>
<td>19</td>
<td>0.17816</td>
<td>35.26</td>
</tr>
<tr>
<td>20</td>
<td>0.18754</td>
<td>33.50</td>
</tr>
<tr>
<td>21</td>
<td>0.19692</td>
<td>31.90</td>
</tr>
<tr>
<td>22</td>
<td>0.20000</td>
<td>30.45</td>
</tr>
<tr>
<td>30</td>
<td>0.28000</td>
<td>22.33</td>
</tr>
<tr>
<td>35</td>
<td>0.33000</td>
<td>19.14</td>
</tr>
<tr>
<td>41</td>
<td>0.38000</td>
<td>16.34</td>
</tr>
<tr>
<td>52</td>
<td>0.49000</td>
<td>12.88</td>
</tr>
<tr>
<td>71</td>
<td>0.66000</td>
<td>9.437</td>
</tr>
</tbody>
</table>

Table 4.2 – Rat-tail order correlations.
Once the data had been corrected, normalised and converted into the correct format it was analysed using the data-fitting program FISH. This program has been discussed previously in Chapter three. Again the data were analysed using the polydisperse hollow spheres model as this model produced the best fit to the data collected. This model was chosen as it was the closest to known geometries of iron oxide particles in aqueous solutions. Such particles are frequently spherical or acicular in shape, as observed by SEM and TEM microscopy.

4.7 Results and discussion

Examination of the spectra showed trends that could be explained in terms of the pH of the solution, counterion and the concentration of the solution. The spectra (Figures 4.8-4.16) are shown below. It should be noted that the data lines refer to increasing time in the direction of the z-axis, i.e. into the plane of the page. Figures 4.8 show a three-dimensional representation of a typical plot, illustrating how the scattering changes over time for 0.03 M (B02) and 0.15 M (B13) FeCl₃ solutions. Figures 4.9-4.16 show the spectra evolution of the runs for the time stepped experiments, with the later signals being those towards the top right of the Figure. It should be noted that no Bragg scattering was observed in the wide angle region suggesting that there was no medium-long range order.
Figure 4.8 – Evolution of SAXS signal with increasing time for
(Top B02) 0.03 M FeCl₃ and
(Bottom B13) 0.15 M FeCl₃.
Chapter 4 – Small and Wide Angle X-ray Scattering From Iron Oxide Colloids

Figure 4.9 – Evolution of SAXS signal with increasing time (arrow) for (Centre B07) 0.03 M Fe$_2$(NO$_3$)$_3$, 0.001 M HNO$_3$.

Figure 4.10 – Evolution of SAXS signal with increasing time (arrow) for (Left B08) and 0.03 M Fe$_2$(NO$_3$)$_3$, 0.01 M HNO$_3$ and (Right B09) 0.03 M Fe$_2$(NO$_3$)$_3$, 0.1 M HNO$_3$. 
Figure 4.11 - Evolution of SAXS signal with increasing time (arrow) for
(Left B17) 0.15 M Fe$_2$(NO$_3$)$_3$ and
(Right B14) 0.15 M Fe$_2$(NO$_3$)$_3$, 0.001 M HNO$_3$.

Figure 4.12 - Evolution of SAXS signal with increasing time (arrow) for
(Left B15) 0.15 M Fe$_2$(NO$_3$)$_3$, 0.01 M HNO$_3$ and
(Right B16) 0.15 M Fe$_2$(NO$_3$)$_3$, 0.1 M HNO$_3$. 
Figure 4.13 - Evolution of SAXS signal with increasing time (arrow) for (Left B03) 0.03 M FeCl$_3$, 0.001 M HCl and (Right B04) 0.03 M FeCl$_3$, 0.01 M HCl.

Figure 4.14 - Evolution of SAXS signal with increasing time (arrow) for (B05) 0.03 M FeCl$_3$, 0.1 M HCl.
Figure 4.15 - Evolution of SAXS signal with time (arrow) for
(Left B13) 0.15 M FeCl₃ and
(Right B10) 0.15 M FeCl₃, 0.001 M HCl.

Figure 4.16 - Evolution of SAXS signal with time (arrow) for
(Left B11) 0.15 M FeCl₃, 0.01 M HCl and
(Right B12) 0.15 M FeCl₃, 0.1 M HCl.
4.7.1 Analysis of SAXS data

The SAXS data were analysed using the FISH fitting program, and it became clear that a variety of models could be used to fit the data, with similar degrees of success. In particular, the data could be fitted to particles whose shape was either a plate or a hollow spherical shell (though not a solid spherical shell). There is no precedent in the literature for growth via plate-like particles, though of course there have been no prior measurements that probe particles in situ, rather than analysing structure on particles extracted from solution, so it is not strictly correct to eliminate this possibility on that basis. For many of the measurements that showed a broad response in $d\Sigma/d\Omega$ versus $Q$, it was also possible to fit the data either to a very broad distribution of particles, or to a collection of particles whose size distribution peaked around two or three mean values. The former of these possibilities gave poorer fits to the data, and indeed the fitting procedure was not stable in terms of convergence of optimised parameters, so in general we found that the data supported the notion that there are small particles present – particularly in the early stages of growth – and that these aggregate to form larger particles. This is apparent for instance in the appearance of the scattering from the more dilute nitrate solutions, shown in Figure 4.9 and 4.10, where the feature at $Q \approx 0.01 \text{ Å}^{-1}$ grows quicker in the initial stages of reaction than the feature at $Q \approx 0.1 \text{ Å}^{-1}$. In all cases the feature at smallest $Q$ corresponded to polydisperse spheres whose radius was $275\pm25$ Å. This size is approximately three times that of the previous SANS experiment, where the mean sphere radius was approximately 100 Å. The SANS experiment used microwaves as the heating source, but in this experiment conventional heating was employed. It is well known that microwaves form nucleation sites (in the bulk of solutions rather than at vessel walls due to their heating properties) and that these sites can then induce the formation of particles. We would expect that under the conditions we employed for our reactions, the rate of heating and the rate of formation of such nucleation sites is faster with microwave heating so it is not unexpected that microwave heating of this system should produce much smaller particles than those obtained by conventional means. At small $Q$, $d\Sigma/d\Omega$ decreases as power law in $Q$ with an exponent of $2.2(2)$, which indicates a fractal structure to the interface with the solution.
The features in dΣ/dΩ versus Q at higher Q correspond to the formation of smaller particles: those in the region Q = 0.2-0.25 Å⁻¹ indicate the presence of particles of radius 15 - 12 Å) while the broad band often seen in the Q range 0.06-0.09 Å⁻¹ indicates particles with radii ranging from 32 - 35 Å.

4.7.2 Dependence of particle growth on acid concentration

Addition of Fe(III) to H₂O leads to hydrolysis with the production of H₃O⁺, so the addition of further acid inhibits particle formation. The pH of the two iron salts at room temperature (298 K) and ambient pressure was measured in deionised water with an electronic meter, and values are given in Table 4.3.

<table>
<thead>
<tr>
<th>Concentration/M</th>
<th>FeCl₃</th>
<th>Fe₂(NO₃)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03 M</td>
<td>2.11</td>
<td>2.28</td>
</tr>
<tr>
<td>0.15 M</td>
<td>1.90</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Table 4.3 – Measured pH of the FeCl₃ and Fe₂(NO₃)₃ at concentrations of 0.03 and 0.15 M in the salts.

The dependence of particle growth on pH can be seen in the time evolution of the intensity of the scattering cross section (dΣ/dΩ). As Table 4.3 shows, the pH of the solutions is already low before any further acid is added; consequently if the pH of the solution is reduced further by the addition of acid then hydrolysis will be inhibited further and fewer particles will be formed in a given period of time. In general, if the spectra for both the chloride and nitrate solutions are examined with respect to added acid, it can be seen that the increase in dΣ/dΩ over time is reduced as the concentration of acid is increased (Figures 4.11 and 4.12 compared with Figures 4.15 and 4.16). This change is particularly marked in the suppression of the features at high Q (≈ 0.1 Å⁻¹ and 0.2-0.25 Å⁻¹) in most samples as pH is lowered, while the feature at lower Q (≈ 0.01 Å⁻¹) continues to evolve with time at the lowest values of pH, albeit at a reduced rate.
4.7.3 Influence of the iron counterion

Fe(III) in aqueous solution is more associated with the counter ion Cl\(^-\) than NO\(_3^-\) under comparable conditions, so one would expect that Fe(III) in chloride solutions will be less involved in hydrolysis than in nitrate solutions. This observation correlates with the values of the stability constants for the two different salts.\(^{10}\) However, it is hard to discern any clear and consistent trend in the evolution of \(d\Sigma/d\Omega\) over time for a given value of acid and Fe(III) concentration so we feel that no reliable conclusions may be drawn on this point.

4.7.4 Influence of the iron concentration

The way in which \(d\Sigma/d\Omega\) responds to changes in the concentration of Fe (III) will also reflect changes in the pH of the solution and the counterion, as these are both dependent on the amount of added ferric salt. It was expected that as the concentration of Fe (III) increased then the intensity of the scattering cross section would also increase. However, this effect is inhibited to some extent by an accompanying decrease in pH, which acts to suppress hydrolysis. The net is that there is relatively little increase in \(d\Sigma/d\Omega\) with added ferric salt.
4.8 Conclusions

This experiment is the first *in situ* SAXS/WAXS measurement on this type of system. The experiment has shown that the mechanism for the growth of iron oxide particles from solution is indeed a complex process. When pH is not particularly low, our data favours a model in which smaller particles form first, followed by formation of larger particles, possibly through aggregation. Unfortunately, our data do not allow us to draw any clear conclusions about the influence of counterion on particle growth, and this is something that would require data taken with higher statistics, in turn requiring a brighter X-ray source. There is some indication that particle growth using microwaves leads to smaller particles, though this conclusion should be treated with some caution because the conditions used were not entirely comparable.

The WAXS part of this experiment showed that no diffraction could be observed. This suggests that the particles, whilst they are still in solution, are not crystalline on lengthscales significantly greater than the wavelength of the X-rays and so do not diffract. The crystallisation process may only occur when the sample is dried out and the particles partially dehydrate. This problem of the local ordering of the iron anion in solution was tackled using an EXAFS experiment (Chapter Five).
4.9 Bibliography

10. Stability Constants of Metal-Ion Complexes, compiled by L. G. Sillén and A. E. Martell, The Chemical Society, London (1964)
Chapter 5 - EXAFS Spectroscopy of Iron Oxide Colloids

5.1 Introduction

The experiment described in this chapter is complementary to the previous chapters describing the SANS and SAXS/WAXS experiments on the iron oxide system. Again the purpose of this experiment was to follow the evolution of both the size and the crystal structure of the particles as the reaction mixture was heated, and therefore determine the reaction route involved in the hydrothermal growth of fine iron oxide powders. The WAXS experiment only showed that the material was not crystalline. Therefore, due to the absence of any long-range structural order, an EXAFS (Extended X-ray Absorption Fine Structure) experiment is an appropriate technique to reveal how the local environment of the iron atoms in solution changes during the course of the reaction. The iron atoms are expected to pass through a variety of stages on hydrolysis, from aqua-ions, through discrete hydroxy coordinated species, then a gel and finally some more condensed forms of iron coordinated by oxygen. EXAFS is the only probe for such short-range order and should be able to distinguish between the various stages of evolution by identifying changes in the local coordination of the metal ion being studied.

Figure 5.1 - EXAFS and XANES (X-ray Absorption Near Edge Structure) region in the X-ray absorption spectra in Iron.
5.2 Experimental background

The mechanism by which ferric (Fe\(^{3+}\)) and ferrous (Fe\(^{2+}\)) ions hydrolyse in aqueous solutions is very sensitive to the reaction conditions, as described previously. As the reaction proceeds, the local environment of the iron ions in solution will change. At the beginning of the reaction, iron will be coordinated by chlorine ions, but as it progresses the chlorine will be substituted by oxygen-containing species to produce an intermediate iron-hydroxy species in the form of a gel. This change in the coordination of iron in solution will give rise to changes in the EXAFS spectra and the purpose of this experiment was to determine such changes and therefore identify any intermediate phases present.

5.3 EXAFS theory

EXAFS is the fine structure in the X-ray absorption coefficient, starting at an absorption edge, and typically extending up to 1000 eV further. The absorption edge corresponds to an X-ray photon which has enough energy to just free a bound electron in the atom of interest. When the electrons are in the most tightly bound shell \(n = 1\) the edge is called the \(K\)-edge. For the \(n = 2\) shell, the corresponding edges are called the \(L\)-edges. Currently these are the only edges used to observe EXAFS, although in principle \(n = 3\) or higher shells could be used as fine structure also exists closer to the absorption edge. However, due to the interaction of the surrounding atoms’ potential with the ejected electrons, the simplifying single-scattering assumption of EXAFS cannot be made. EXAFS can be used to gain information about the local arrangement of atoms surrounding the absorbing atom, in this case Iron. EXAFS experiments, when successful, produce many useful results, such as:

1. Long-range order is not required. Hence, crystalline and non-crystalline solids can be treated in the same way.
2. The local atomic co-ordination can be determined for each atom type individually. To obtain this information using diffuse elastic electron scattering would require isotopic labeling or anomalous scattering, which prolongs experimental time and increases error margins and can also be very expensive.
Structural information is obtained from EXAFS through simple and direct computer refinement using packages such as Excurve98, Exbrook and Excalib.\textsuperscript{11-13}

Due to the intensity of synchrotron radiation, the measurement is quick (a pattern can be obtained in a matter of minutes) and is relatively easy to set-up.\textsuperscript{4}

Many of the assumptions and approximations made in EXAFS break down in the XANES (X-ray absorption near edge structure) region (between the threshold and the point where EXAFS begins) and so different analysis methods are required. This severely limits the structural information obtained from EXAFS, particularly in extremely disordered systems. This means that EXAFS as a technique is only useful over a short-range and that no information about long-range order may be obtained. This results in EXAFS being a complementary technique to other diffraction methods.

