In-vacuum and In-air Ion Beam Analysis Techniques for the Investigation of Diffusion in Materials

By

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Abstract

In-vacuo and in-air ion beam analysis techniques have been developed to investigate diffusion in materials at the University of Surrey 2MV Tandem accelerator. Following Energy calibration of the accelerator, two main systems were studied using these techniques.

Lithium intercalation into thin films of vanadium pentoxide was investigated using both nuclear reaction analysis and backscattering spectrometry in-vacuo. Energy loss techniques were used for both proton backscattering and the reaction $^7\text{Li}(p,\alpha)^4\text{He}$. Simulated annealing software enabled both data sets to be analysed simultaneously to give the Li profile.

An in-air scanning micro-PIXE technique was developed to investigate diffusion into cementitious materials. Internal and external normalisation methods for elemental diffusion studies have been developed, applied and compared. Both Chloride and Sulphate ingress in cement, mortars and concrete have been studied. Results were obtained both from samples prepared in the lab and from large core samples taken from concrete blocks exposed to a saline environment for 30years. Additional studies were performed both to compare results from scanning micro-PIXE and micro-XRF techniques and to compare results from an abraded small core. Another application of the technique is the study of chloride and heavy element distributions in paste, mortar and brick samples before and after electrochemical extraction methodologies. A CdTe detector was used for the first time with an external beam, to detect $K_\alpha$ X-rays induced from the heavy elements.
Dedication

I would like to dedicate this thesis to my father, my mother, my parents in law, my family members and to my beloved wife Rafah.
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Chapter One: Introduction

1.1 Ion beam analysis techniques

Ion beam analysis is the field of experimental physics that deals with a variety of interactions between energetic ions and the atoms and nuclei in a target. These interactions create inter alia characteristic X-rays or charged particles which can be detected to provide information about the target. To perform ion beam analysis, it is necessary to have a beam of charged particles of MeV energies and appropriate detectors.

1.2 Applying ion beam analysis techniques to study diffusion in materials

Ion beam analysis methods have been devised to study diffusion in materials [1]. Since they are classified as non-destructive, high precision quantitative and qualitative measurements can be obtained without any significant chemical or mechanical change to the sample. They offer spatial resolution in the range of 1 to 100 microns depending on the application and the analysis method used.

Diffusion profile information can be obtained by means of either a beam energy loss or a beam scanning technique [2]. In the first case, as the beam travels in the material it losses energy. This can be used to give extremely valuable information about the diffusion concentration profile by the detection and energy measurement of either backscattered beam particles or any resultant charged particles produced in nuclear reactions. Kinematic calculations can then be performed to calculate the beam energy at which the scattering or nuclear reaction event occurred. The beam energy loss can then be used to determine a depth scale. The technique is used where the diffusion process takes place in thin films (nm to several μm thick).

If the diffusion occurs over long distances (i.e. a few mm), then the sample can be cut parallel to the diffusion direction and subsequently a beam can be raster scanned across it.
The products (usually induced X-rays, γ-rays or charged particles) from the interaction of the beam and an elemental component of the diffusant are detected. These can then be associated with the scan position to generate elemental maps and subsequently to obtain the diffusion profile. If the diffusion occurs over greater distances (several cm), then the scanning technique can also be used, doing a raster scan at one position then moving the sample a few mm to the next position. For instance, this procedure is performed to study chlorides and sulphates diffusion into cementitious materials exposed to saline environments.

1.3 The aims of this work

There are two main objectives of this work,

- To apply in-vacuo nuclear reaction analysis (NRA) and backscattering (BS) measurements to the investigation of Li intercalation in V$_2$O$_5$ thin films.
- To apply in-air scanning micro-PIXE measurements to the investigation of diffusion in cementitious materials.

In addition to this introductory chapter, this thesis consists of seven other chapters. In Chapter Two, ion beam analysis techniques, their applications, advantages and limitations are introduced. Chapter Three gives a brief description of the University of Surrey Ion Beam Centre experimental facilities. This includes the tandem accelerator and its beam lines. Chapter Four explains the basic principles of diffusion. The energy calibration of the tandem accelerator at the University of Surrey Ion Beam Centre is described in Chapter Five. NRA and BS measurements applied to the investigation of lithium intercalation profiles in vanadium pentoxide thin films are discussed in detail in Chapter Six, including the use of the novel IBA DataFurnace simulated annealing software [3]. In Chapter Seven an extended study of applying external scanning micro-PIXE to the investigation of diffusion in cementitious materials is described in detail. The last chapter (Chapter Eight) presents overall conclusions.
Chapter Two: MeV Ion Beam Analysis

Techniques Overview

2.1 Introduction

Ion Beam Analysis (IBA) techniques [4] depend on the interaction of energetic charged particles and matter. When a sample is bombarded with an energetic ion beam (in the MeV energy range), both elastic scattering and different atomic and nuclear processes occur leading to the possible emission of X-rays, charged particles, neutrons, and gamma rays. Detection of such events can be used, in conjunction with a focused mono-energetic incident beam or a focused scanning microbeam, to obtain information about the elemental composition of a target and the depth and areal distribution of elements.

IBA is a general term that involves several techniques such as Rutherford Backscattering Spectrometry (RBS), Nuclear Reaction Analysis (NRA) and Particle Induced X-ray Emission (PIXE). They can be used singly or in combination to obtain more information about the system being studied. Also they can be used with either a static mono-energetic beam or a scanning microbeam.

They combine the advantages of being non-destructive and quantitative. They can be applied [5] to analysis problems where elemental composition and depth information are required. The next section gives an overview of general terms used in the Ion Beam Analysis. A discussion of the IBA techniques used in this thesis is introduced.
2.2 Ion beam analysis techniques

2.2.1 Particle Induced X-ray Emission (PIXE)

When an electron from an electronic inner shell of an atom is removed leaving a vacancy, another electron from an outer shell fills this vacancy and a quantum of energy, equal to the energy difference between the two shells, is released at the same time. This quantum of energy, in the form of an X-ray, is characteristic of the atom and can be used to identify it. The inner core electron can be removed by means of the collision of an energetic charged particle as shown schematically in Figure 2-1. The production of characteristic X-rays is then called Particle Induced X-ray Emission (PIXE) and was first discovered by Johansson et al. in 1970 [6]. This technique is now well documented [7, 8].

As mentioned above, the production of characteristic X-rays is caused by electrons moving from one electronic shell to another. Characteristic X-rays are identified as (K, L, M,...) according to the electronic shell being filled with the electron from the outer shell and subscripted by (α, β, γ) in relation to that outer shell as is shown in Figure 2-2. It should be mentioned that K, L, M... shells are not mono-energetic but are each split into multiple subshells causing the X-rays to be split as well. The electron transitions, in which the production of characteristic X-rays occurs, is governed by quantum selection rules.

Solid state lithium drifted silicon (Si(Li)) detectors are widely used in PIXE spectroscopy due to their high efficiency and excellent energy resolution [9]. Elements with atomic numbers up to Z=50 are detected through their K X-rays and heavier elements are measured using their L X-ray lines because their K X-ray lines have too high energy to be detected by a Si(Li) detectors. Its efficiency becomes lower at high X-ray energies due to their incomplete stopping in the Si crystal. CdTe detectors can then be used (see chapter 3) in association with Si(Li) detectors [10]. Very low X-rays (from light elements) are difficult to detect as they are absorbed in the detector window (usually Be).
The energy range of the detector can be extended, using a thin composite polymer window, down to carbon X-rays.

Figure 2-1: The basic principle of PIXE

Figure 2-2: X-ray characteristic transitions
PIXE identifies elements by the emission of their characteristic X-rays and it can be used for quantitative analysis by measuring the number of emitted X-rays at a particular angle. The basic formula used in PIXE quantitative analysis for thin target is a simple product of several quantities and is given by Equation 2-1 [8]:

\[ N = nI\sigma_p \Omega T \varepsilon \]

Equation 2-1

Where:

- \( N \): The total number of counts in the photopeak in the energy spectrum produced by X-ray interactions with the detector per unit time.
- \( n \): The total number of atoms of the element being studied per unit area of the sample.
- \( I \): The total number of charged particles in the beam per unit time.
- \( \sigma_p \): The X-ray production differential cross-section.
- \( \Omega \): The solid angle subtended by the detector.
- \( T \): The transmission factor of the X-rays through the filter between the sample and the detector.
- \( \varepsilon \): The photopeak efficiency of the detector at the X-ray energy.

For a thick target the analysis is complex due to the change of the energy of the particles whilst they penetrate the sample and hence the change of the X-ray production cross-section, which is a function of particle energy. Furthermore, X-rays produced at depth have a possibility of being absorbed in the sample rather than being detected by the X-ray detector. These two factors must be taken into account in the calculations when doing PIXE on thick targets (TT-PIXE) [11] by determining the elements with the largest concentration in the sample (matrix elements).

The typical method of estimating the concentration of an element in a sample using PIXE is to compare the yield with that of a standard material containing the same elements with known concentrations. The absolute method, which involves the fitting of a model PIXE spectrum to the experimental one, is used to obtain concentrations in a standardless
analysis using a database containing the energies and relative intensities of the K and L X-rays for all elements and relying on a complex computer codes such as GUPIX [12].

The main origin of the background in the PIXE spectrum is due to the bremsstrahlung (braking) radiation emitted by either the projectiles or the secondary electrons produced by ionization when they undergo slowing down in the presence of Coulomb field of the nucleus. The electron contribution is more significant. The best way to minimise this radiation is by placing a suitable filter in front of the X-ray detector window.

Another source of background arises because of the charge built up on thick insulating samples, i.e. the beam spot position charges to a high positive voltage. This causes the electrons to be accelerated towards this region and gives rise to a bremsstrahlung background. Coating the insulating sample by a thin conducting layer of carbon or gold can minimize this effect.

PIXE has great advantages [13] since it is multi-elemental, highly sensitive, capable of analysing very small samples, quantitative without standards, fast, non-destructive and less costly. It has been used and applied in many applications of elemental analysis in fields such as medicine, zoology, geology, atmospheric aerosols and archaeology.

2.2.1.1 PIXE comparison with other X-ray based analytical techniques

Other well known analytical methods can be classified as X-ray detection techniques based on the same detection principle of PIXE but different in the ionisation mechanism. They are Electron Probe Micro Analysis (EPMA) [14] and X-ray Fluorescence Spectroscopy (XRF) [15], where the ionisation is caused by electrons or a beam of X-ray, respectively. The first technique has the advantages of being cheaper than PIXE. The electron beam can be focused to ~50Å. A disadvantage of EPMA is mainly the production of a high level of background in the X-ray spectra due to primary electron bremsstrahlung. Also the range of electrons in the sample is very short compared with the charged particle beams making this method appropriate only for thin samples. Also for
thick samples the electron beam is broadened strongly due to the scattering of the electrons.

Like EPMA, the second technique (XRF) also has the advantage of being more readily available than PIXE. Special attention has been paid here to the XRF technique to compare it with the PIXE technique since they have both been used to investigate sulphate and chloride diffusion in cementitious materials. The next section is introduced for this reason.

2.2.1.2 PIXE and XRF technique comparison

X-ray Fluorescence Spectrometry (XRF) is widely used for the quantitative elemental analysis of environmental, geological, biological, industrial and other applications. XRF has the advantage of being non-destructive, multi-elemental, fast and cost-effective. Furthermore, it provides a fairly uniform detection limit across a large portion of the periodic table [16].

The X-ray fluorescence principle is similar to that of PIXE. An inner shell electron is excited by an incident photon in the X-ray region (instead of an energetic charged particle in the case of PIXE). During the de-excitation process, an electron moves from a higher energy level to fill the vacancy. The energy difference between the two shells appears as an X-ray, emitted by the atom.

In the past, the fact that the X-rays are difficult to focus and raster scan on the sample made (XRF) less suitable for obtaining two-dimensional elemental maps. The production of intense narrow X-ray beams is achieved nowadays by passing the X-Ray from the generator through a small aperture usually in the range of a few millimetres down to a few tens of micrometres in diameter. The developments in X-ray optics [17] have led to the generation of narrow X-Ray beams, ranging from 1 mm down to 10 μm.
In the XRF technique the sample is rapidly moved (i.e. scanned) through the X-Ray beam and XRF spectra are continuously read from the detector and correlated to a particular position on the sample.

Many investigators have been interested in comparing PIXE and XRF techniques [18, 19]. Willis [20] has given a comprehensive comparison between PIXE and XRF. Advantages and disadvantages of both methods are introduced. Both of them share the advantages of being non-destructive, multi-elemental and capable of ppm detection limit with no standards. The advantages of both techniques are discussed below.

The advantages of XRF are:

- The cost of running an XRF machine is much cheaper than PIXE. The XRF system is smaller in size and easier to be handled.
- XRF has more sensitivity than PIXE for heavy elements since the X-ray production cross-section in XRF is higher for heavy elements. This positive effect can be accompanied with the low self-absorption of high energy emitted X-rays to make this technique even better for heavy elements.
- XRF is more suitable than PIXE for studying thick samples since the penetration depths are larger.
- Large scan areas can be performed to obtain whole sample elemental maps.

By contrast the advantages of PIXE are:

- The PIXE technique can be accompanied with other IBA techniques simultaneously to give more information about the sample being analysed.
- The X-ray production cross section for light elements is higher in PIXE than that in XRF. This balances the self attenuation of soft X-rays from light elements.
- PIXE is ideal for investigating thin samples (or to obtain information from the first few couple microns of the sample surface). This is due to the limited range of energetic charged particles in the sample.
- PIXE is more flexible in terms of sample preparation. This is mainly observed when using an external beam where the sample can be placed in air just opposite the beam exit window regardless of the size and the shape of the sample.
- Event by event data collection can be performed to produce data that can be replayed off line to produce new elemental maps and their corresponding spectra, selected for specific regions of the maps.

In conclusion, both techniques are complementary rather than competitive. Their usage depends on the samples and the application being studied.

2.2.2 Rutherford Backscattering (RBS) and Non-Rutherford Backscattering (N-RBS) Spectrometries

In 1908 Ernest Rutherford, together with Geiger and Marsden first investigated alpha particle scattering. The name Rutherford Backscattering (RBS) was derived from his name. RBS is based on the elastic scattering of highly energetic beam of ions from nuclei in a sample by pure Coulomb interaction. This is shown schematically in Figure 2-3. These backscattered particles can be detected using a silicon surface barrier detector.