A general expression\textsuperscript{5} used in the interpretation of EXAFS data, which relates the structural parameters to the measured EXAFS oscillations using the plane wave theory, is given by:

\[
\chi(k) = -A(k) \sum_j \frac{N_j}{kR_j^2} |f_j(k, \lambda)| \exp(-2\sigma^2_j k^2) \exp \left( - \frac{2R_j}{\lambda_j} \right) \sin(2kR_j + 2\delta_j + \psi_j)
\]

Here \( \chi(k) \) is the magnitude of the EXAFS as a function of the photoelectron wavevector \( k \); \( N_j \) is the number of identical scattering atoms at an average interatomic distance \( R_j \), in the \( j \)th coordination shell; the terms \( 2\delta_j + \psi_j \) are phase shifts experienced by the photoelectron during the outgoing scattering process, and \( f_j(k, \pi) \) is the backscattered amplitude of the phototelectron wave; \( \lambda_j \) is the mean free path of the photoelectron. There is also a Debye-Waller factor, which depends on \( \sigma_j^2 \), the mean variation in \( R_j \). The elastic mean free path \( \lambda_j \) and the amplitude factor \( A(k) \) measure the proportion of absorption events that result in excitation of a single photoelectron.
An EXAFS wave is therefore determined by the backscattering amplitude \( N_j f_j(k, \lambda) \) modified by several reduction factors.

1. The amplitude reduction factor \( A(k) \) which acts upon \( \frac{N_j}{kR_j^2} \) and \( |f_j(k, \lambda)| \) and allows for losses due to multiple excitations at the central atom.

2. The damping factor \( \frac{-2R_j}{\lambda_j} \) is due to inelastic losses in the scattering process due to neighbouring atoms and the medium in between. This is dependent upon the ratio of the distance \( R_j \) and the mean electron free path \( \lambda_j \) are chemically sensitive to the local chemical environment.

3. The Debye-Waller factor \( \exp\left(-\frac{2\sigma_j^2}{k^2}\right) \) which accounts for thermal vibrations (assuming harmonic vibration) and static disorder (assuming a Gaussian pair distribution) at a distance \( R \).

Fitting of the experimental data in \( k \) space involves calculating a spectrum using an assumed set of parameters \( R, N, A \) and \( E_i \) until a best least squares fit is obtained.\(^6\)

### 5.3.1 EXAFS Data Analysis

Once an EXAFS measurement has been taken at SRS, Daresbury the analysis package Excurve98 is used to obtain a structural model of a material that agrees best with the EXAFS spectra. In order to refine a structure, the model must first be defined in terms of one or more clusters of atoms, weighted according to the overall composition of the material. These clusters may represent different atomic sites in a single-phase or multiple phases. A cluster requires the following description:

1. The radial or Cartesian co-ordinates of the scattering atoms about each absorbing atom for which spectra are available.

2. A pair distribution function for each symmetrically unique excited atom/scattering atom pair.

3. The point group of each cluster.
These definition parameters for the model are refined to optimise the fit to the EXAFS data. Structural data from other diffraction methods (such as bond length and bond angles) can also be used in the model. This is particularly true for crystalline samples with known structures.\(^4\)

5.4 EXAFS spectrometer on experiment station 9.3 at the SRS, Daresbury

The experiment was performed on station 9.3 at the Synchnotron Radiation Source (SRS) located at the Daresbury Laboratories.

Station 9.3 is an EXAFS facility for materials science experiments. The combination of a mirror and a stable, D.C. servo driven monochromator is a flexible arrangement for a wide range of experiments as a very wide energy range can be observed. A dispersive EXAFS facility has also just been commissioned which will allow complete EXAFS measurements in transmission in a timescale of 10-100 ms. The wiggler I source enables experiments in the range 6-30 keV. The one metre long plane Pd mirror is situated 18 m from the source and is used for collecting the whole vertical fan, focussing the beam onto the sample, and for harmonic rejection.

Station 9.3 has been used to develop the quick scanning EXAFS experiments by making use of the capability of the D.C. servo drive system to scan at constant angular speed. It is possible to record transmission spectra in around ten seconds and fluorescence samples with a concentration 10 mM or greater in a similar time. More dilute systems of concentrations of down to around 1 mM can be recorded with sufficient signal to noise ratio for qualitative analysis in around thirty seconds. The table has also been equipped with D.C. motors and this allows the table to move simultaneously with the monochromator, providing an effective exit system, which operates even in quick EXAFS mode.\(^7\) This station had the first quick EXAFS double crystal monochromator; the reflection used in the monochromator is Si (220). The first crystal is water cooled, and the second is controlled for alignment and harmonic rejection using three inchworms. This monochromator can be withdrawn and a second horizontally diffracting Si (111) crystal can then be inserted for energy
dispersive experiments. The timescale for a typical EXAFS experiment using this experimental arrangement is only a few minutes.

The experimental hutch contains an adjustable sample table capable of taking large, heavy items. The design allows easy, rapid change of experimental configurations. The table is mounted on a horizontal 20 arm that allows equipment to be aligned for dispersive experiments.

The station is equipped with a thirteen-element solid state detector, with semi automatic windowing and dead time correction for measurement of dilute systems. For diffraction, an Inel 120° position sensitive detector is available and for dispersive experiments a Hamamatsu S4874 1024 element photo diode array is used.

Due to the flexibility of the monochromator and experimental table, station 9.3 has been used to pioneer the combined EXAFS/powder diffraction experiments which are unique to Daresbury Laboratories. This arrangement is ideal for studying materials processing in which long and short-range structural order co-exist e.g. the synthesis of cadmium oxide from a hydroxyl gel.8,9

The station has a wiggler I source with 3 mrad horizontal acceptance and a Pd coated plane mirror one metre in length. The mirror has a variable angle of incidence and is bent to provide vertical collimation or focusing. The double crystal harmonic rejecting Si (220) monochromator is water-cooled, and is Bragg axis D.C servo driven, and also has a rectangular 4-point mounted, horizontally diffracting, energy dispersive Si (111) monochromator.

During our scanning EXAFS experiment the following conditions were typical.

1. Beam conditions: 150-250 mA minimum at 2 GeV.
2. Beamline: 7 mrad, mirror focusing onto a 200 µm slit.
3. Beam size: 10 mm horizontal.
4. Si (220) monochromator set at 50% harmonic rejection detune.
5. Detectors: standard ion chambers filled with Argon; 20% absorbing $I_0$ (incident beam intensity) and 80% absorbing $I_t$ (transmitted beam intensity). The ion chambers are backfilled to 1000 mbar with Helium.
6. Amplifiers: Keithley 427, gain $10^7$, a rise time of 10 ms, zero adjusted.
7. Scan conditions: fast 300 second scan to 15 Å⁻¹.

The data are then background subtracted and normalised using ECABS.⁹,¹⁰ These procedures are described in Section 5.7. The resulting data will typically have a signal to noise ratio greater than 50 at $Q = 10$ Å⁻¹ and 15 at $Q = 12$ Å⁻¹ where $Q = \frac{2\pi}{\lambda}$, the wavenumber.⁴

5.5 Apparatus for sample heating
The sample heater apparatus was designed and made by Dr. G. Sankar of the Royal Institution, London.¹⁰ The sample was sandwiched between two sheets of Kapton (50 μm thick); the cell and its holder was then inserted into the brass heating block (figure 5.2). Four cartridge heaters were then inserted into heating block, two at the front and two at the rear of the sample holder. The cartridge heaters were connected to an Eurotherm controller and a Variac controller. A thermocouple was then inserted into the heating block, and this was connected to the Eurotherm controller.

![Figure 5.2 - Photograph of the mounted R.I. EXAFS cell, showing the brass heating block, with X-ray aperture and aluminium sample cell (inside brass block).]
5.6 Experimental procedure
Aqueous solutions of FeCl₃ were made up in volumetric flasks with concentrations in the range of 0.03 - 0.15 M; some solutions also contained HCl with concentrations ranging from 0.001 - 0.1 M. These solutions were then transferred using a Pasteur pipette into the Kapton window sample cell. The second Kapton window was then placed over the sample and the cell was closed. Typically, only 3-4 drops of each solution were required to fill the cell. The second Kapton window was then carefully placed over the sample and the cell was sealed. The cell in its holder was then placed into the brass heating block. The samples were heated to approximately 100°C for the duration of the EXAFS scan and the subsequent X-ray scan; this typically lasted 10 minutes in total. It was noted that the solution had changed from a clear orange-brown solution into a dark brown precipitate after this time.

5.7 Data analysis
A series of data manipulations were performed before it could be analysed. First the background subtraction was made. Using the program Excalib and then Exbrook a pre-edge subtraction was performed in order to obtain a normalised absorption spectrum with asymptotes parallel to the x-axis. This was achieved using a linear extrapolation between two points on the pre-edge. A post-edge subtraction then produces the EXAFS wave, which has an even envelope about the x-axis and a Fourier transform of minimal intensity below the range of 1 Å. The Fourier transform of the EXAFS represents the shells of the backscattering atoms around the central atom (in this case iron). However, at this stage the distances are unphase-shifted, meaning that the position of the peaks does not accurately correspond with the distance between a shell and the central atom. After the data had been corrected, the program Excurv98 was used to calculate the theoretical spectrum for the data. This gives an indication of the species in the sample and what their surrounding environment will be. By using Excurv98 the bond lengths in the sample can be determined, as well as the number and type of atom surrounding the central atom.
5.8 Results and discussion

A variety of data were analysed. It was found that for lower concentrations, the amount of sample in the beam was not enough to be detected through EXAFS by either transmission or fluorescence. One data set (experiment 83799) did show a response that could be analysed, being taken for a 0.15 M solution of FeCl₃, heated at 95°C counting for 10 minutes data collection. This sample produced the densest colloid prepared during this experiment. Analysis, using the method described in Section 5.7, yielded the actual and theoretical EXAFS waves (figure 5.3), which in turn gave the Fourier transform (figure 5.4) and consequently the environment of the iron atoms in solution (Table 5.1).

![Figure 5.3 - Refined X-ray absorption spectrum data output for experiment 83799 (0.15 M FeCl₃, 95°C, 10 minutes).](image)
Figure 5.4 – Fourier transform output for experiment 83799
(0.15 M FeCl₃, 95°C, 10 minutes).

<table>
<thead>
<tr>
<th>Atom type</th>
<th>Coordination number</th>
<th>Distance/Å</th>
<th>Debye-Waller Factor (2σ²)/Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1.5</td>
<td>1.944</td>
<td>0.013</td>
</tr>
<tr>
<td>O</td>
<td>1.5</td>
<td>2.117</td>
<td>0.013</td>
</tr>
<tr>
<td>Fe</td>
<td>1</td>
<td>3.012</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Table 5.1 – Results for experiment 83799
(0.15 M FeCl₃, 95°C, 10 minutes).

The errors associated with this table are ± 0.02 Å for the bond distances and ± 10% for the Debye-Waller factors and coordination number (a measure of the size of the thermal ellipsoid of an atom). The Debye-Waller factor can be viewed as a result of averaging the single-scattering EXAFS formula over many near-neighbour pairs with a given pair distribution factor. Fluctuations in the near neighbour distances resulting from small vibrations or small degrees of disorder can be observed as changes in the size of the thermal ellipsoid of an atom or ion. An increase in the Debye-Waller factor can be thought of as an increase in the size of the thermal ellipsoid of that atom or ion.
These results were compared with various iron species held on the CDS database (Table 5.2). The local environment of common iron oxide species was compared with the experimental local environment in order to identify the species in solution. It was subsequently found that this reaction had formed nanosized particles of $\alpha$-Fe$_2$O$_3$ rather than bulk $\alpha$-Fe$_2$O$_3$.

<table>
<thead>
<tr>
<th>Atom type</th>
<th>Coordination number</th>
<th>Distance/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>3</td>
<td>1.944</td>
</tr>
<tr>
<td>O</td>
<td>3</td>
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<tr>
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<td>3</td>
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<tr>
<td>Fe</td>
<td>1</td>
<td>2.895</td>
</tr>
<tr>
<td>Fe</td>
<td>3</td>
<td>3.362</td>
</tr>
</tbody>
</table>

Table 5.2 – CDS database values for $\alpha$-Fe$_2$O$_3$.

This would explain why the EXAFS shows a lower coordination than expected. EXAFS determines the average coordination number of all of the iron atoms; the presence of small particles results in a large number of surface atoms which are not fully coordinated, which in turn lowers the total average coordination number for iron.
5.9 Conclusions

EXAFS is a powerful technique for determining the local environment of atoms in solutions, films and materials. In this case it has been shown that a relatively dilute solution of FeCl₃ when heated will produce small particles of α-Fe₂O₃. The cell used in this experiment was designed to study the transformation of a liquid into a gel suspension. Future modifications to the cell design may further optimise the conditions required for this reaction. In any case, it will be necessary to increase the iron concentration in order to obtain a good signal to noise ratio so that EXAFS spectra can be obtained in very short timescales. Further beamtime has been awarded (autumn 2001) in order to complete this experiment, and it is hoped that the next experiment will yield more information on this complicated problem.
5.10 Bibliography


7. http://www.srs.dl.ac.uk/xrs/


10. G. Sankar et al, manuscript in preparation (2001)

11. *Excalib manual*, SRS Daresbury Laboratories, UK

12. *Exbrook manual*, SRS Daresbury Laboratories, UK

Chapter 6 – Microwave-assisted Diffusion in Porous Materials

6.1 Introduction

This chapter describes experiments involving the microwave assisted diffusion of ions into porous materials. There is evidence that during the formation of haematite particles that Fe$^{2+}$ ions diffuse with the assistance of microwaves into the lattice of an intermediate iron oxyhydroxide species. Normally, intercalation reactions often require long reaction times (several days or even weeks) and elevated temperatures. Even under extreme conditions such as these the reactions are not guaranteed to be successful. Ultrasound methods have been shown to enhance the rate of reaction, but as with traditional heating methods the crystallinity of the final product can be poor, but better than would have otherwise been obtained using traditional methods. Due to the coupling of microwave electric dipole with the ions or small molecules it may be possible to use them to enhance diffusion through porous functional materials in particular iron and manganese oxides.$^{2-4}$

There are various materials that are suitable for studying how microwaves may affect the intercalation kinetics involved in the diffusion of ions into a host lattice. Materials such as $X_{1.9}$Fe$_2$OOH (where $X$ = Co, Ni and Li) and LiMnOOH are of interest in the electronics industry as magnetic recording media and as new battery materials.