To establish this technique, the classical elastic scattering of two rigid balls under the influence of the Coulomb force is considered. When an energetic charged particle of mass $M_1$ scatters elastically from a target nucleus $M_2$ (greater than $M_1$ in mass) at an angle $\theta$, the energy and momentum laws are preserved before and after the collision. Taking into account this fact one can predict the energy of the scattered particle after the collision via the so-called Kinematic Factor ($K$), which is the ratio between the energy of the projectile before and after the collision. It is given by Equation 2-2 [21],
\[
K = \frac{E_{\text{scattered}}}{E_{\text{incident}}} = \left[ \frac{1-(M_1/M_2)^2 \sin^2 \theta}{1+(M_1/M_2)} \cos \theta \right]^{1/2} + (M_1/M_2) \cos \theta
\]

Equation 2-2

K is characteristic of each nucleus and tabulated [22] for given angles and given incident particles. By determining the energy after scattering from the RBS spectrum at a known scattering angle and knowing the energy before the scattering, the existing elements in the sample can be determined using the tabulated values of K.

Introducing the concept of the Kinematic factor leads to the understanding of the capability of backscattering spectroscopy for mass resolution. By plotting K versus the scattering angle for C and O, for instance, using a proton and He beam respectively, it is clear from the Figure 2-4 that the energy difference between the particles scattered from C and O (scattered particle energy is proportional to K) is greatest at or near 180° (i.e. at backscattered angles).

Thus the detection of scattered particles at backward angles is required to obtain good mass resolution. The behaviour of K near 180° has given rise to the field of Backscattering Spectrometry (BS) [21]. The same graph shows also that the mass resolution is better if a projectile of large mass is used. He ions are often used, these backscatter from all elements with mass >4. If He is used as the energetic beam particle, elastic backscatters from H or He can only occur in the forward direction. A charged particle detector can be placed so that these forward particles can be detected and thus the light elements H and He can be measured using the complementary technique to BS with similar principle involved, called either Forward Recoil Spectroscopy (FRS) or Elastic Recoil Detection Analysis (ERDA) [23].
Energetic particle $M_1, E_0$

Target nucleus $M_2$

Charged particle Detector

Backscattered particle $M_1, E_1$

Figure 2-3: An outline of the backscattering process

Figure 2-4: Demonstrating the influence of the particle detection angles on the Kinematic factor and hence the mass resolution
The differential scattering cross section was introduced in RBS spectrometry to give a measure of the probability that an incident ion will be scattered into unit solid angle at a scattering angle $\theta$. It is given by Equation 2-3 [21]:

$$\frac{\partial \sigma}{\partial \Omega} = \left[ \frac{Z_1 Z_2 e^2}{4E} \right]^2 \frac{4}{\sin^4 \theta} \left[ \frac{1 - \left( \frac{M_1 \sin \theta}{M_2} \right)^2 + \cos \theta}{\sqrt{1 - \left( \frac{M_1 \sin \theta}{M_2} \right)^2}} \right]^2$$

Equation 2-3

Where:

- $Z_1$: the atomic number of the incident beam
- $Z_2$: the atomic number of the target atom
- $E$: the energy of the incident ion
- $M_1$: the mass of the incident ion
- $M_2$: the mass of the target atom
- $\theta$: the scattering angle
- $e$: the electron charge

The differential scattering cross sections for different elements $Z_2$ is tabulated [22] for a variety of target elements $Z_2$ and different energies. We can conclude from Equation 2-3 that $\frac{\partial \sigma}{\partial \Omega}$ is proportional to the square of the atomic number of the target $Z_2$ giving RBS more sensitivity for detecting heavy elements than light ones. Using heavy incident particles is better for the yield. Quantitative analysis can be achieved once the RBS spectrum is collected. The yield ($Y$) of the RBS spectrum is governed by $\frac{\partial \sigma}{\partial \Omega}$, the solid angle subtended at the target by the charged particle detector ($\Omega$), the total number of the atoms being studied in the target per unit area ($n$) and the total number of charged particles that hit the target ($N$). This can be illustrated in Equation 2-4:
If the scattering process takes place at energy in which the Coulomb barrier of the nucleus is exceeded by the energetic particle and the scattering is still elastic (i.e. no new products are induced), then the scattering is called \textit{non-Rutherford (elastic) scattering} (N-RBS or simply BS). This means that the Rutherford scattering is a special case of elastic scattering. Dealing with elastic scattering for quantitative measurements should be considered carefully since Equation 2-3 is not valid then. The scattering cross section is energy dependent. Scattering cross sections relative to Rutherford values are experimentally determined and tabulated \cite{24} and can be used for quantitative measurements.

Figure 2-5 illustrates how RBS/BS spectrometry can tell at which depth the atoms of a certain element are situated (i.e. elemental depth profiling). As the projectile particles travel through the sample to a depth “d” they lose energy due to the interaction with the electrons in the sample. This is translated into the RBS/BS spectra as follows: the long vertical edge in the spectrum in Figure 2-5 corresponds to ions scattered at the surface. Ions that penetrate deeper lose more energy and therefore their energy is lower and shifted to the left in the spectra. Thus the energy scale in the RBS/BS spectrum is a measure of the depth of the atoms in the sample whilst the yield scale corresponds with the quantity of these atoms at that depth.

Obtaining the depth scale can be achieved using tabulated stopping power and range equations \cite{25}. As an alternative, there are various commercially available programs for analysing RBS/BS data. The best one by far is in routine use at Surrey – the IBA DataFurnace \cite{26}. It is a code based on the simulated annealing algorithm \cite{3} that can rapidly, accurately and automatically extract depth profiles from the RBS/BS data (see chapter 6).
In conclusion, Backscattering Spectrometry has many features that make it an excellent analytical method. It is capable of obtaining multi-element depth concentration profiles, is fast and non-destructive. It has quantitative ability without need of standards and has high sensitivity. RBS/BS has several analytical applications especially in thin film analysis. Absolute thicknesses of thin films, coatings and surface layers (in atoms/cm²) can be obtained. Quantitative dopant profiles in semiconductors can be verified. RBS/BS is often used in combination with other IBA techniques to obtain more information about the system being studied.
Figure 2-5: Diagram of how an elemental depth profile can be obtained by collecting backscattered particles. The top figure shows two backscattering processes are taking place at the surface of a sample and the other at a given depth “d”. The bottom figure shows the corresponding spectrum and how the energy scale is translated into depth scale.
2.2.3 Nuclear Reaction Analysis (NRA)

When an incident particle hits a nucleus in an atom with sufficient energy to exceed (or tunnel through) the Coulomb barrier, either an elastic (i.e. non-Rutherford elastic scattering) or an inelastic interaction occurs. When an ion undergoes an inelastic reaction with the target, a rearrangement of the component nucleons take place leading to different product nuclei and particles. These particles can be charged particles, neutrons and gamma rays. Detecting these products gives extremely important qualitative and quantitative information about the sample in the Nuclear Reaction Analysis technique (NRA) [27, 28]. NRA is used for profiling light elements (where we have seen in section 2.2.2 that Backscattering does not usually occur) as a complementary technique to ERDA.