Iron oxyhydroxy compounds provide potential host lattices for the intercalation of metal cations.$^{5}$ Goethite ($\alpha$-FeOOH) is the most abundant and stable of this group of compounds. The structure is based on hexagonal close packing of oxygen and hydroxy ions with Fe$^{3+}$ ions arranged in the octahedral interstices in a series of double rows, separated by a vacant double row. Each double row of atoms, with associated anions, constitutes a double chain of edge sharing octahedra, which extend along the [001] direction. The shared vertices at the chain edges connect the double chains to each other (Figure 6.1).
The close packed anion stacking is along the [001] direction with the oxygen and hydroxy anions alternating within the ion plane. The vacant rows of octahedral sites give rise to channels in the structure along the [001] direction and it is these channels that allow the diffusion of ions. Those channels that occur on the surface of the goethite are called grooves and act as sites of attachment for the adsorption of foreign ions or molecules.

Naturally occurring samples of goethite exhibit such absorption processes in nature and are good indicators of pollution as they absorb heavy metals such as lead. The insertion of $\text{Fe}^{2+}$ into the $\text{Fe}^{3+}$ lattice suggests that other metal cations such as $\text{Co}^{2+}$, $\text{Cu}^{2+}$, $\text{Ni}^{2+}$ and $\text{Cr}^{3+}$ could be inserted into the host lattice. It is hoped that the insertion of such metal ions into the iron-oxygen lattice will result in materials with useful characteristics e. g. Nb and Ge doped into haematite (made from goethite by a simple process) to improve its semiconducting properties. Goethite doped with barium is of use as a perpendicular magnetic recording medium. An example of such a material is $\text{BaFe}_{12}\text{O}_{19}$, which is easy to magnetise in the longitudinal direction of the particles which gives rise to a higher magnetic recording density.
The intercalation compound LiCoO$_2$ has been made using microwaves. This intercalation compound is important as it was one of the first rechargeable lithium ion battery materials. These cells consist of layered electrodes, usually made of metal oxides or graphite, which store positive ions between the crystal layers of an electrode. In this instance lithium ions form an intercalation compound with the graphite electrode when charged. As the cell is discharged the ions move through the electrolyte to the manganese dioxide electrode (Figure 6.2).

![Diagram showing the diffusion of Li$^+$ between the electrodes during the charge and discharge processes in a Lithium intercalation cell.](image)

These cells show no appreciable change in their structure during charging and discharge; the electrolyte does not decompose and acts as a conductor of ions which may be recharged thousands of times making it suitable as a power cell for a variety of applications.

Microwave routes to similar lithium cathode materials based on iron and manganese systems are described here. Such a preparative route may prove to be cleaner, with energy savings and so should mean that future lithium battery materials are cheaper than their predecessors were.
6.2 Apparatus

A commercial 0-1 kW variable power microwave source (microwave heating type GU14) was used to generate microwaves of frequency 2.45 GHz, which were delivered to the sample via a compact waveguide arrangement. Two different waveguide configurations were used depending upon the type of reaction being studied.

6.2.1 Reactions in solution

When the reaction required the reagents to be heated under reflux, the waveguide was set up in the configuration shown in Figures 6.3 and 6.4. A water condenser was connected to the round-bottomed flask to allow the vapour to condense and prevent its loss. The water condenser also behaves as a water load by absorbing excess microwave power, thus preventing leakage. The variable microwave power output from the microwave generator was under P.C control using software written in Visual Basic 5.0, specifically for this instrument. The software allows temperature control by monitoring the microwave output power to hold the temperature of the sample to within ±0.5 K for the duration of the experiment. The temperature of the reaction was monitored using a fibre-optic thermometer (Nortech ReFlex); the fibre-optic was immersed in the reactants and was connected to the P.C via its control unit. The fibre-optic thermometer consists of an optical fibre tipped with a fluorescent material (manganese activated magnesium fluorogermanate) as the sensor and was capable of accuracy of greater than ± 1 K plus 0.003 K per metre of fibre, with a response time of 0.25-1.0 seconds (probe length dependent).
6.2.2 Solid state reactions

In the case of solid state reactions, samples were in the form of a pellet which was placed into a silica crucible situated in the waveguide under the brass choke section. As brass is a microwave reflecting material, this ensures that no microwave radiation will escape from the waveguide. In contrast, silica is a microwave transparent material and was therefore used as the reaction vessel. A Platinum/Rhodium thermocouple was inserted (perpendicular to the field) into the bottom of the silica crucible through a small hole and linked to the temperature controller; this allows the temperature to be monitored throughout the reaction (Figures 6.5 and 6.6).
Figure 6.5 - Schematic of the arrangement of microwave applicator for use in the solid state reactions.

Figure 6.6 - Photograph of the apparatus when in solid state configuration.

6.2.3 28 GHz microwave applicator

In addition to constructing and using our own apparatus, we also gained access to a 28 GHz microwave applicator located at the Department of Material Chemistry at Tohoku University, Japan. Experiments were performed using this apparatus during an eight-week exchange Fellowship as part of the Monbusho program.

The 28 GHz microwave applicator (Fujidempa FMS-10-28, 10 kW, pressure range 13.3 Pa - 0.95 KPa) was used to heat certain reactions involving channeled...
manganese oxides. The design of this applicator (Figure 6.7) was very different to the 2.45 GHz applicator. Microwaves are generated by a gyrotron and are then transferred to the cavity by copper (10.7 cm diameter) cylindrical waveguide. The cylindrical (75x100 cm) stainless steel cavity has mirror-finish walls inside to allow a uniform distribution of the electromagnetic field.

The samples were loaded into a silica crucible, which was mounted on a Platinum/Rhodium (10%) thermocouple encapsulated in a silica sheath. The samples were then irradiated (at 1 kW unless specified) with microwaves of 28 GHz frequency and the variation of the sample temperature was followed via the microwave control software. Typically the sample was irradiated for fifteen minutes.

Figure 6.7 – 28 GHz microwave applicator (cavity open, approximately 1m in diameter), note the silica crucible in the centre of the cavity.
6.3 Experimental procedure

The experiments we performed fall into two categories: diffusion into natural and synthetic iron oxide materials; and diffusion into synthetic manganese oxide materials.

6.3.1 Diffusion into channeled iron oxides

6.3.1.1 Diffusion of divalent metal cations into natural goethite

The reactions involving microwaves were carried out in a 50 ml thick-walled silica test tube, which was covered with a transparent polythene sheath in case of explosion, and fitted with an air-tight screw top allowing pressure control via a pressure transducer. This vessel is also known as a Fischer-Porter tube (Figure 9.2). The vessel was placed vertically into the cavity at and held in position by a simple clamp arrangement. Typically, the samples were heated for three hours at 5 bar pressure with a microwave power of 950 W. In each case the most soluble salt of each metal cation was used.

A sample of natural goethite (source: J. M. Davidson, Department of Chemical Engineering, The University of Edinburgh) was initially examined using a scanning electron microscope (SEM). The micrograph showed that the sample contained parallel needles of goethite (Figure 6.8).

![SEM micrograph of natural goethite](image)

Figure 6.8 – SEM micrograph of natural goethite.
In order to monitor the extent of diffusion, we performed measurements to map the elemental distribution at micron lengthscales. Element specific images can be obtained for materials in two ways, either by wavelength dispersive (WD) or energy dispersive (ED) techniques. The electron microprobe is a WD technique and SEM can provide an ED technique for elemental mapping of a material. The electron microprobe can analyse all but the lightest elements in the periodic table (boron being the limit) with a spatial resolution of about 1μm and good analytical precision. Typical detection limits are in the order of 0.01 wt% to 0.05 wt%, depending on the element. The Cameca Camebax Microbeam is equipped with four vertical crystal spectrometers and an Oxford Instruments Isis 300 energy dispersive analyser. Backscatter electron, secondary electron, X-ray and cathodoluminescence imaging facilities are available. The SEM Facility operates a Philips XL30CP with an Oxford Instruments Isis 300 X-ray analysis system. The resolution of the microscope is 3.5 nm at 30 kV. The backscatter detector allows the imaging of specimens that have a mean atomic number difference of greater than 0.1.

Both techniques measure the change in intensity of an X-ray peak as an electron beam scans across the surface of the material. Scanning the electron beam over the sample using the ED detector can create element maps within seconds.

Electron microprobe X-ray maps require stage scanning under a stationary beam and therefore takes longer. However, it does allow the imaging of smaller variations and elements present at lower concentrations. The higher X-ray energy/wavelength resolution largely removes the problems of peak overlaps, commonly found when using ED spectrometry, which gives improved detection limits.

6.3.1.1.1 Diffusion of Co$^{2+}$ into natural goethite
A small chip of goethite was added to an aqueous solution of 0.1 M CoSO$_4$ and heated for 3 hours at a microwave power of 950 W in the Fisher-Porter tube at 5 bar pressure. The chips were then washed in distilled water and acetone and dried for 20 hours in a silica gel desiccator. The chips were analysed using PXRD, SEM and electron microprobe elemental mapping.
To compare the results and identify any specific differences between microwave driven intercalation and any standard thermal effects, the experiment was repeated placing a Teflon/steel bomb (a reaction vessel capable of reaching high pressures and temperatures) into a muffle furnace at 70 °C. A pressure of 5 bar was again maintained for 15 hours. The time was extended to allow the bomb and its contents to reach the desired temperature and pressure. The sample was analysed using PXRD and electron microprobe elemental mapping in order to detect the extent of absorption of the cobalt ion.

The size of the ion being intercalated will determine the degree to which the ion is inserted into the host lattice; the experiment was repeated using Ni\(^{2+}\) as the absorbing ion since it has an atomic radius slightly smaller (124 pm) than cobalt (125 pm). Goethite has a pore size of 1.4 Å by 2.4 Å which is large enough to allow cations to enter the channels.

6.3.1.1.2 Diffusion of Ni\(^{2+}\) into natural goethite
A small chip of goethite was added to an aqueous solution of 0.1 M NiCl\(_2\) and heated for 3 hours at a microwave power of 950 W in the Fischer-Porter tube at 5 bar pressure. The chip was not washed with water or acetone as it this may leach out any ions that had adsorbed near the surface of the chip. Electron microprobe mapping was carried out on the sample once dry.

The size of the ion being intercalated will determine the degree to which the ion is inserted into the host lattice; the experiment was repeated using Ba\(^{2+}\) and Sr\(^{2+}\) as the absorbing ions since these ions are larger than Co\(^{2+}\) and Ni\(^{2+}\). Their atomic radii are 217, 215, 125 and 124 pm respectively.

6.3.1.1.3 Diffusion of Ba\(^{2+}\) into natural goethite
A small chip of goethite was added to a solution of 0.1 M BaSO\(_4\) and heated for 3 hours at a microwave power of 950 W in the Fischer-Porter tube at 5 bar pressure. The chip was not washed with water or acetone as it was thought that this might
wash out any ions that had adsorbed near the surface of the chip. ED mapping was carried out on the sample after drying.

### 6.3.1.4 Diffusion of Sr$^{2+}$ into natural goethite

A small chip of goethite was added to a solution of 0.1 M Sr(OH)$_2$ and heated for 3 hours at a microwave power of 950 W in the Fischer-Porter tube at 5 bar pressure. The chip was not washed with water or acetone as it was thought that this might wash out any ions that had adsorbed near the surface of the chip. ED mapping was carried out on the sample once dry.

These reactions were then repeated on powder samples of goethite so that PXRD analysis could be performed on the samples. The natural sample of goethite was very hard and did not form a uniform powder when ground so goethite was synthesized using the method described here. Lepidocrocite was also synthesized to investigate its diffusion properties relative to goethite.

### 6.3.1.2 Diffusion of metal cations into synthetic goethite

#### 6.3.1.2.1 Synthesis of goethite

Ferrihydrite (Fe$_5$HO$_8$.4H$_2$O) was precipitated by adding 180 ml of 5 M aqueous KOH solution to 100 ml of 1 M Fe(NO$_3$)$_3$ solution. The resulting suspension was diluted to 2000 ml with distilled water in a screwcapped polypropylene flask. The flask was closed and heated in an oven at 70°C for 60 hours. The brown ferrihydrite suspension converted into a compact yellow precipitate (goethite) during this time. The yellow precipitate was collected by sedimentation and was washed several times with distilled water. The final solid was dried in an oven at 50°C and characterised using PXRD and SQUID magnetometry. This synthesis yielded 9 g of goethite.

#### 6.3.1.2.2 Synthetic goethite diffusion studies

Approximately 1 g of synthetic goethite was heated under reflux (using the microwave configuration in Figure 6.3) with 0.1 M solutions of (a) CoSO$_4$, (b) NiCl$_2$, (c) BaSO$_4$ and (d) Sr(OH)$_2$ for 6 hours. The samples were then filtered under vacuum.
and dried overnight in an oven at 110°C. The samples were then characterised using PXRD and SQUID magnetrometry.

6.3.1.2.3 Synthesis of LiFeO$_2$ from goethite and lepidocrocite
Stoichiometric quantities of (a) LiI and synthetic lepidocrocite and of (b) LiI and synthetic goethite were ground using a mortar and pestle and pelleted. Pellets 1cm in diameter were made by applying an uni-axial pressure of 10 tons. LiI was chosen as it has the lowest lattice energy of all the lithium halides and so should dissociate to produce Li$^+$ at the lowest temperature. The pellets were placed in a silica crucible and irradiated with microwaves using the solid state configuration shown in Figure 6.5. The microwave power was held at 400-500 W, which corresponded to a temperature of 370-380 °C, for 30 mins. The temperature was monitored using a thermocouple connected to a LCD display unit.

The pellets from mixtures (a) and (b) were heated separately. It was found that after 30mins, the temperature of mixture (a) had fallen to 120-140°C and in contrast the temperature of mixture (b) after 30mins had risen to 700-720°C. The products were allowed to cool and then characterised by PXRD.

6.3.1.2.4 Syntheses of CoFeO$_2$, NiFeO$_2$ and LiFeO$_2$ from goethite
Stoichiometric quantities of synthetic goethite with (a) CoO (b) NiO and (c) LiI were ground using a mortar and pestle. The mixed powders were packed into a silica tube (one end had been sealed previously), and glass wool was used to block the open end. The sealed tube was placed in the middle of the waveguide. Table 6.1 shows the reaction conditions.
### Table 6.1 – Reaction conditions required for synthesis of CoFeO₂, NiFeO₂ and LiFeO₂.

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>Microwave power/W</th>
<th>Reaction time/minutes</th>
<th>Product Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO/FeOOH</td>
<td>500</td>
<td>30</td>
<td>CoFeO₂</td>
</tr>
<tr>
<td>NiO/FeOOH</td>
<td>500</td>
<td>30</td>
<td>NiFeO₂</td>
</tr>
<tr>
<td>LiI/FeOOH</td>
<td>100</td>
<td>10</td>
<td>LiFeO₂ (I₂ evolved)</td>
</tr>
</tbody>
</table>

6.3.1.3 Diffusion of metal cations into synthetic haematite

Stoichiometric quantities of synthetic haematite with (a) CoO (b) NiO and (c) LiI were ground using a mortar and pestle. The mixed powders were packed into a silica tube (one end had been sealed previously), and glass wool was used to block the open end. The sealed tube was placed in the middle of the waveguide. Table 6.2 shows the reaction conditions.

### Table 6.2 – Reaction conditions required for synthesis of CoFeO₂, NiFeO₂ and LiFeO₂.

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>Microwave power/W</th>
<th>Reaction time/minutes</th>
<th>Product Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO/α-Fe₂O₃</td>
<td>500</td>
<td>30</td>
<td>CoFeO₂</td>
</tr>
<tr>
<td>NiO/α-Fe₂O₃</td>
<td>500</td>
<td>30</td>
<td>NiFeO₂</td>
</tr>
<tr>
<td>LiI/α-Fe₂O₃</td>
<td>100</td>
<td>10</td>
<td>LiFeO₂ (I₂ evolved)</td>
</tr>
</tbody>
</table>

The silica tube and its contents were allowed to cool. The contents were reground and characterised by PXRD.

6.3.2 Diffusion into channeled manganese oxides

6.3.2.1 28 GHz microwave irradiation

Powder samples of various mixed metal manganese oxides were prepared by grinding the metal salt (usually the carbonate) with manganese dioxide (MnO₂) using a pestle and mortar. All chemicals were of reagent quality and were used without further purification.
The samples were loaded into a silica crucible, which was mounted in contact with a Platinum/Rhodium (10%) thermocouple encapsulated in a silica sheath. The samples were then irradiated (at 1 kW unless specified) with microwaves of 28 GHz frequency and the variation of the sample temperature was followed via the microwave control software. Typically the sample was irradiated for fifteen minutes.

The samples were then characterised using PXRD. The pattern produced was then compared with the patterns contained within the Midi Jade™ database. Initially, a mixture of BaCO₃ and MnO₂ (1:8) was irradiated, but no reaction occurred. Another mixture was prepared using Ba(NO₃)₂ in the same ratio as before, but again no reaction occurred. Another batch of the second mixture was prepared, pelletised, sintered in a muffle furnace at 700°C for 12 hours and was then irradiated; however no reaction occurred. It is possible that the temperature used to sinter the mixture was not high enough to produce the intermediate oxide compound necessary to be heated by microwave irradiation.

Barium salts (carbonate, sulphate, nitrate, hydroxide, chloride and fluoride) were irradiated in order to ascertain their microwave absorbing properties. It was found that all of the salts tested were very poor at absorbing microwaves and showed only a small temperature change during the period of irradiation. A mixture of BaCO₃, K₂CO₃ and MnO₂ (1:1:18) was irradiated at 3 kW; reaction occurred after 30 minutes. PXRD analysis showed the sample to be multi-phase. In order to minimise the number of possible phases in the final product, samples were prepared with BaCO₃ and MnO₂ (1:16) along with carbon in various weight percentages (1.0, 2.5 and 5.0 wt%). As each series of samples was irradiated at various power settings (1, 2 and 3 kW) the maximum temperature for each sample was recorded. These results are shown in Table 6.3. There seems to be no clear correlation between power setting, carbon content and the maximum temperature.
### Table 6.3 – Maximum sample temperature at various power settings and carbon content.

<table>
<thead>
<tr>
<th>Carbon /wt%</th>
<th>Power = 1.0 kW</th>
<th>Power = 2.0 kW</th>
<th>Power = 3.0 kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>505 K</td>
<td>379 K</td>
<td>636 K</td>
</tr>
<tr>
<td>2.5</td>
<td>636 K</td>
<td>446 K</td>
<td>376 K</td>
</tr>
<tr>
<td>5.0</td>
<td>575 K</td>
<td>363 K</td>
<td>497 K</td>
</tr>
</tbody>
</table>

Another mixture of BaCO$_3$ and MnO$_2$ (1:16) was prepared containing 5 wt% of carbon. This was irradiated in air for 3 minutes and as before, the temperature did not change rapidly. The microwave cavity was then evacuated and this caused a rapid increase in temperature over a short period of time because the microwaves were coupling more efficiently with the sample. Reaction was seen to occur over a period of 4-5 minutes with the final temperature reaching 871°C. PXRD analysis showed that the final product for this reaction was a mixture of Mn$_3$O$_4$ and BaCO$_3$, thus showing that the desired reaction had not occurred.

#### 6.3.2.2 2.45 GHz microwave irradiation

##### 6.3.2.2.1 Reaction in solution

LiMnO$_2$ was synthesised by a the solid state ion exchange reaction between NaMnO$_2$ and LiBr.$^{13}$ The precursor, NaMnO$_2$, was prepared from stoichiometric quantities of (I) Na$_2$CO$_3$ and MnO$_2$ and (II) Na$_2$CO$_3$ and Mn$_2$O$_3$. The mixtures were ground together using a mortar and pestle and pelletised. Pellets 10 mm in diameter were made by applying an uni-axial pressure of 10 tons in a pellet press.

The pellets were (a) placed in the conventional tube furnace (Carbolite CTF 12/65/550) at 800 °C for 24 hours and (b) placed in a silica crucible and irradiated with microwaves at 950-1000 °C, at 100 W microwave power, for 1 hour using the configuration shown in Figure 6.3. The temperature of the microwave reaction was monitored using a thermocouple.
The products of both reactions were characterised by PXRD. Characterisation showed that product formed using mixture (I) formed the desired precursor in both cases.

For the purpose of this experiment the precursor that was prepared by microwave heating using mixture (I) was used in the ion exchange reaction to prepare LiMnO₂. NaMnO₂ was ground together with excess LiBr and placed in a 100 ml round-bottomed flask to which 50 ml of n-pentanol was added. The mixture was set up to reflux for 5 hours under microwave irradiation using the configuration shown in Figure 6.3. The temperature of the reaction, controlled using a fibre-optic thermometer, was held at 120-125 °C and the microwave power set at 500 W.

After cooling at room temperature, the product was filtered under suction and washed with n-pentanol and then water, to remove any unreacted LiBr. The product was characterised using PXRD.

To justify the use of pentanol as the solvent and the use of water to wash the product, solubility tests were performed on LiBr. A small portion of LiBr was added to a few millilitres of pentanol and of water. It was found that LiBr was soluble in pentanol but only when heated, hence the use of pentanol in the reaction. During the reaction LiBr dissolves in pentanol, facilitating mobility of Li⁺ ions, which can then undergo substitution with Na⁺ to form the product. LiBr was found to be soluble in water at room temperature, so water was used to remove any unreacted LiBr.

To ascertain whether microwave heating was able to accelerate the intercalation reaction, the reaction described above was repeated and a representative sample was extracted from the reaction vessel every hour using a syringe. Samples of approximately 15 ml were extracted for a total of 5 hours. The samples were filtered under suction and the filtrate added back into the reaction vessel immediately. The removed samples were washed with n-pentanol and then water and dried and finally characterised by PXRD.
6.3.2.2.2 Solid state reaction
Stoichiometric quantities of LiI and MnO₂ were ground using a mortar and pestle. The mixed powders were packed into a silica tube (one end had been sealed previously) and glass wool was used to block the open end. The mixture was heated for 500 W for 30 minutes.

6.4 Results and discussion
6.4.1 Diffusion into channeled iron oxides
6.4.1.1 Natural goethite
The time available for the most informative analysis, electron microprobe elemental mapping, was very limited; it was therefore decided to concentrate the results on the cobalt samples heated with microwaves for 3 hours as this was expected to give the highest concentration of cation diffusion into the sample.

ED spectrometry showed five assigned peaks: O at 0.6 keV, Si at 1.8 keV, (Fe, Kα) at 6.4 keV, (Co, Kα) at 6.95 keV and (Fe, Kβ) at 7.05 keV. The Si peak was most probably due to absorbed silicon species, such as quartz, in the ore’s natural environment. The intensity of these peaks was approximately proportional to the percentage of each element in the area under analysis. The cobalt was estimated to be 3% of the total composition of goethite in this particular area.

WD spectrometry showed peaks at sinθ = 0.401 (Co, Kβ), 0.435 (Fe, Kβ), 0.443 (Co, Kα) and 0.481 (Fe, Kα). The WD measurements could also be represented as a map showing areas of relative high element intensity (Figure 6.9).
Figure 6.9 – Electron microprobe X-ray map showing cobalt diffusion. (Left) Iron content and (Right) cobalt content. Each map covers an area of 100 μm² with the needles running from top to bottom.

The cobalt-doped goethite clearly shows the diffusion of cobalt, along the channels, parallel to the needles, as expected. Cobalt can also be observed at the edges and in breaks in the sample. The mapping of the iron content in the sample also appears to show a deficit in iron in the area where the cobalt was abundant. This could be due to direct substitution of iron by cobalt or alternatively iron may undergo withdrawal from the goethite during the reaction, which was then being replaced by cobalt via the channels. Further studies would have to be carried out to determine the mechanism.

The electron microprobe map of goethite doped with cobalt using conventional heating shows minimal intercalation. The PXRD showed no change to that of the natural sample again suggesting no diffusion had taken place.

The PXRD pattern of the goethite doped under microwave irradiation was slightly different to that of the natural goethite showing a low composition of cobalt. It should be noted that this result was for the whole sample, not just for the outer
surface area so a low level of detection of cobalt was expected. However, if the PXRD had been of the outer area of the sample only, where the ions are migrating from, then higher intensity peaks would be expected.

The electron microprobe X-ray map shows the doping of nickel into goethite also shows the ions migrating into the structure (Figure 6.10).

![Electron microprobe X-ray map showing nickel diffusion.](image)

**Figure 6.10** – Electron microprobe X-ray map showing nickel diffusion. (Left) Iron content and (right) nickel content. Each map covers an area of 100 \( \mu m^2 \) with the needles running from top to bottom.

When the strontium and barium samples were analysed using ED, it was found that no strontium or barium could be detected in the natural goethite chip. This was likely to be because they are larger in comparison to the pore sizes found in the chip.

When the reactions were repeated using synthetic goethite under reflux with conventional heating no diffusion was found. PXRD and SQUID analysis remained unchanged from the unreacted goethite. Had diffusion of the metal cation occurred then structural changes would have taken place resulting in different reflections in the PXRD data and SQUID measurements. Instead of diffusion occurring inside the
goethite needles, diffusion is actually occurring between the needles. As the space between the needles is much greater than the channel size of the needle then it is more likely for this intra-needle diffusion to be occurring. Chloride ions are found in the channel; their presence is vital to maintaining the channel structure. Attempting to substitute this ion for a small, positively charged metal cation will not be a favourable process. There are no such substitution problems found between the needles, making this a more suitable environment for diffusion.

### 6.4.1.2 Insertion reactions of synthetic goethite and haematite

It was found that when the apparatus was used in the solid state configuration (Figure 9.3) arcing occurred between the pellets and the thermocouple probe. Such arcing results in highly elevated temperatures and uneven heating through the sample. As a result the powders obtained from these pellets were shown to be multiphase when analysed by PXRD, containing the desired product, starting materials and a spectrum of intermediate compounds in some cases. Such purity problems were avoided when the samples were microwaved as compacted powders in silica tubes. As the thermocouple probe had been removed there was no problem with arcing and the samples were heated more evenly at the desired power level. Pellets could have been heated in this way, but this method had been used effectively with the 28 GHz microwave described previously. This method (for both goethite and haematite) yielded the desired product using a quick convenient method.

### 6.4.2 Diffusion into channeled manganese oxides

#### 6.4.2.1 Lithium Insertion

Lithium insertion in the synthesis of LiMnO₂ and of LiFeO₂ may take place by two different mechanisms. The synthesis of LiMnO₂ involves an ion exchange reaction in which Li⁺ displaces Na⁺ in NaMnO₂. The starting material NaMnO₂ has a layered structure consisting of layers of Na atoms and Mn atoms, held together through the coordination of oxygen atoms (Figure 6.11).
Figure 6.11 – Structure of MMnO$_2$ (M=Li, Na) showing the layers of MnO$_6$ octahedra and M atoms (yellow) between the layers.