When a nuclear reaction takes place, an energy $Q$ (MeV) equal to the difference between the rest masses of the initial particles and the products is released. It called the Q-value of the reaction. If $M_1$, $M_2$, $M_3$ and $M_4$ are the masses (in MeV/c^2 units) of the incident particle, the target nucleus, the emitted particle and the residual nucleus respectively, then the energy released from the reaction is given by Equation 2-5:

$$Q = [(M_1 + M_2) - (M_3 + M_4)]c^2 \quad \text{(MeV)}$$

Equation 2-5

where $c$ is the velocity of the light. The Q-value can be positive (an exothermic reaction), negative (an endothermic reaction) or equal to zero in the case of compound elastic scattering, which is a special case of a nuclear reaction. When $Q$ is positive, the nuclear reaction can happen at any energy of the incident particle (with much decreased probability below Coulomb barrier). When $Q$ is negative the reaction does not happen unless the incident particle reaches or exceeds a minimum required energy, which is called the threshold kinetic energy.
Taking into account the conservation of the energy and the momentum and considering Figure 2-6, which represents a schematic drawing of a nuclear reaction, the kinetic energy $E_3$ of the detected particle $M_3$ is given by Equation 2-6 [29],

$$E_3 = \frac{E_i M_1 M_3}{(M_1 + M_3)^2} \left[ 2 \cos^2 \theta + \frac{M_4 (M_1 + M_3)}{M_3} \left( \frac{Q}{E_i} - 1 - \frac{M_1}{M_4} \right) + 2 \cos \theta \left( \cos^2 \theta + \frac{M_4 (M_1 + M_3)}{M_3} \left( \frac{Q}{E_i} - 1 - \frac{M_1}{M_4} \right) \right)^{1/2} \right]$$

Equation 2-6

Where $E_i$ is the energy of the incident particle and $\theta$ is the angle between the direction of incident beam and the emitted particle.

Figure 2-6: An outline of the nuclear reaction process
Detecting the emitted particles requires a surface barrier detector placed at an angle to the direction of the beam. This can be used to collect elastically backscattered particles at the same time. Obtaining the depth profile from NRA data can be achieved in similar way to that discussed for the RBS. Some reactions result in inverse kinematics at backward angles. A plot of the detected particle energy $E_3$, versus the energy of the incident beam $E_i$ is shown in Figure 2-7 for the case of the $^3\text{He}(\alpha,p)^4\text{He}$ reaction at a detection angle of $165^\circ$. The graph shows that the less the energy of the incident $^3\text{He}$ the more the energy of the emitted protons. If a thick fully deuterated polystyrene sample (DPS) is used as a target, this translates into the spectra in Figure 2-8, where the abscissa represents the channel number of the multi channel analyser used to collect the data. Here the left edge of the peak represents the protons produced at the surface. When the $^3\text{He}$ beam goes into the sample it loses energy and its interaction with deuterium results in emitting protons at higher energies shifted to the right in the spectra towards higher energies. Therefore the energy scale in the NRA spectra is a measure of the depth, $d$, of the atoms being studied by NRA.

Nuclear reactions (wanted or unwanted) can result in high levels of radiation including the emission of gamma rays (and/or neutrons) and activation of the sample and the beam system. Health and safety aspects should be considered before or while undertaking any measurement where nuclear reactions can occur. On the other hand, these products can be used, if detected by suitable detectors, to give valuable information about the sample. Detecting the gamma rays induced by the beam from particular elements in a sample using a high purity germanium (HPGe) detector and comparing the resulting gamma-ray spectrum with one from a reference material containing known concentrations of these elements, the concentration of atoms of interest in the sample can be obtained. This technique is called Particle induced Gamma-ray Emission (PIGE) [30]. For instance, using the $^{19}\text{F}(p,\alpha)^{16}\text{O}$ reaction is a major application of this technique for detecting fluorine in teeth and hair [31, 32]. It is also used for accelerator energy calibration (see Chapter 5). Detecting the neutrons induced from the $^7\text{Li}(p,n)^8\text{Be}$ reaction in forward direction near threshold is also used as a standard method for calibrating the accelerator energy [33] as will be discussed in details in chapter (5).
NRA is now well accepted as a standard analytical method. It is specially used in the semiconductor industry since most of the materials used contain light elements (N, O and C) [34]. The NRA scanning microbeam technique has been applied here at Surrey to investigate diffusion of deuterated water into materials using the D(\(^{3}\)He,p)\(\alpha\) reaction [2, 35-40].

Figure 2-7: The protons energy induced from D(\(^{3}\)He,p)\(\alpha\) reaction versus \(^{3}\)He beam energy at detection angle of 165°. The inverse kinematics effect is shown
2.2.3.1 Some specifics of the nuclear reaction applied in this thesis

$^7\text{Li}(p,\alpha)^4\text{He}$ reaction

This reaction is excellent for $^7\text{Li}$ detection due to its high Q-value ($Q = +17.347 \text{ MeV}$) and its fairly high cross-section [41]. The induced alpha particles lose enough energy in matter to make this reaction ideal for Li depth profiling [42]. The $^7\text{Li}(p,\alpha)^4\text{He}$ reaction obeys inverse kinematics at backward detection angles. The $^7\text{Li}(p,\alpha)^4\text{He}$ reaction has been utilised in many applications. It has been recommended in the investigation of the intercalation compounds containing Li [43] to study the performance of the Li-based rechargeable batteries. The corrosive behaviour of lithium in stainless steel can also be investigated using this reaction [44] as can the study of white blood cells during Li treatment [45].
The $^7\text{Li}(p,\alpha)^4\text{He}$ reaction has a maximum total cross section at ~3 MeV for protons as is shown in Figure 2-9 [46]. Furthermore, at this energy, when the backscattered protons are collected at the same time, the non-Rutherford scattering cross-section of protons on $^7\text{Li}$ is more than 50 times than Rutherford one if the detection angle is 165°. The presence of $^{19}\text{F}$ may cause interference since it will undergo the $^{19}\text{F}(p,\alpha)^{16}\text{O}$ reaction ($Q = 8.1137$ MeV). The choice of proton energy should be taken with care depending on the energy dependent cross-section of the $^{19}\text{F}(p,\alpha)^{16}\text{O}$ reaction (i.e. choose a proton beam energy in which its cross-section is low). This will be discussed in detail in chapter (6).

Bombarding Li with protons is accompanied with the emission of neutrons from the $^7\text{Li}(p,n)^8\text{Be}$ reaction ($Q = -1.644$) if the energy of the protons exceeds the threshold (1.88 MeV). Furthermore, gamma rays are produced simultaneously from the $(p,\gamma)$ reaction. Therefore attention should be paid, when bombarding Li with energetic protons, to minimising the radiation hazards.
Figure 2-9: The total cross-section of the $^7$Li(p,$\alpha$)$^4$He reaction versus proton beam energy [46]
Chapter Three: The University of Surrey Ion Beam Centre Analysis Facility

3.1 Introduction

In this chapter an overview is given of the University of Surrey Ion Beam Centre Facility [47], which includes a brief description of the 2MV tandem accelerator and its ion source, the two microbeam lines, one in-vacuum and the other in-air, the focusing and scanning systems, the detectors used and the data acquisition system. These components are shown schematically in Figure 3-1. The accelerator and the beam lines are all kept under vacuum pressure of \( \sim 10^{-7} \) mBar. A variety of ion beam applications, including RBS, PIXE and NRA are possible using \(^1\mathrm{H}^+, \ ^3\mathrm{He}^+, \ ^3\mathrm{He}^{++}, \ ^4\mathrm{He}^+\) and \(^4\mathrm{He}^{++}\) beams. The next sections give descriptions of the components starting from the left end of Figure 3-1.
Figure 3-1: An outline of the main components of the University of Surrey Tandem accelerator facility
3.2 The ion source and the charge exchange canal

This is a gas fed duoplasmatron ion source [48] (model 358) and is shown schematically in Figure 3-2. It has two stages. The first one is the production of electrons by means of thermo ionic emission from a filament. These electrons are guided via a confining magnetic field into a region of flow of the gas (H₂ or He), which is ionised as a result of the collisions. The second stage is the extraction of the desired ions by a strong electric field (20kV). The extraction may be either positive or negative depending whether it is H₂ or He gas respectively. A negatively charged H⁻ beam is obtained directly from the duoplasmatron when H₂ gas is used. In the case of He gas, He⁺ ions are more likely to be created. They then pass the charge exchange canal, which contains hot alkali metal vapour (Li in our case) that converts only ~1% of He⁺ into He⁻. The alkali metals strongly tend to lose electron. The Li vapour is obtained by heating metallic Li to 500-600 °C. The resulting negatively charged particles are focused and guided into the low energy magnet.