This can then be compared to the unit cell structure of the product LiMnO$_2$. Again it can be seen to be a layered structure consisting of layers of Li atoms and Mn atoms, held together by coordination with oxygen atoms. Although the atomic radii of Li$^+$ and Na$^+$ differ by 33 pm, they both belong to crystals with the same space group and we can therefore conclude that Na$^+$ ions are being displaced by Li$^+$ ions during the reaction to form LiMnO$_2$.

The starting materials for the synthesis of LiFeO$_2$ adopt a different structure and therefore there is a different mechanism of formation taking place. Figure 6.1 shows the structure of goethite. It has orthorhombic symmetry and consists of double chains of octahedra alternating with double chains of vacant sites. The vacant sites appear as tunnels into which Li$^+$ ions may be inserted to form LiFeO$_2$.

Lepidocrocite, has a layered structure, quite different from goethite (Figure 6.12). Lepidocrocite consists of double chains of octahedra sharing edges with adjacent double chains. Each chain is displaced by half a unit cell with respect to its
neighbour, thus forming corrugated sheets of octahedra. These sheets are stacked and are separated by double rows of empty octahedral sites. Li$^+$ ions can therefore be inserted into the empty sites to form LiFeO$_2$ (Figure 6.13).

![Layered structure of lepidocrocite showing the FeO$_6$ octahedra.](image)

The structure is layered, consisting of layers of Li atoms and Fe atoms, coordinating with oxygen atoms. This structure was obtained regardless of the starting material (goethite or lepidocrocite) used in the synthesis.
6.4.2.2 Synthesis of LiMnO$_2$

Characterisation of the products for the synthesis of LiMnO$_2$ was achieved by comparison of the experimental PXRD patterns with reference PXRD patterns. The reference patterns were obtained from the Phillips diffraction software identification package. This was used in conjunction with the powder diffraction file search manual Inorganic Phases.$^{14}$ These reference patterns were used to assign observed peaks in all of the data.

Analysis of the XRD patterns allowed the progress of the ion exchange reaction to be followed. Characteristic peaks of LiMnO$_2$ only conclusively appeared after 3 hours under microwave irradiation. Figure 6.14 shows the PXRD pattern obtained after 5 hours irradiation.
Figure 6.14 – PXRD of LiMnO₂ sample after irradiation for 5 hours.

To determine whether the unassigned peaks in the PXRD patterns were due to the starting materials, the starting mixture was prepared as in Section 6.3.2.2. NaMnO₂ and excess LiBr were ground together using a mortar and pestle and added to 50 ml of n-pentanol. This mixture was left at room temperature and underwent no additional heating. The mixture was then filtered and washed as before and a PXRD pattern obtained (Figure 6.15). From this PXRD pattern the most intense peaks were marked and compared to the unassigned peaks in patterns. This was able to confirm that in fact these peaks were due to the starting material.

Figure 6.15 – PXRD of NaMnO₂ and LiBr starting mixture.
Again it is undesirable for the final material to be multiphase. The method described in Section 6.3.2.2.2 was found to be a quicker, cleaner way of producing the desired product dispensing for the need to have several complicated steps.

6.4.2.3 Synthesis of LiFeO₂

LiFeO₂ was successfully synthesised, using both synthetic goethite and ledipocrocite, as starting materials, using microwave irradiation. Characterisation of the products was achieved by comparison of the experimental PXRD patterns with reference PXRD patterns, as before. Analysis of the PXRD patterns (Figures 6.16 and 6.17) of both products show characteristic peaks of LiFeO₂.

![Figure 6.16 - PXRD of LiFeO₂ using lepidocrocite as the starting material.](image)

![Figure 6.17 - PXRD of LiFeO₂ using goethite as the starting material.](image)
From the PXRD patterns it was observed that more LiFeO$_2$ was formed from lepidocrocite than goethite. This is consistent with the more open structure. Unassigned peaks in the PXRD patterns for LiFeO$_2$ were thought to be due to the presence of complicated mixtures of phases in the sample. FeOOH undergoing dehydroxylation to Fe$_2$O$_3$ can occur under the influence of either heat or mechanical stress. It is known that goethite proceeds directly to haematite in the dry state without any intermediate phase and that lepidocrocite transforms upon dry heating first to maghaemite ($\gamma$-Fe$_2$O$_3$), through the collapse of the conjugated layers, and then to haematite. The thermal dehydroxylation reaction of the different forms of FeOOH takes place at widely varying temperatures, between 140-500°C. On comparison of the reference PXRD pattern of haematite and that of the synthesised product, it was observed that haematite was present in the samples. PXRD is not a good method for “fingerprinting” samples, particularly whenever mixed phases are present.
6.5 Conclusions

The experiments described in this chapter have shown that the use of microwaves may result in materials being synthesised more quickly than by using traditional synthetic routes. Although the results for diffusion into natural goethite were initially disappointing, the subsequent results for synthetic iron and manganese systems showed that diffusion does occur at a microscopic level. The importance of the stability of the host lattice was found to be an important factor when deciding upon reaction conditions. Manganese dioxide has a particularly stable lattice at high temperatures (and is therefore less likely to collapse) and so reactions involving it occurred at higher temperatures for longer times than the equivalent iron reactions, which have less stable lattices.

The way that the starting materials were prepared proved to be less important than in traditional solid state reactions. Normally, pelletisation of the reactants is necessary for solid state reactions to ensure intimate mixing of the starting materials. However, this was found to be unnecessary in the microwave reactions. It has been shown that a tightly packed ampoule was sufficient because the materials were being heated directly by the microwaves as opposed to thermal conduction in a tube furnace. This makes the microwave method more attractive as it was more convenient than traditional methods.
6.6 Bibliography

9. H. Yan, J. Power Sources, 68, 530 (1997)
11. K. Tamaura and T. Horiba, J. Power Sources, 81, 156 (1999)
Chapter 7 - Effect of Microwaves on H-bonding in Aspirin

7.1 Introduction

Microwaves are becoming increasingly used in a wide variety of chemical syntheses. For organic reactions in particular they are used as an alternative type of heating source and in many cases have been shown to increase the rate of reaction due to superheating of the solvent (Section 1.4.6.1). For many years there has been speculation about a "non-thermal microwave effect" with very little in the way of hard evidence. Much of the supposed evidence can be explained by conventional phenomena, that are more easily induced with microwaves e.g. solvent superheating\(^1\) or poor temperature measurement.\(^2\) If there really are other differences between conventional and microwave heated samples, there is a need for more evidence of anomalous heating effects e.g. through the observation of anomalous motion of atoms/molecules during microwave irradiation.

When living tissue is exposed to microwave irradiation they are heated resulting in the expression of heat shock proteins\(^3\) (HSPs) whose function is the protection of the cell by encouraging the refolding of globular proteins that are unfolded by heat. However, this response is puzzling for two reasons.

1. Expression of the HSPs is sometimes observed even when the power level of the radiation is too small to produce a significant or even measurable rise in temperature; this has been referred an athermal effect.

2. Typically, microwave radiation frequency in the range of GHz, while most of the modes of excitation of a biological macromolecule that can couple to electromagnetic radiation correspond to local vibrations that lie in the THz range. Despite this frequency mismatch, circular dichroism studies of β-lactoglobulin under microwave irradiation indicates an unusually high folding/unfolding rate compared to conventional heating at the same temperature.

The modes\(^4\) with which microwave radiation couple most effectively are believed to be collective torsional modes of large amplitude that involve relatively large regions
of the molecule. Normal mode analysis\textsuperscript{5} of protein excitations has been used to calculate atomic mean square displacements and compare them with X-ray crystallographic data, to reveal a significant density of states for such low-frequency modes, correlated over distances similar to the protein diameter.\textsuperscript{6} Recent work on the rate at which heat is equilibrated in a macromolecular material in relation to the rate of repartition of energy of relatively large amplitude torsional modes, indicates that the latter is much slower (timescales for such processes occurring in the range $10^{12} - 10^9$ s and in the region of $10^6$ s respectively).\textsuperscript{7} Therefore, it is possible that low-level microwave radiation may be particularly effective at directing energy selectively at precisely those modes that are involved in the conformational rearrangements seen in gating, hinge-bending and even protein folding. This area of research is important due to the proliferation of mobile telephones and their possible detrimental health effects.

One promising technique for such studies is neutron diffraction, which can reveal anomalous motion through observation of changes in the size and orientation of atom thermal ellipsoids. Previous neutron diffraction studies on materials related to aspirin (acetyl salicylic acid) such as paracetamol ($p$-hydroxyacetanilide) and benzoic acid dimers have shown that it is possible to model the atomic disorder associated with these molecules at specific temperatures.\textsuperscript{8-10} During the refinement process positional and anisotropic displacement parameters (ADPs) were refined for all atoms, including the hydrogens. The paracetamol molecule at 100 K has methyl hydrogen atoms that have very large thermal ellipsoids, suggesting libration or disorder of this group. Benzoic acid dimers have also been studied at specific temperatures (20, 50, 100 and 175 K) in order to determine hydrogen atom disorder in the hydrogen bonded carboxylic acid dimer motif. Refinement of the crystal at the four temperatures showed that the disorder of the hydrogen bonded hydrogen atom increases as the temperature increases. This disorder is observed as an increase in the size of the thermal ellipsoids as the temperature increases. This trend is also seen in the length of the two carbon-oxygen bonds of the carboxylic acid groups. The structure of aspirin is related to that of paracetamol and benzoic acid and it has
exhibited disorder in its hydrogen bonding similar to that described for paracetamol
and benzoic acid.

One aim of this experiment was to investigate the influence of microwaves on the
structure of aspirin and to investigate the possibility of a non-thermal microwave
effect. A microwave field of power 50 W was applied across a single crystal of
aspirin in order to determine whether the applied field caused a change in the
hydrogen motion in the crystal. The experimental set up of the neutron diffractometer
was such that the thermal contribution of the field was kept to an absolute minimum.
The second aim was to develop apparatus that can be used to produce a microwave
field across the sample, with the sample being analysed in situ for any resulting
structural changes. For this work neutron diffraction was employed as the most
appropriate analytical technique.

7.2 Experimental background: thermal disorder in aspirin
Aspirin molecules have hydrogen bonds between the hydrogen of the carboxylic
hydroxyl and the carboxylic carbonyl oxygen of an adjacent aspirin molecule (Figure
7.1). It has been observed that as temperature increases, the oxygen-hydrogen bond
length increases. This is observed as an increase in the size of the thermal ellipsoids
of the two atoms. Aspirin was chosen because of the hydrogen bonding described
above, but any hydrogen-bonded molecule could be used. Also, aspirin is a very
simple molecule with only a few atoms and a small unit cell thus making the
refinement process easier and allowing conveniently short data collection times.
Chapter 7 – Effect of Microwaves on H-bonding in Aspirin

Figure 7.1 – Depiction of the hydrogen bonds between the hydrogen of the carboxylic hydroxyl and the carboxylic carbonyl oxygen of an adjacent aspirin molecules.

Microwaves are known for their ability to enhance diffusion in many systems. It is expected that the application of microwaves to the aspirin system will enhance the movement of the hydrogen atom. The microwave power was set to 50 W so that the thermal contribution to this process was minimised, the only contribution being due to the presence of the microwave field.

7.3 Station instrument SXD at ISIS
The experiment was performed on the single crystal diffractometer (SXD) located at the ISIS Facility at the Rutherford-Appleton Laboratories, UK.

SXD is a general-purpose single crystal diffractometer, using a Laue technique. Utilising both the time-of-flight technique to separate the white beam, and large-area position-sensitive detectors, it is possible to access large volumes of reciprocal space in a single measurement. Standard crystallographic refinements are very successful, and use can be made of the epithermal, short wavelength neutrons that are available on a pulsed neutron source such as ISIS, to allow measurements to very high resolution.
SXD is situated on beam line S3. It receives neutrons from a 316 K H₂O moderator, poisoned with Gd at a depth of 2 cm to narrow the range of neutron energies. The distance of the sample from the moderator is 8 m and the diameter of the beam at the sample is a maximum of 15 mm. The beam size may be modified using B₄C inserts, located in the collimation box immediately before the sample.

There are three position-sensitive detectors. Two of the detectors are mounted on arms, which allow limited rotation and also manual adjustment of the sample to detector distance (L). The angle 20 for the centre of detector one can change between 90° and 130° (mounted on the high angle arm) and 50° and 90° for detector two (mounted on the low angle arm). The sample to detector distance has a user selectable range of 70<L<500mm depends upon the sample environment and the detector. Detector three is located on the opposite side of the neutron beam to detectors one and two, and can be fixed at one of three angles (20 for the detector centre at -55°, -90° or -125°). The detectors consist of a square array of 4096 3x3mm² fibre-optic pixel elements, with a thin Gd₂O₃ coated metal grid separating the four optic fibres required for each pixel from its neighbours. The total active area of the detectors is 192x192 mm². During this experiment a liquid helium ‘orange’ cryostat was employed; this is capable of producing a temperature range of 1.5-300 K in the sample tank. The tails of the cryostat have been adapted to provide reliable ω-rotation and minimise unwanted scattering. Additional scattering caused by the presence of air in the sample tank was removed by evacuating the sample tank (Figure 7.2) by means of a vacuum pump prior to data collection.¹¹

![Figure 7.2 – SXD sample tank.](image-url)
7.4 Microwave apparatus
A commercial 0-1 kW variable power microwave source (ASTeX 5-1000) was used to generate microwaves of frequency 2.45 GHz, which were delivered to the sample tank via a flexible 200 W co-axial cable. A water flow dummy load was used to protect the source. The co-axial cable was connected to a custom made circuit consisting of copper plates connected to vanadium plates which are situated on either side of the sample, which was an aspirin crystal. Vanadium was chosen because its coherent scattering cross-section is very small. It is the vanadium plates that operate as a parallel plate waveguide, generating the microwave field across the crystal.

![Diagram of E-field between vanadium plates.](image)

A 10 mm thick block of PTFE (Figure 7.4) separated the copper plates which were in turn connected to a standard n-type co-axial connector.
Figure 7.4 – (left) Shows the vanadium plate/copper co-axial circuit. (right) Shows sample (sandwiched between the two Vanadium plates) orientation relative to the vanadium plates.

A second co-axial cable was used to dump the microwaves into the dummy load located outside the sample tank (Figures 7.5 and 7.6).

Figure 7.5 – Schematic of the co-axial circuit. Power is lost to the dummy load. The arrows show the path of the microwaves through the circuit.
Due to space limitations within the SXD pit the microwave controller and generator were positioned remotely. The co-axial cable was passed through a hole in the side of the neutron shielding, as were the water pipes connected to and from the dummy load. The three-stub tuner was used to minimise the reflected microwave power.

The aspirin crystal was mounted on a custom-made AlN sample pin using Kapton tape. The sample pin was machined to be as similar as possible to the aluminium sample pin which are normally used in an SXD experiment. AlN was selected as this material is microwave transparent and has a high thermal conductivity. The sample temperature regulation was achieved using the thermal controller drawing heat from the sample pin (Figure 7.7) and hence the crystal. No neutron scattering from either the sample pin or the Kapton tape was detected during the course of the experiment.
7.5 Experimental procedure
The aspirin crystal was made prior to the experiment by dissolving aspirin in acetone. This solution was left in a lightly stoppered sample vial. Over the course of five days the acetone evaporated, resulting in the formation of a 8x4x1.5 mm single crystal of aspirin. The crystal was mounted the sample pin which was centered in the beam whilst in the sample tank.

Data were collected for the crystal at 100, 200 and 300 K, in the presence and absence of a microwave field. The cryostat was used to set the temperature. The microwave power was manually set at 50 W, and the power of the reflected microwaves was typically in the range 8-13 W.

7.6 Data refinement
The data were refined by a least-squares refinement method using the software package SHELXL-97.

The position of reflections in a diffraction pattern is determined by the geometry of the unit cell, and the intensity of these reflections is determined by the structure
factor $F_{kl}^2$, which depends on the position and nature of the atoms in the unit cell. Single crystal diffraction studies are capable of extracting the maximum amount of information about the structure of a material. A least-squares refinement is used to generate a best fit between the observed diffraction pattern as a whole, and the calculated model. This is achieved by the refinement of a series of factors relating to specific parameters (particularly the size of the unit cell and the atom positions), as well as those associated with the instrument involved (X-ray wavelength etc). Individual reflection profiles will overlap but the method does not attempt to allocate observed intensity to any specific Bragg reflections, instead it treats the profile as a whole. The quantity $S_y$ is minimised during the least squares refinement and is given by:

$$S_y = \sum_i w_i (y_i - y_{ci})^2$$ \hspace{1cm} 7.1

where $w_i = (y_i)^2$, $y_i$ is the observed intensity at the $i$th step and $y_{ci}$ the calculated intensity at the $i$th step. The sum is performed over all data points.

The least squares minimisation leads to a set of normal equations containing the derivatives of all the calculated intensities, $y_{ci}$, with respect to each of the adjustable parameters, which are then solved by an inversion of the normal matrix. This solution is performed iteratively; shifts are then applied to the initial parameters in order to improve the model. Since the adjustable parameters and intensities are related non-linearly the starting model must be close to the correct model, otherwise the refinement will not reach an overall minimum. There are certain criteria of fit used to judge the refinements; the term used is designated the R-weighted pattern or $R_{wp}$ value, which is given by

$$R_{wp} = \left\{ \frac{\sum_i w_i[y_i(\text{obs}) - y_i(\text{calc})]^2}{\sum_i w_i[y_i(\text{obs})]^2} \right\}^{1/2}$$ \hspace{1cm} 7.2
where \( w_i \) is defined as above, and \( y_i(\text{obs}) \) and \( y_i(\text{calc}) \) are the observed and calculated intensity at the \( i \)th reflection respectively.

Another statistic calculated during a typical refinement cycle is the ‘goodness of fit’, \( \chi^2 \), which is given by:

\[
\chi^2 = \left\{ \sum w_i[y_i(\text{obs}) - y_i(\text{calc})]^2 \right\} \frac{1}{(N_{\text{obs}} - N_{\text{var}})}
\]

where \( N_{\text{obs}} \) is the number of data points and \( N_{\text{var}} \) the number of variables in the fit. Should a perfect fit between the observed and calculated data be obtained then the value of \( \chi^2 \) will be equal to one. A fit with a value of \( \chi^2 \) less than four is considered good enough for publication for data taken on SXD.

### 7.7 Results and discussion

Previous neutron diffraction studies had determined the thermally-induced changes in crystal structure for aspirin. In order to obtain good control studies, consecutive crystal structures were obtained at 100 K, 200 K and 300 K both in the presence and in the absence of microwave radiation. In the absence of the microwave radiation, the observed ADPs were consistent with those obtained using conventional neutron diffraction.

The ADPs (Figure 7.8) obtained under microwave irradiation were less straightforward to explain. There was a clear increase in the vibrational motion of the atoms, most notably at instrument temperatures of 100 K and 200 K, where the structure corresponds to those observed at some several tens of Kelvin higher. The structure obtained at 300 K, however, was consistent with that obtained conventionally. It is probable that the microwaves were coupling with the vibration of the bridging protons. However, this energy was repartitioned through the molecule in times corresponding to a few tens of vibrations (<10^{-11} seconds), several orders of magnitude less than that required for one cycle of the microwave field.
(approximately $10^{-9}$ seconds). However, this still does not explain the variation in the observed temperature differences. One possible explanation could be that the uniform heating effect of the microwaves over this temperature range is not uniformly matched by the cooling efficiency of the cryostat through the sample pin.

Figure 7.8 - Comparison of ADPs in aspirin at 100K, showing the effect of microwave irradiation. 
(left) microwaves off (right) microwaves on
7.8 Conclusions
This chapter has shown that the apparatus designed for this experiment can be used to apply a microwave field across a single crystal and that the crystal can be probed in situ using neutrons to determine its structure. This experiment will provide the basis for similar studies on the relaxation processes in proteins, where the lower frequency (<10^9 Hz) of some large-scale vibrations shows some potential for non-thermal microwave effects.
Chapter 7 – Effect of Microwaves on H-bonding in Aspirin

7.9 Bibliography

11. [http://www.isis.rl.ac.uk/crystallography/sxd.htm](http://www.isis.rl.ac.uk/crystallography/sxd.htm)
Chapter 8 – Cation Diffusion Studies in Beta Aluminas

8.1 Introduction

The experiment described in this chapter is complementary to the experiment performed on SXD located at the ISIS Facility (Chapter Seven). There has been much speculation that microwaves may have a “non-thermal” contribution to their heating properties. Particularly in the case of organic reactions heated with microwaves, the “non-thermal” effects reported have now been explained in terms of superheating of the solvent, which can result in rate enhancement of the reaction. In the solid-state, anomalous effects might be anticipated when there are relatively mobile ions present. A good example of such materials are solid electrolytes that are designed as ‘fast ion conductors’. Beta aluminas are fast ion conductors and so were chosen for this experiment.

Sodium $\beta^+$ alumina and silver $\beta^+$ alumina (Figure 8.1) are members of the family of nonstoichiometric aluminates and may be synthesised from the corresponding oxide and alumina. They have the general formula $(\text{Ag/Na})_{1+x}M_x\text{Al}_{1-x}\text{O}_{17}$ where $M = \text{Mg}^{2+}$, $\text{Ni}^{2+}$ or $\text{Zn}^{2+}$.

Figure 8.1 – Structure of $\beta^-$ alumina. The blue atoms show the position of the sodium and silver atoms in the alumina framework.
Both sodium and silver $\beta^+$ alumina are layered structures in which dense slabs with a spinel structure are bridged by oxygen atoms at widely spaced intervals. The conducting ions ($\text{Na}^+$ and $\text{Ag}^+$) populate the plane between the spinel slabs, but not all of the sites are occupied. As the temperature of the material rises the conducting ions become disordered in this conduction plane, and this disorder occurs over a broad range of temperature. $\beta^+$ alumina has the remarkable property of supporting the rapid diffusion of a large fraction of the cations in the periodic table. The divalent $\beta^+$ aluminas have provided new materials for use as batteries and sensors, whilst the trivalent $\beta^+$ aluminas have potential uses in optics, phosphors and lasers due to their ability to act as single crystal or powder hosts for lanthanide ions. Sodium $\beta^+$ alumina has a sodium ion conductivity at 300°C that is comparable to that of an aqueous sodium chloride solution, thus making it suitable for solid electrolyte batteries.\(^{2-4}\)

One aim of the experiment was to investigate whether or not microwaves enhanced cation diffusion in the fast ion conductors sodium $\beta^+$ alumina and silver $\beta^+$ alumina. To provide a contrast, the two conductors were also heated using conventional methods. The second aim of the experiment was to show that the apparatus can be used to heat a sample controllably \textit{in situ} using microwaves whilst a high resolution powder X-ray pattern of that material is collected.

\section*{8.2 Experimental background}

The $\beta$ alumina family have been used as solid electrolytes in for example sodium-sulphur batteries. The $\beta$-aluminas possess a very stable host lattice (Figure 8.1) and this consequently allows very precise examination of their ionic conductivities. At elevated temperatures (>300°C) the conductivity increases greatly as the sodium and silver ions are able to move through the host lattice more easily.
8.3 The instrument on experiment station 9.1 at the SRS

The in situ diffraction experiment was performed on station 9.1 at the SRS, Daresbury.

Station 9.1 houses a general purpose powder diffractometer facility, which can operate in either Debye-Scherrer or flat plate sample geometries. The typical wavelength range is between 0.4-1.7 Å. The instrument has a high angular resolution and a well-defined peak profile. It is possible to collect data at high and low temperatures and high-pressure phases may be studied using an image plate system (Figure 8.2).

The radiation source consists of a 5 T wiggler located 15 m from the tangent point and has an energy range of 7-30 keV. The instrument has two monochromators: a Si (111) channel-cut and a four-bounce Si (111). The beam has a maximum linear polarisation of 96%, but at present cannot be focussed. The geometry of the instrument is a vertically scattering, two-axis diffractometer with a curved image plate. The gonimometer can move through step sizes of 20 and ω = 1 mdegree.5
8.4 Microwave apparatus

A commercial 0-1 kW variable power microwave source (ASTeX 5-1000) was used to generate microwaves of frequency 2.45 GHz, which were delivered to the sample via a flexible 200 W co-axial cable. The apparatus was designed so as to enable rapid and convenient switching between conventional to microwave heating to be as simple and convenient as possible. The apparatus also ensured that the X-rays could penetrate the sample easily and consequently be detected by the goniometer, but at the same time did not allow microwaves to leak out (Figure 8.3).

![Figure 8.3](image)

*Figure 8.3 – (Left) Shows the microwave co-axial cable (black) and Al foil X-ray window.*

*(Right) Shows the heatgun and insulated tube used during the conventional heating.*

The apparatus was machined in stainless steel and had a 180° rectangular section cut out directly above the sample, to act as the X-ray window. However, to ensure that microwaves did not leak out, the window was blocked with a 10 μm thick film of aluminium foil. The foil was thick enough to stop microwave leakage, but not thick enough to affect the detection of the scattered X-rays. The sample was mounted on a 30 mm diameter rod of a machinable ceramic (*Macor*). This ceramic is transparent to
microwaves, but is thermally conducting, thus ensuring that the material is heated directly by the microwaves and not by thermal conduction through the sample holder. The macor support was machined to provide a flat plate geometry suitable for this diffractometer, the sample area 25 x 15 mm.

Microwaves were introduced to the sample cavity by means of a $\frac{\lambda}{4}$ (30 mm) long antenna connected to a co-axial feedthrough, to the base of the cavity. A heat gun was used to heat the sample conventionally, and an aperture perpendicular to the antenna allowed an hot air gun (Steinel HG 4000 E, 1750 W) to be pass heated air over the sample during course of the experiment. The temperature of the heat gun may be set at any temperature in the range of 25-600 °C. For both the conventional and microwave heating experiments the inside of the apparatus was insulated using furnace lagging in order to minimise heat loss to the surroundings and to protect the goniometer.

8.5 Experimental procedure

Two experiments were performed. The first using sodium $\beta^+$ alumina and the second with silver $\beta^+$ alumina; the experimental procedure was the same for both materials.

8.5.1 Conventional heating experiments

During these experiments only the heat gun was using to heat the samples during data collection. The samples were mounted onto the Macor sample plate and the aluminium foil window was closed. The heat gun was then set at 300°C and the apparatus and the sample were allowed to heat to the desired temperature; this took approximately 10 minutes. After this equilibration period data were collected, see Section 8.5.3. The temperature was monitored using a fluoro-optic thermometer in contact with the sample surface. This ensured that the temperature was measured exactly at the point of diffraction.
8.5.2 Microwave heating experiments

During these experiments a heat gun was used to provide a constant thermal background, whilst the microwave generator was used to supply a background of microwaves. This ensured that the two experiments were as similar as possible to allow a valid comparison of the results to be made. The samples were mounted onto the Macor sample plate and the aluminium foil window was closed. The microwave power was set at 50 W for the duration of the data collection. Again, an equilibration period of 10 minutes was allowed before data collection began.

8.5.3 Data collection

The data collection for the two sets of experiments was set as shown in Table 8.1.