Figure 3-2: An outline of the duoplasmatron ion source. The charge exchange canal is shown
3.3 Low energy magnet

This is a bending magnet, with a radius of curvature "r", used to inject an ion beam with the desired mass into the tandem accelerator. It is called the multi purpose injector (MPI). Only ions with the suitable mass M and charge q having the correct radius of curvature r will come out of the exit slits of the injecting magnet according to Equation 3-1:

\[
r = \frac{\sqrt{2ME}}{Bq}
\]

Equation 3-1

where E is the energy of the ions and B is the value of the magnetic field. Once the ions leave the MPI magnet they are injected into the accelerator tank. Any other ions, which do not obey Equation 3-1 are stopped by the exit slits (see Figure 3-3).

![Diagram showing the working principle of the analysing magnet](image)

Figure 3-3: Diagram showing the working principle of the analysing magnet
3.4 The accelerator

This is an HVEE 2MV Tandetron™ accelerator [49] installed in 2002. It has a positive high terminal voltage located in the centre of the tank. Figure 3-4 shows that its working principle is based on two stages of particle acceleration. The first stage involves the acceleration of the negatively charged particles, which were injected into the accelerator from the source via the MPI magnet, to a terminal high voltage located in the middle of the tank. Here a stripper gas removes two or more electrons from each particle (i.e. a charge exchange takes place). The resulting positive ion is then accelerated in a second stage towards ground potential. Thus the particle acquires energy both before and after the terminal. The final energy of ions with final charge state \( q_e \) is given by Equation 3-2:

\[
E = eV_e + (q + 1)eV_t,
\]

Equation 3-2

Where \( V_e \) is the extraction voltage in the source, \( e \) the electron charge and \( V_t \) is the terminal voltage, which is generated using a Cockroft-Walton high voltage generator [50]. A generating voltmeter (GVM) [51] measures the voltage at the terminal. This device must be calibrated since the reading it gives is affected by the thermal drift of its mechanical dimensions and its position relative to the high voltage terminal [47]. The calibration procedures of the GVM are discussed in chapter 5. After the accelerator, the beam enters the high energy switching magnet.

3.5 High energy switching magnet

The switching magnet has the main purpose of directing the accelerated charged particles to the desired beam line with the required energy and the required ion charge (single or doubly charged). (See Figure 3-4).
Figure 3-4: Diagram showing the working principle of the tandem accelerator. The negative ions from the source are accelerated towards the high voltage terminal $V_t$. They are subjected to a gas stripping process at the high voltage terminal where a charge exchange takes place. The resulting positive ions are accelerated again towards ground potential (potential of the sample). Analysing magnets at both the low and high energies ends of the accelerator are shown.
3.6 Beam focusing

Originally IBA techniques were used with a focused beam of areal dimensions of mm\(^2\). This gives results averaged over a similar sized portion of the sample. In order to obtain smaller dimensions of the beam, in the case that higher spatial resolution is needed in order to allow more details to be seen in the sample, micro-beams with areal dimensions of a few µm\(^2\) were developed [52, 53]. Legge [54] has given a comprehensive discussion of the history of ion micro-beams.

Initially micro-beams were simply achieved by using fine collimators. This has the limitation of a substantial reduction in the beam current. The best way of producing ion micro beam is by focussing using magnetic or electrostatic fields. One way this can be achieved is to use a system of suitable slits and quadrupole lenses. Two groups of slits are placed in the beam line, one called the object slits and the other collimated slits. Single quadrupole lenses create magnetic field, in which the beam is focussed in one plane and defocused in the orthogonal plane. By placing another quadrupole lens at 90\(^\circ\) orientation relative to the first one, a beam focussed in one spot is produced as is shown in Figure 3-5. Using a third quadrupole lens, (i.e. a triplet quadrupole lenses in total), reduces the astigmatism of the resulting image of the object [7].
Figure 3-5: Diagram showing the basic working principle of the beam focusing system. A doublet quadrupole focusing magnet and both the object and collimator slits are shown.
3.7 Beam scanning

Taking the data while scanning the microbeam in two directions over the sample results in a picture or "map" of the location of the elements within the scan area (i.e. 2-D elemental maps are generated). Scanning the beam across the sample is achieved by passing the beam through two electric fields, one vertical and one horizontal. The scan-controlling software OM-DAQ \[55\] ("an acronym for Oxford Microbeam Ltd Data Acquisition System) determines the field strength at any one moment.

If an energy window, corresponding to a peak in a spectrum, from, say, an X-ray detector is selected, any counts in that window are associated by the scan-controlling software with the momentary position of the beam. The microbeam spot stays at the same place while scanning for \(~10^{-6}\) sec before moving to the next point. Hence, as the peak is characteristic of an element, an elemental map is obtained.

Collecting the data using the list mode option results in every event read by the data acquiring system being stored sequentially in a file as a list of \((E,X,Y)\) triplets, where \(E\) is the energy of the detected X-ray, \(X\) and \(Y\) are the positions of the beam spot. The file can then be played back after the run (i.e. off line) to generate new maps from selected regions of the scan and subsequently new corresponding spectra.

3.8 In-vacuum microbeam line

This line is set at the -30° port of the switching magnet. It is mounted on two massive concrete blocks to reduce any vibration effects, one at the beginning of the beam line where the object slits are placed and the other where the end stage of the microbeam is located. This includes the target chamber, triplet quadrupole lenses, scanning system deflection coils and the collimator slits all mounted on an integral support table. Scanning plates are placed just before a triplet of magnetic quadrupoles to enable focussed MeV
ions (~5×5 μm²) to raster scan over the sample of up to 2×2 mm², depending on the energy, the mass and the charge state of the ion.

The beam line is kept under a vacuum of the order of 10⁻⁹ mBar. A retractable Faraday cup is placed in the middle of the beam line to enable current measurements before focussing the beam. A fast-acting automatic valve is situated at the beginning of the beam line (just after the switching magnet) to protect the accelerator from any leak in the beam line vacuum. Another (manual) valve is situated in the beam line before the collimator slits to allow the scattering chamber to be isolated from the beam line – for example whilst the sample ladder is being installed in the scattering chamber.