<table>
<thead>
<tr>
<th>2θ range</th>
<th>5-50°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Omega</td>
<td>Fixed</td>
</tr>
<tr>
<td>Step size</td>
<td>0.01 θ</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.0 Å</td>
</tr>
<tr>
<td>Time per step</td>
<td>2 seconds</td>
</tr>
</tbody>
</table>

Table 8.1 – Diffractometer settings.

These settings allowed high resolution data to be collected in approximately 3.5 hours.

8.6 Data refinement

After the data had been collected it was normalised and corrections were made to allow for the decay of the synchrotron beam radiation. The program PODSUM was used for this purpose. The data were refined using the Rietveld refinement method. This was performed using the refinement software package GSAS (general structure analysis system). This method of refinement was described previously in Chapter seven.
8.6 Results and discussion

Examination of the thermal parameters using GSAS showed that the samples did heat (modestly) with microwaves.

For comparable temperatures there was no obvious difference between conventional and microwave heating (see Figures 8.4 – 8.7).

Figure 8.4 – PXRD of silver β” alumina heated to 183°C.
No microwave field applied.

Figure 8.5 – PXRD of silver β” alumina heated to 183°C.
50 W microwave field applied.
Figure 8.6 – PXRD of sodium \( \beta'' \) alumina heated to 250°C. No microwave field applied.

Figure 8.7 – PXRD of sodium \( \beta'' \) alumina heated to 250°C. 50 W microwave field applied.

The Rietveld analysis identified a major problem with the data. The strongest reflection in at least one data set was split in a manner such that it cannot be indexed on any of the known versions of the cell plus all likely distortions. This means that the current data sets cannot be refined. Satisfactory resolution will require single crystal data obtained on a high-resolution diffractometer. The peak splitting is too small to be seen on a standard laboratory X-ray instrument; it is only at very high resolution that the problem becomes apparent.
8.7 Conclusions

High-resolution X-ray analysis has shown that there was no discernable difference for samples of sodium and silver $\beta^+$ alumina heated at 183 and 250°C either in the presence or absence of a 50 W microwave field. Due to the presence of a previously unreported peak splitting Rietveld analysis could not be adequately performed. A proposal has been submitted to the SRS, Daresbury in order to gain more beamtime in order to repeat this measurement but this will occur outside of the time of this thesis.
8.9 Bibliography

Chapter 9 - Microwave Reactions Under Pressure

9.1 Introduction
The application of pressure in the range of 1-20 kbar can strongly influence the rate and equilibrium position of many chemical reactions. Reactions where the volume of activation ($\Delta V^*$) is negative will be accelerated by the application of an external pressure and the equilibria are shifted toward the side of the products. Conversely, reactions where $\Delta V^*$ is greater than zero will be inhibited by pressure and the equilibrium point will be shifted toward the side of the reactants. Therefore, the application of high pressure may be particularly useful to control the course of a reaction and may be used to drive a reaction that is not feasible under standard conditions of temperature and pressure.

The experiments described in this chapter were performed in a microwave pressure vessel. This vessel designed by Dr. Gavin Whittaker of The University of Edinburgh has a radically new design which allows microwave pressure reactions to be performed at pressures of up to 70 bar. This new pressure cell allows microwave chemistry to be performed under pressure conditions not previously possible with current designs of vessel. The experiments in this chapter were among the first to be carried using this vessel.

9.1.1 Units of pressure
It should be noted that pressure (force per unit area) has the SI units of Pascals (Pa), where one Pascal is equal to one Newton per square metre ($\text{Nm}^{-2}$). However, in practice, in the laboratory, a number of other pressure scales may be employed, particularly units of bar, where one bar is equal to $10^5$ Pa. In the chemical literature, pressure is usually cited in MPa; thus standard atmospheric pressure is 0.1 MPa and 1000 bar = 1 kbar = 100 MPa. In this thesis the bar unit of scale will be used.
9.1.2 Theoretical background

We will only consider theory for reactions in the liquid state because this is the only type of phase in which reactions were performed. Two viewpoints of pressure theory can be used by chemists to explain and predict the effect of pressure on a chemical reaction, namely thermodynamics, and the applications of thermodynamic principles within the absolute reaction rate (kinetic) theory. Pressure can affect either the equilibrium constant, \( K \), \( (\Delta G^0 = -RT\ln K) \) for the reaction, or the free energy of activation \( (\Delta G^\dagger) \). If pressure causes an increase in the magnitude of \( K \), or reduces \( \Delta G^\dagger \), the reaction will have a greater yield or a faster reaction rate respectively. These effects come about due to the differing pressure effects on the chemical potentials of the reactants and the products (equilibrium), or the reactants and the transition state (kinetics). When considering the effect of pressure on such quantities it is common to then consider the volume of one mole of the initial state, the transition state and where appropriate, the product state. For a reaction where the transition state volume is smaller than the initial state volume the reaction will be accelerated with pressure. Also, if the product state and the transition states have different volumes, pressure will induce a change in the position of equilibrium. The volumes of these states are considered as follows.

The volume of a chemical species in solution is different to that of the pure chemical species. As the volume per mole can be calculated from the density then the partial molar volume \( (V_{A,m}) \) for the chemical species \( A \) can be given by

\[
V_{A,m} = \frac{\delta V}{\delta n_A}_{PT,n_B}
\]

where the partial derivative signifies the change of volume \( V \) when the number of moles of \( A \) \( n_A \) is increased in a binary system (\( A \) and \( B \) present). This change occurs at constant temperature \( T \), pressure \( P \) and the number of moles of \( B \) \( n_B \). The partial molar volume can be thought of as the effective volume per mole of a species when its intrinsic volume is modified by the influence of solvation.
The volume of activation ($\Delta V^\ddagger$), is defined as the difference between the partial molar volumes of the transition state $\bar{V}_{TS}$ and the initial state $\bar{V}_{IS}$

$$\Delta V^\ddagger = \bar{V}_{TS} - \bar{V}_{IS}$$  \hspace{1cm} (9.2)

$\bar{V}_{TS}$ cannot be measured directly, it can only be obtained if the volume of activation can be measured and the partial molar volume(s) of the reactant(s) are either known or can be measured. Kinetic measurements at several pressures lead to the determination of $\Delta V^\ddagger$, since the rate constant for a reaction and $\Delta V^\ddagger$ are connected by the expressions

$$\left(\frac{\delta \ln k}{\delta P}\right) = -\frac{\Delta V^\ddagger}{RT}$$  \hspace{1cm} (9.3)

$$\ln k = \ln k_0 - \left(\frac{\Delta V^\ddagger}{RT}\right)_P$$  \hspace{1cm} (9.4)

where $k$ and $k_0$ are the rate constant at pressure $P$ and at a pressure of one bar respectively and $R$ is the ideal gas constant. If a plot of $\ln k$ against $P$ is linear then equation 9.4 (the integrated form of equation 9.3) is valid and $\Delta V^\ddagger$ is independent of pressure. This is often found to be the case and curvature of this dependency is not observed when the pressure is greater than 1.5 kbar. To avoid complications of non-linearity, fitting procedures and interpretation of the pressure dependence of $\Delta V^\ddagger$, most experiments designed to obtain this parameter use a pressure range no higher than 2 kbar. The form of equation 9.4 allows a negative value of $\Delta V^\ddagger$, which comes from an increase in the rate of reaction with pressure. It is this region that is of particular interest for chemists who employ pressure to modify chemical reactions. Diels-Alder condensations and ligand transfer reactions in metal complexes are examples of reactions that can be enhanced by increasing pressure as they have negative volumes of activation. If the rate of reaction is independent of pressure then $\Delta V^\ddagger$ is equal to zero and if the reaction is inhibited by pressure then $\Delta V^\ddagger$ is positive (see Figure 9.1).
For many reactions $\Delta V^e$ is rarely larger than 30 cm$^3$ mol$^{-1}$. This value corresponds to a rate acceleration or inhibition of a factor of three and a half times between atmospheric pressure and a pressure of 1 kbar.$^5$ Consequently, it is often easier (and cheaper) to increase the temperature of a reaction, rather than the pressure for purely practical reasons as it is easier. It should be noted that the effects described here will be very small in the experiments considered in this chapter.

9.2 Apparatus
The apparatus cannot be fully described here as it is currently undergoing a patent application.$^6$ This thesis, under patent law, is considered to be the public domain and so would invalidate the current patent application should the details of the vessel be published here, so we will merely outline its construction. The new vessel allows microwaves to enter the cavity directly, with the reaction vessel also acting as the pressure vessel. As the cavity has a dual purpose it can be made of metal which has been designed to withstand very high pressures. The vessel has been pressure tested to 250 bar and has been used experimentally to a pressure of 70 bar to produce supercritical acetone and methanol.

High pressure vessels are usually made of metal as opposed to polymers/ceramics as they are very strong and is more resistant to extremes of temperature and pressure. Metals (such as stainless steel) also tend to be chemically inert and so will not react with the reagents. An example of a common high pressure vessel is the stainless
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steel/PTFE bomb. The vessel has thick walls made of stainless steel. The reaction mixture is placed inside a PTFE container that is then closed and put inside the steel vessel. The vessel is then screwed shut and placed in a muffle furnace. The vessel has a blast seal to allow the vessel to lose pressure safely should the vessel fail. This sort of vessel can reach pressures of 25 bar and temperatures of approximately 240°C and tend to be a reliable and safe way to reach elevated conditions of temperature and pressure in the laboratory.

This design of pressure vessel is not suitable for use with microwaves. Microwaves couple with metals and so placing a metal pressure vessel in the path of a microwave field would be dangerous due to arcing and scattering of the electromagnetic field. Previous microwave pressure vessels have been made out of PTFE, which is transparent to microwaves; such vessels allow microwave penetration whilst remaining pressure tight. However, very high pressures cannot be reached as PTFE tends to deform at temperatures greater than 250°C and at very high pressure and so this type of vessel can fail. The Fischer-Porter tube has also been used to obtain elevated pressures in the presence of a microwave field (Figure 9.2).

A Fischer-Porter tube was made up of a thick walled silica test tube with a screw top. The screw top has two openings, one to a safety value and one to a pressure transducer, which was linked to the P.C. by a control cable. The tube was covered in plastic to absorb the force of an explosion should the tube fail. The sealed tube was

Figure 9.2 – Diagram of a Fischer-Porter tube used for microwave reactions at moderate pressure.

A Fischer-Porter tube was made up of a thick walled silica test tube with a screw top. The screw top has two openings, one to a safety valve and one to a pressure transducer, which was linked to the P.C. by a control cable. The tube was covered in plastic to absorb the force of an explosion should the tube fail. The sealed tube was
lowered into the waveguide where it was held in place by a simple clamp arrangement. The microwave power was increased manually until the desired pressure was reached. The pressure was monitored using the P.C. control software and microwave pressure LED display. This apparatus could be used up to a pressure of 15 bar, but it failed on several occasions.

9.3 Experimental procedure

From this point it may be assumed that the new design of pressure vessel was used in the experiments described. A variety of inorganic and organic reactions were performed; the general experimental procedure is described below, but each reaction is described in detail during the following Sections.

After the reaction mixture was added to the pressure vessel, it was sealed and the microwave applicator was then attached, as was the cable connecting the P.C. to the pressure transducer. The entire apparatus was then lowered into a cylindrical steel blast tube and wadding was then placed on top of the apparatus to keep the vessel in place during the reaction and to act as a blast absorber. The vessel and blast tube was located in a fume cupboard. The microwave power was increased manually until the desired pressure was reached. The pressure was monitored using the P.C. control software and microwave pressure LED display.

Once the reaction time had elapsed the microwave power was switched off and the vessel was allowed to reach ambient pressure and temperature, reaction time and microwave power were controlled manually. Typically, this took approximately 15 minutes. Once the pressure vessel had cooled and reached approximately atmospheric pressure, it was opened and the contents were filtered under vacuum using a Büchner funnel and flask. The solid collected in this manner was then washed with a small volume of cold solvent. In some instances the product was a liquid and was treated accordingly. The products were then submitted for chemical analysis. Analysis methods used were NMR, CHN, mass spectroscopy and where appropriate PXRD. This experimental procedure was applicable for all of the reactions performed here.
The first test reaction involved the substitution of reactive complexes of Ru$^{3+}$ and Rh$^{3+}$, and were chosen because they are kinetically inert due to their electronic configuration (d$^6$). In order for these ions to react they require extreme conditions such as high temperature or pressure. Once activated, the ligands (Figure 9.3) then act as thermodynamic sinks which then help to drive the reaction to completion. Chelation of 1, 4, 7-trithiacyclononane (9S3) does not require any conformational changes to take place in the ligand the ring as the lowest conformation of the ring is one in which the sulphur lone pairs point to a single location resulting in the sulphur 3$p^4$ orbitals bending towards the metal ion when bonding occurs. This effect does not occur for the ligand 1, 4, 8-trithiacyclodecane (10S3) as this ligand can change its conformation by puckering the ring allowing overlap of the metal-ligand orbitals without them having to bend. Thus we performed the following reactions.

![Figure 9.3](image)

**Figure 9.3** – (a) cyclooctadiene, (b) 1, 4, 7-trithiacyclononane and (c) 1, 4, 8-trithiacyclodecane

### 9.3.1 Reaction of 1, 4-cyclooctadiene (cod) with RhCl$_3$.3H$_2$O

RhCl$_3$.3H$_2$O (0.26 g: 1.24x10$^{-3}$ M) and cyclooctadiene (cod) (0.2 ml: 1.63x10$^{-3}$ M) were dissolved in 10 ml of a 4:1 mixture of ethanol and water in a beaker. The mixture was then transferred to the pressure vessel. The reaction mixture was then heated for 3 minutes at 15 bar pressure, with a microwave power between 500-600 W. It was noted that the reaction mixture had changed colour from a dark orange/red solution to a yellow solid (yield = 40%) which was collected by Büchner filtration and was submitted for analysis.$^7,^8$
9.3.2 Reaction of 1, 4, 7-trithiacyclononane (9S3) with RhCl₃·3H₂O

RhCl₃·3H₂O (0.13 g: 6.21x10⁻⁴ M) and 1, 4, 7-trithiacyclononane (9S3) (0.08 g: 4.44x10⁻⁴ M) were dissolved in 10ml of methanol in a beaker. The mixture was then transferred to the pressure vessel. The reaction mixture was then heated for 45 minutes at 20 bar pressure, the microwave power of 200 W. The reaction mixture was then collected by Büchner filtration in order to remove the solid waste product (Ru(9S3)₂²⁺), the filtrate was a yellow colour. A saturated solution of NH₄PF₆ in methanol was added to the filtrate. A white precipitate formed (yield = 60%) which was collected by Büchner filtration and was submitted for analysis.⁸,⁹

9.3.3 Reaction of 1, 4, 8-trithiacyclodecane (10S3) with RhCl₃·3H₂O

RhCl₃·3H₂O (0.13 g: 6.21x10⁻⁴ M) and 1, 4, 8-trithiacyclodecane (10S3) (0.25 g: 1.29x10⁻⁴ M) were dissolved in 10ml of methanol in a beaker. The mixture was then transferred to the pressure vessel. The reaction mixture was then heated for 45 minutes at 20 bar pressure, at a microwave power of 200 W. The reaction mixture was then filtered under suction in order to remove the solid waste product (Ru(10S3)₂²⁺), the filtrate was a yellow colour. A saturated solution of NH₄PF₆ in methanol was added to the filtrate. A white precipitate formed (yield = 65%) which was collected by Büchner filtration and was submitted for analysis.⁸,⁹

The second test reaction involved the synthesis of a sterically hindered ester and the synthesis of an ether. Both reactions are difficult to perform without the going through a variety of highly reactive intermediates (such as acid chlorides) but at high pressures the reactions should occur readily.

9.3.4 Reaction of 2-bromoethyl benzene with methanol

PhCH₂CH₂Br (0.33 g: 1.76x10⁻³ M) was dissolved in 10 ml of methanol and water in a beaker. The mixture was then transferred to the pressure vessel. The reaction mixture was then heated for 3 minutes at 15 bar pressure and the microwave power of 400-600 W. It was noted that the reaction mixture had formed two immiscible layers; the ether layer was extracted using DCM, dried with MgSO₄ and then rotary evaporated to give an acrid oil which was submitted for analysis.
9.3.5 Reaction of 2, 4, 6-trimethyl benzoic acid with acidic methanol

(CH$_3$)$_3$(Ph)COOH (0.23 g: 1.4x$10^{-3}$ M) was dissolved in 10 ml of methanol containing a few drops of H$_2$SO$_4$ in a beaker. The mixture was then transferred to the pressure vessel. The reaction mixture was then heated for 3 minutes at 15 bar pressure, at a microwave power of 400-600 W. It was noted that the reaction mixture had formed two immiscible layers; the ester layer was extracted using DCM, dried with MgSO$_4$ to give a green liquid (yield = 50%) which was submitted for analysis.

![Diagram](image)

Figure 9.4 – Organic reaction products for (a) 9.3.4 and (b) 9.3.5

9.4 Results and discussion

9.4.1 Reaction of 1, 4-cyclooctadiene (cod) with RhCl$_3$.3H$_2$O

9.4.1.1 CHN analysis

The theoretical proportions of carbon, hydrogen and nitrogen were calculated and the sample was submitted for analysis. The following result was obtained.

Expected  C 39%, H 4.9%, N 0%
Actual    C 38.36%, H 4.57%, N 0%

This analysis shows that the desired product was formed during this reaction.

9.4.1.2 Mass spectroscopy

Expected  m/z (FAB-MS) 494 [(M+H)$^+$]
Actual    m/z 493 [Rh(cod)Cl]$_2$, 457 [Rh(cod)$_2$]Cl, 348 [Rh(cod)]Cl

Several fragments of the product were identified in the spectrum, suggesting that the product for this reaction had been formed.
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9.4.1.3 NMR
The spectrum consisted of a singlet at 4.21 δ corresponding to the “alkene” CH protons, a multiplet at 2.45-2.52 δ corresponding to CH₂ and a multiplet at 1.67-1.79 δ corresponding to CH₂. The multiplets were thought to correspond with the axial or equatorial protons, although an absolute assignment could not be made.

Therefore, the product was shown to be [Rh(cod)]₂.

9.4.2 Reaction of 1, 4, 7-trithiacyclononane (9S3) with RhCl₃·3H₂O

9.4.2.1 CHN analysis
Expected C 19.2%, H 3.2%, N 0%
Actual C 19.05%, H 3.26%, N 0%
This analysis shows that the desired product was formed during this reaction.

9.4.2.2 Mass spectroscopy
Expected m/z (FAB-MS) 753 [(M+H)⁺]
Actual m/z 607 [Ru(9S3)₂][PF₆], 460 [Ru(9S3)₂]
Several fragments of the product were identified in the spectrum, suggesting that the product for this reaction had been formed.

9.4.2.3 NMR
The spectrum consisted of a multiplet at 2.87-2.877 δ corresponding to the three groups of symmetrical -CH₂CH₂- protons.

Therefore, the product was shown to be [Ru(9S3)₂][PF₆]₂.

9.4.3 Reaction of 1, 4, 8-trithiacyclodecane (10S3) with RhCl₃·3H₂O

9.4.3.1 CHN analysis
Expected C 21.6%, H 3.6%, N 0%
Actual C 21.12%, H 3.59%, N 0%
This analysis shows that the desired product was formed during this reaction.
9.4.3.2 Mass spectroscopy

Expected m/z (FAB-MS) 781 [(M+H)⁺]
Actual m/z 635 [Ru(10S3)₂][PF₆], 489 [Ru(10S3)₂]

Several fragments of the product were identified in the spectrum, suggesting that the product for this reaction had been formed.

9.4.3.3 NMR

The spectrum consisted of a singlet at 2.08 δ corresponding to the middle CH₂ in the -CH₂CH₂CH₂- bridge and a multiplet at 2.86-2.87 δ corresponding to the -CH₂CH₂- bridges.

Therefore, the product was shown to be [Ru(10S3)₂][PF₆]₂.

9.4.4 Reaction of 2-bromoethyl benzene with methanol

9.4.4.1 CHN analysis

Expected C 79.4%, H 8.82%, N 0%
Actual C 42.42%, H 3.89%, N 0%

This analysis shows that the desired product was not formed during this reaction.

9.4.4.2 Mass spectroscopy

Expected m/z (EI-MS) 136 [(M)⁺]
Actual m/z 184/186 PhCH₂CH₂Br, 105 PhCH₂CH₂, 91 PhCH₂, 77 P

Several fragments of one of the reactants were identified in the spectrum, suggesting that the product for this reaction had not been formed.

9.4.4.3 NMR

The spectrum consisted of a multiplet at 7.24-7.44 δ corresponding to the aromatic protons, a triplet at 3.58-3.66 δ corresponding to the CH₂ protons adjacent to the bromine atom and a triplet at 3.18-3.25 δ corresponding to the CH₂ protons adjacent to the phenyl ring.
Therefore, the product was shown to be PhCH₂CH₂Br. This route to the ester is not the favoured synthetic approach to the compound; other better routes can be used, such as going via the acid chloride, tend to react more easily. However, this route was chosen as it was expected to be favoured by using high pressures.

### 9.4.5 Reaction of 2, 4, 6-trimethyl benzoic acid with acidic methanol

#### 9.4.5.1 CHN analysis

**Expected**  
C 74.2%, H 7.9%, N 0%

**Actual**  
C 71.07%, H 7.5%, N 0%

This analysis shows that the desired product was formed during this reaction.

#### 9.4.5.2 Mass spectroscopy

**Expected**  
m/z (EI-MS) 181 [(M)⁺]

**Actual**  
m/z 178 (CH₃)₃PhCOOMe, 119 (CH₃)₃Ph, 164 (CH₃)₃PhCOOH

Several fragments of the product were identified in the spectrum, suggesting that the product for this reaction had been formed.

#### 9.4.5.3 NMR

The spectrum consisted of two singlets at 7.24 and 6.88 δ corresponding to the aromatic protons, a singlet at 4.14 δ corresponding to the protons on the methoxy group and two singlets at 2.4 and 2.29 δ corresponding to the protons of the methyl groups and the benzene ring.

Therefore, the product was shown to be (CH₃)₃PhCOOMe.

The complementary reaction using iso-propanol instead of methanol was attempted, but no reaction occurred. This was most likely due to steric hindrance between the bulky iso-propyl and the trimethyl benzoic groups.
9.5 Conclusions

This chapter has shown that the new design for the pressure vessel can be used over a wide range of pressures and can be used for a variety of reactions, both inorganic and organic. Since this work the current design of the vessel has been tested at pressures up to 250 bar and has been used experimentally up to 60 bar. Supercritical synthesis in acetone, carbon dioxide and ammonia are now feasible options for this vessel and experiments are planned to be carried out using such supercritical solvents.

The reactions described previously are usually performed at high temperature and require long reaction times. In the case of the reaction of cod with RhCl₃.3H₂O, heating under reflux for 18 hours gives a yield of 94%. Using microwaves the reaction time is only 3 minutes resulting in a yield of 40%. Despite the reduced yield, the use of microwaves results in a huge reduction in reaction time and in energy costs. Similar time and energy saving are noted for the other reactions.
9.6 Bibliography

6. Patent application number 9910065.3
Chapter 10 – Conclusions

10.1 Conclusions and Next Steps

The aim of this thesis was to investigate the interaction of microwaves with matter for a particular set of reactions, primarily formation and modification of metal oxides and oxy-hydroxides. These investigations required new apparatus to be designed and built to produce specific reaction environments. Sections of brass wave-guide were designed in order to perform solid and solution state reactions. The apparatus was also able to be adapted to perform the first in situ SANS experiment on iron oxide colloids. Other apparatus was made in order to apply a microwave field across a single crystal whilst neutron diffraction data was collected. A sample chamber incorporating a powder sample plate and co-axial cable was made in order to collect powder diffraction data from a sample in the presence of a microwave field. Finally, a novel design of microwave pressure vessel was used to perform microwave pressure reactions at pressures not yet attained through traditional pressure cell technology.

Mechanistic studies of the hydrothermal synthesis of iron oxide particles using the techniques SANS, SAXS and EXAFS have provided an insight into how these particles are formed from solution. SANS data has shown an evolution of particle size from 50 Å in the first 30 minutes to final particle size of 100 Å after 7.5 hours. However, the complementary SAXS data showed that the mean particle size was in the range of 250-300 Å. This apparent size discrepancy may be due to the difference in the heating methods for each experiment, and it would appear that under the reaction conditions we employed, nucleation was faster with microwave heating, and led to smaller particles. The EXAFS data determined that small particles of \( \alpha \)-Fe\(_2\)O\(_3\) were formed. Taken together, these results favour a mechanism in which the initial formation of small particles is followed by aggregation to produce larger particles. However, the precise evolution of the products was very sensitive to conditions and more work is required to obtain more consistent data and establish more firmly the mechanism for wider range of conditions. In the near future the first steps in this direction will be taken through further EXAFS experiment, and complementary TEM
measurements might prove very useful in determining more clearly the microstructure of the larger particles grown from solution.

The microwave-assisted diffusion reactions have shown that in some cases – for example insertion of cations into channeled oxides and oxyhydroxides of iron – diffusion is enhanced and reaction times are reduced compared to conventional means of heating. The results for diffusion into natural goethite did not yield the anticipated result, but diffusion of ions into synthetic iron and manganese systems was shown to have occurred. However, the host lattice must be thermally stable so that lattice does not collapse before the final product is formed. In the case of the iron systems, the host lattices tended to collapse to form the thermally stable product haematite before the reaction had finished. This led to mixed phases in the material as shown by PXRD. Through modification of the experiment conditions the presence of such mixed phases could be minimised although could not be completely removed. The manganese host lattice is thermally more stable and can be heated to higher temperatures before collapse. The main advantage of using microwaves was that the reaction could proceed in one step. Previous reactions to the product LiMnO₂ had required the synthesis of the intermediate material NaMnO₂. Obviously, reducing the numbers of steps in a reaction affords advantages in yield maximisation and time savings. Further work in this area could be in other microporous host systems such as zeolites, accelerating insertion or deinsertion of molecules in processes such as catalysis or extraction of template molecules used in their synthesis.

The two new pieces of in situ apparatus for applying microwaves across single crystal and powder samples during diffraction experiments have been shown to work effectively and opens the scope for analysing solid-state reactions in real time. Despite disappointing initial results, future beam-time should be able to elucidate the structural changes fully for both aspirin and beta alumina. The single crystal apparatus can be extended to problems of biological interest – for instance to investigate the influence of microwave irradiation on proteins, an important issue in trying to assess the effect of mobile phones on health. In the near future this work
will be extended to the specific case of the protein β-Lactoglobulin. This has been chosen as a starting point because it is a protein whose structure is well characterised, and on which *in situ* spectroscopic measurements have already been performed during irradiation. The powder diffraction apparatus could also be used for this kind of work, using careful powder profile refinement (Rietveld analysis) to model detailed structural parameters such as thermal parameters, which in turn provide an indication of the way that energy is partitioned in the molecule. Powder methods may also be used to follow the course of a reaction as a mixture of reactants are heated by microwaves – provided of course that the powder patterns of likely intermediates are already known and can therefore be used as structural fingerprints.

Finally, the new design pressure vessel has been tested and used at much higher pressures than other current designs of microwave pressure vessels. Although the reactions described here are conventional the vessel now allows for microwave reactions to be performed in media such as supercritical acetone, ammonia and carbon dioxide, and may open the door to effective, lower-energy routes to new materials – ‘greener’ chemistry both from the point of view of energy costs and some of the solvents that may be used.