The target chamber is made from stainless steel with 8-access ports to enable mounting of a wide range of detectors, a microscope assembly (for sample and beam viewing) and a viewing window. It is at earth potential. A microscope connected to the chamber is equipped with a camera connected to a TV monitor to enable sample viewing. The vacuum in the chamber is in the order of 10⁻⁶ mBar. This is possible; whilst the beam line vacuum is 10⁻⁷ mBar as the beam line is very narrow (~5mm). In theory, if there were no leaks in the vacuum system, then the pressures would be the same if the manual valve between the beamline and the chamber is opened, as expected. However, at these levels of vacuum, everything leaks. Some areas are easier / harder to pump than others, due to the size of the tubes etc, and the rate of leakage. The target chamber has more seals than the main beamline, and thus leaks quicker. The pressure is gradually, within long time, tends to be the same in both the beam line and the chamber. A 3-axis XYZ goniometer controlled-sample stage is available.

A Si(Li) detector, for PIXE analysis, is placed at an angle of 135° to the direction of the beam in IBM geometry. Detection of the NRA and RBS products is achieved by a thick silicon surface barrier detector located at backward angle of 165° in Cornell geometry. Figure 3-6 shows an outline of the in-vacuum microbeam line.
Figure 3-6: An outline of the main components of the in-vacuum micro-beam line.

An upper view of the in-vacuum chamber is shown.
3.9 In-air microbeam line

The use of an external microbeam is necessary for the investigation of samples which are unstable under vacuum conditions (e.g. soft organic tissue or liquids) or which are too large to be mounted in a vacuum chamber (e.g. historical artefacts, bones, papers, paintings etc.) [56]. The development of an external microbeam facility at the University of Surrey [57] has led to wide range of research possibilities such in Clough et al [58]. It is located at the +10⁰ port of the switching magnet. Similar to the case of the in-vacuum beam line, the end stage of the external beam line is mounted on a massive concrete block. It has a scanning system and doublet quadrupole lenses for beam focussing as is seen in Figure 3-7. A doublet quadrupole is used rather than a triplet as, when the focussed beam is brought into air, a substantial amount of lateral scattering occurs, increasing the size of the beam spot. This far outweighs the reduction in spherical aberrations enabled by a third quadrupole.

The microbeam is brought into air through a nozzle of 3mm diameter covered by a Kapton™ foil (C₂₂H₁₀N₂O₂)n [59] 8 microns thick. Using Kapton™ foil as exit window is ideal due to its several special characteristics. It has low beam-induced background emission, low energy loss, high resistance to radiation damage and to the massive pressure difference between the vacuum and the air. A lithium drifted silicon detector (Si(Li)) with an area of 80mm² is used to enable in-air PIXE measurements. It is placed at an angle of 135⁰ to the direction of the beam in IBM geometry. To pick up backscattered particles, a silicon surface barrier detector is set up at a backward angle of 135⁰ in Cornell geometry. Both detectors are equipped with nozzles that allow helium gas to flow in between each of them and the sample. This both minimises, in the case of RBS detector, the energy loss of the backscattered particles, as they lose much more energy in air than in He, and decreases the beam straggling. In the PIXE situation this decreases the attenuation of soft X-rays in the air. This will be established in detail in chapter 7.

An optical system consisting of a set of mirrors, a camera and a TV screen with cursors defining the beam spot position together with an independent alignment laser is used to
position the sample in the beam. The alignment of the sample along the beam using the optical system is discussed in Chapter 7. The samples are viewed on the TV monitor through the optical system. This enables the correct positioning of the sample, using a 3-axis traversing table, for it to be raster scanned by the beam. Monitoring of the beam intensity is achieved by detecting the particles backscattered from a rotating chopper located upstream in the evacuated section of the beam line.

Figure 3-7: An outline of the main component of the external micro-beam line. The exit window arrangements are zoomed in to be shown clearly. (photo from Merchant et al [57])
3.10 Measuring the beam current

Measuring the number of particles hitting the target is an essential procedure in the IBA measurements since it affects the quantitative analysis. The fact that the ion beam from an accelerator is not steady (i.e. it fluctuates), due to many factors, makes measuring the current of the particles hitting the target a complicated issue. Different methods have been reported [22, 52] to determine the number of particles hitting the sample.

The Faraday cup in Figure 3-8 is a device that is widely used for measuring the current in a beam of charged particles. Its simplest form consists of a conducting metallic chamber or a cup, which intercepts a particle beam, in which the charged particles impinge on it to induce secondary electrons that can be measured. An electrical connection is attached to the cup which conducts the resulting current to a measuring instrument. A bias voltage applied to the cup is usually used to prevent secondary electron emission loss that would distort the reading.

![Figure 3-8: Outline of the Faraday cup used for monitoring the beam current](image)
The Faraday cup is normally placed behind the sample and records the beam transmitted through it. The beam current from the sample is also recorded and their sum is the measure of the overall beam current. The sample has to be thin enough that the beam does not stop in the specimen. Charge collection using thick samples can be evaluated by connecting the charge integrator to the sample holder directly. The target sample is normally electrically isolated from the chamber. This is the method that is being used here at Surrey in the in-vacuum microbeam chamber. Another possibility is to electrically isolate the whole chamber from earth. Any charged particles going into the chamber can then be recorded as a true beam current if the chamber is connected directly to a current monitor.

The use of a rotating vane or chopper is ideal for monitoring variation in the beam intensity. It can be placed within the beam line in vacuum. Its blades intercept and sample the beam (cut the beam) periodically and backscattered particles are detected. The blades are covered with an element chosen to be sensitive to the backscattering process (i.e. heavy metals such as a thin layer of gold). They are set to be narrow enough that they are exposed to the beam for less than 10% of the total time that is needed for the experiment. The particles scattered from the gold are collected using a silicon surface barrier detector and then discriminated in a single channel analyser (SCA), the amount of which is recorded as a scalar. Figure 3-9 shows an outline of the beam chopper used for monitoring the beam. The current intensity in the external beam line measurements here at Surrey is obtained by,

1. a chopper to monitor the beam variation during the run.
2. a retractable in-vacuum Faraday cup to record the beam current before and after each run.

Beam current normalisation measurements can also be obtained from the backscattering particles from the matrix composition of the sample (i.e. internal normalisation). Alternatively a measure may be obtained by reading the number of particles backscattered from a thin film placed in front of the sample.
Figure 3-9: Outline of the beam chopper used for monitoring the beam current in the external beam line
3.11 Data acquisition system

Oxford Microbeam Data Acquisition System (OM_DAQ) [55] includes a complete hardware and software package for the collection of PIXE, RBS, NRA elemental maps and energy spectra from a scanning high energy ion microbeam. It has the following interesting features:

- It can be coupled with the scanning system to collect data simultaneously from up to 8 X-ray or particle detectors to generate online energy spectra and online 2-D elemental maps.

- A user-friendly Windows® interface (see Figure 3-10) allows a mouse selection of the programme functions in a simple way.

- Display of the beam current, the accumulated charge and the dead time on-screen.

- Automatic generation of the run numbers and storage of experimental conditions.

- On-screen identification of PIXE emission lines and RBS surface energies.

- Capability of saving the data in a list mode option.

Figure 3-10: OM_DAQ software Windows® interface
3.12 Radiation detectors

The basic principle of radiation detection is based on the transfer of part or all of the radiation energy to detectors that have the ability to convert it into a measurable form. They are based on the interaction of the radiation with the matter that the detector is made of. Figure 3-11 shows different types of detectors used for ion beam analysis techniques. The best descriptions of the working principles of the radiation detectors are given by Knoll [60] and Leo [61].

3.12.1 Surface barrier detector

This detector [60] is widely used for charged particle detection. It is formed by depositing a very thin layer of p-type Si on a surface of n-type pure Si crystal. A p-n junction is thus obtained. Electrical contacts to the p-type and n-type Si are made by evaporating thin layers of gold and aluminium respectively. A bias voltage is applied in a reverse direction across the p-n junction to form an active (depletion) layer in the p-n junction. Electron-hole pairs are produced by the charged particles in this region to form an electric signal that is proportional to the deposited energy of the charged particles.

3.12.2 Lithium drifted silicon Si(Li) detector

This is a semiconductor detector (similar to the previous case) usually used for the X-ray detection [52]. It is fabricated using high pure p-type silicon crystal doped with lithium atoms. The purpose of Li atoms is to produce an n-type layer (since Li is classified as a donor element) to create a p-n junction that has a large depletion layer. This is required to detect X-rays, owing to their highly penetrative characteristics. The electrode contacts in this diode are formed with thin gold layers. The Si(Li) detector should be operated at low temperatures (boiling point of liquid nitrogen “77 K”) to minimise the Li diffusion out of the Si crystal and reduce electronic noise.
3.12.3 Cadmium Telluride CdTe detector

Cadmium Telluride (CdTe) [60] is a large band gap semiconductor with a high atomic number \(Z\). It has particular advantages such as room temperature operation and high efficiency with good energy resolution and low cost.

Choosing either Si(Li) or CdTe detectors for X-ray detection depends on the application that is being studied. For X-ray energies below 25 keV, the Si(Li) detector is the detector to be used then. It has 100% efficiency up to 25 keV. For higher energy X-rays, above 25 keV, CdTe is the perfect detector. It has better stopping power, with very good efficiency up to 100 keV.

3.12.4 High purity germanium (HPGe) detector

As a result of the deep penetration of high energy \(\gamma\) rays, a large depletion region is required in a gamma ray semiconductor detector. Increasing the inverse bias on the p-n junction and decreasing the crystal impurity will result in giving larger depletion layer. Using high purity germanium is ideal for gamma ray detection via photoelectric effect since it has high atomic number and the photoelectric effect cross section is proportional to \(Z^5\). The germanium detector requires cooling to 77 K in order to limit thermal excitations. This detector has very good energy resolution.

3.12.5 Scintillation detector

A popular method for the detection of gamma-rays involves the use of NaI(Tl) scintillators. The scintillator is a material that emits light (i.e. scintillates) when absorbing radiation. These devices are often portable and easy to handle. The gamma rays that hit the crystals are absorbed. The crystal then gives off light flashes. These flashes of light are detected by a photomultiplier tube and an electrical response is produced. The energy of the radiation is proportional to this signal. This detector has poor energy resolution but very high count rates compared with the HPGe detector.
3.12.6 Neutron detectors

Detecting neutrons is difficult since they are electrically neutral. Therefore the neutron does not typically cause ionization in the matter. Its detection is based on the production of secondary charged particles, from a nuclear reaction, that can be easily detected. For instance the production of protons from the $^3\text{He}(n,p)^3\text{H}$ reaction ($Q = 764$ keV) is used for neutron monitoring. The detector consists of a sealed tube or sphere filled with $^3\text{He}$ gas. Energetic protons are generated inside the detector by the neutrons via the $^3\text{He}(n,p)^3\text{H}$ reaction. When such protons pass through the gas in the tube, some of the gas molecules are ionized. The produced ions and electrons are accelerated by applying an electric field between a central electrode in the detector tube and the tube wall, and hence producing a current pulse. The number of current pulses generated per unit time (pulse rate) is thus related to the number of neutrons entering the detector per unit time.
Figure 3-11: Different types of detectors used for the ion beam analysis techniques
Chapter Four: Diffusion Basics

4.1 Introduction

Diffusion is defined as the process of matter transportation from one part of a system to another due to random molecular motion. It leads eventually to the homogenisation of a mixture of two molecules [62]. In general the diffusion velocity is fast in gases, slower in liquids and much slower in solids. The diffusion process in gases and liquids is well predicted. This is not the case in the solids since it is governed by a large range of variables [63].

The study of diffusion in materials has become of great interest in recent decades since it is extremely important to have good knowledge of transport phenomena in many practical fields such as foods, polymers, cementitious materials, semiconductors, etc. Many techniques have been introduced to study diffusion in materials resulting in a better knowledge of the material structures, the transport phenomena and the physical models of diffusion [63].

It has been demonstrated that Fickian (Case I) and Non-Fickian (Case II and anomalous) diffusions represent the two extremes of solvent transports [64]. Fickian diffusion, which scales linearly with square root of time $t^{1/2}$, is observed for many systems. In contrast, Case II transport (mainly observed in glassy polymers where the polymer chains are not sufficiently mobile to permit the immediate penetration of the solvent in the polymer) is characterized by a linear scaling with time. The transport process is limited by the swelling of the polymer matrix by the penetrant. Anomalous diffusion lies in between Fickian and case II diffusion where mass uptake $M_t$ of the penetrant is proportional to $t^n$ where $\frac{1}{2} < n < 1$ (i.e. $M_t = kt^n$ with $k=\text{constant}$)
4.2 Fickian Diffusion

In 1855, Adolph Fick put matter transport on a quantitative foundation by introducing a mathematical description analogous to the flow of heat, as both were considered to be due to the random motion of molecules [62].

Fick's First Law states that the flux (the amount of substance diffusing across unit area in a material per unit time) (e.g. mol/m²·sec) is proportional to the concentration gradient. It describes diffusion in the steady state when the concentration does not vary with time (flux is constant $J_{in}=J_{out}$). It is given (for diffusion in one dimension) by the formula:

$$J = -D \frac{\partial C}{\partial x}$$

Equation 4-1

where $J$ is the flux, $C$ is the concentration of atoms or molecules of interest (e.g. mol/m³) and $x$ is the position of penetrant. $D$ is a constant called Diffusion Coefficient, which has dimensions (length²·time⁻¹) (e.g. m²/sec). It expresses the transfer rate of a substance by random molecular motion. The negative sign denotes that the diffusing mass flows in the direction of decreasing concentration.

If the concentration gradient changes with time, then Fick's Second Law will describes the diffusion in that case (non-steady state). The change of the concentration profile is given by the partial differential equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Equation 4-2

For diffusion in two or three dimensions Fick's Second Law is:

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$

Equation 4-3
4.3 Glossary of some terms related to the diffusion process

There are many terms in connection with diffusion [65]. Some of them include absorption, which represents the atoms or molecules uptake by a host material. The accumulation of molecules at the surface of a solid or liquid is described as adsorption. Sorption is the collective term for both absorption and adsorption processes. The reverse process of sorption is called desorption. The transport of a gas or liquid through a material is named permeation.

4.4 Solutions to diffusion equation for some special cases

Solution of Equation 4-3 gives the concentration profile as a function of the time and distance. In order to solve Fick's law, initial boundary conditions are required. These can be achieved for special cases that involve symmetries that have special geometrical features e.g. studying matter transport in a plane sheet, a cylinder or a sphere. Two special cases are discussed here, the diffusion in planar and cylindrical geometries.

4.4.1 Fickian diffusion into a planar matrix

Fick's Second Law describing planar diffusion along one axis, say in x axis, is give by Equation 4-2 above. Two special cases are discussed here [66]. See Figure 4-1.

4.4.1.1 Infinite source diffusion

Infinite source diffusion requires a constant surface concentration of the diffusing molecules or atoms. In this case, one initial and two boundary conditions are considered. They are:

\[ C(x,0) = 0 \] (i.e. concentration is initially zero in the medium)
\[ C(0,t) = C_0 \] (i.e. the surface is maintained at concentration \( C_0 \)).
\[ C(\infty,t) = 0 \] (i.e. the concentration far enough from the surface is zero)
The solution to Fick’s second law under these conditions is given by Equation 4-4:

\[ C(x,t) = C_0 \times \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \]

Equation 4-4

Where (erfc) is called the complementary error function.

4.4.1.2 Limited source diffusion

In this case, a fixed quantity of diffusant is plated onto the material. One initial and two boundary conditions are taken into account:

\[ C(x,0) = 0, \quad C(0,0) = \infty \quad \text{(i.e. concentration is initially zero in the medium and remains only in the surface)} \]

\[ \int_0^\infty C(x,t)dx = m \quad \text{(i.e. the total amount of diffusing substance is constant)} \]

\[ C(\infty,t) = 0 \quad \text{(i.e. the concentration far enough from the surface is zero)} \]

The solution to Fick’s second law under these conditions is given by Equation 4-5:

\[ C(x,t) = \frac{m}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \]

Equation 4-5

Equation 4-5 can be linearised by taking logarithms, i.e.

\[ \ln C(x,t) = \ln \frac{m}{2\sqrt{\pi Dt}} - \frac{x^2}{4Dt} \]

Equation 4-6

Linear regression of \( \ln C(x,t) \) versus \( x^2 \) yields a slope \( -\frac{1}{4Dt} \) from which we can obtain the diffusion coefficient \( D \).
Figure 4-1: One dimensional diffusion from both limited (left) and infinite (right) sources
4.4.2 Fickian diffusion into cylindrical matrix

The Fickian diffusion in cylindrical co-ordinates, considering a long cylinder in which the diffusion is everywhere radial, is given by Equation 4-7 \([62, 67]\),

\[
\frac{\partial C(r,t)}{\partial t} = D \frac{\partial}{\partial r} \left( \frac{r \partial C(r,t)}{\partial r} \right)
\]

**Equation 4-7**

Considering a constant surface concentration \(C_0\) and an initial concentration of zero in a cylinder of radius \(a\), that is mean,

\[
C = C_0, \quad r = a, \quad t \geq 0
\]

\[
C = 0, \quad 0 < r < a, \quad t = 0
\]

then the solution of Equation 4-7 is given by Equation 4-8,

\[
\frac{C}{C_0} = 1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{\exp(-D \alpha_n^2 t) J_0(r \alpha_n)}{\alpha_n J_1(a \alpha_n)}
\]

**Equation 4-8**

where,

\(C\) : Concentration of the diffusing molecule.

\(C_0\) : The surface concentration of the diffusing molecule.

\(D\) : Diffusion coefficient.

\(a\) : The radius of the cylinder.

\(t\) : The exposure time.

\(r\) : The radial distance from the centre.

\(J_0\) : Bessel function of the first kind of order zero.

\(J_1\) : Bessel function of the first kind of order one.

\(\alpha_n\) : The roots of \(J_0(a \alpha_n) = 0\)
Chapter Five: The Energy Calibration of the Tandem Accelerator at the University of Surrey Ion Beam Centre

5.1 Introduction

As mentioned in chapter (3) the terminal voltage is measured by a generating voltmeter (GVM) that is mounted inside the accelerator tank just opposite the high voltage electrode. It consists of two sets of vanes the rotor and the stator. The rotor vanes spin in front of the stator, alternately hiding and exposing it to the electric field of the terminal. This generates an electrical signal from the stator proportional to the terminal voltage. This is shown schematically in Figure 5-1.

The GVM readout is affected by the thermal drift of its mechanical components and its position relative to the high voltage electrode [47] and needs frequent calibration. This calibration can be performed by bombarding a target sample with an ion beam and scanning through a known strong resonant cross-section or of reaction threshold by varying the terminal voltage (and hence the energy of the ion beam).

To calibrate the Tandetron™ at the University of Surrey Ion Beam Centre, four energy points of calibration were established. The first one was obtained by detecting near-threshold neutrons from the $^7\text{Li}(p,n)^7\text{Be}$ reaction. The other three were known resonant reactions – two resonances in the $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ reaction and one in the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ reaction.
Figure 5-1: Schematic diagram of GVM
5.2 Neutron threshold

The $^7\text{Li}(p,n)^7\text{Be}$ reaction is an endothermic reaction that can not occur if the energy of the bombarding particles is less than the threshold energy. At threshold the induced neutrons are kinematically focussed in the beam direction. As the energy is increased above threshold, a corresponding spread of the neutrons at forward angles occurs [68] as shown in Figure 5-2. The fact that near-threshold neutrons are produced only in the forward direction of the beam has the advantage that the total yield may be measured using a single detector placed in the forward direction [69]. The total neutron yield $Y$ is approximately proportional to the difference between the bombarding energy and the threshold energy raised to the power of 3/2 [70]. That is $Y \sim (E_p - E_t)^{3/2}$. Hence, In order to determine the neutron threshold energy, $Y^{2/3}$ is plotted versus the bombarding energy. Subsequently a linear fit is obtained and the threshold energy estimated by an extrapolation to the zero neutron yield [22].

Neutrons induced from the $^7\text{Li}(p,n)^7\text{Be}$ reaction (Q-value = -1.644 MeV) near threshold (1880.42keV) will be considered in this study. It is one of the major accelerator energy calibration standards.

5.2.1 $^7\text{Li}(p,n)^7\text{Be}$ threshold

A LiF standard (~48.9 μg/cm²) deposited on Mylar™ was bombarded by protons of energies near the threshold of $^7\text{Li}(p,n)^7\text{Be}$ reaction to induce neutrons in the forward direction of the beam. A JCS® NMS017 neutron monitor was used to accumulate neutron counts per unit time and was placed outside the microbeam chamber just behind the sample as is shown Figure 5-3.
Two sets of measurements were carried out by changing the terminal voltage of the tandem accelerator and reading the neutron monitor readout (counts per second). This was corrected to the collected charge. The resulting normalised neutron yield to the power of $2/3$ is plotted versus the terminal voltages for the two sets of measurements in Figure 5-4. The corresponding thresholds were obtained by doing a linear fit to each set of measurements. The mean terminal voltage threshold, corresponds to energy threshold of 1880.42 keV, was calculated to be $905.8 \pm 0.4 \text{ kV}$.

![Angular energy distribution of the $^7\text{Li}(p,n)^7\text{Be}$ reaction](image)

**Figure 5-2**: Angular energy distribution of the $^7\text{Li}(p,n)^7\text{Be}$ reaction
Forward induced neutrons

The microbeam line
LiF sample
Neutron monitor

Figure 5-3: Experimental arrangements to perform neutron emission from the $^7\text{Li}(p,n)^7\text{Be}$ reaction in the microbeam chamber

Neutron Threshold Measurements

$y = 0.0098x - 8.895$
$R^2 = 0.9934$

$y = 0.0092x - 8.3057$
$R^2 = 0.9779$

Figure 5-4: Linear fit for the two near-threshold measurements
5.3 Gamma resonances

In order to determine the resonance energy for a gamma ray reaction, an excitation curve (gamma yield versus beam energy) may be obtained for a thick target. The energy of the resonance, corresponding to the mid point of the resonance step, can be obtained by fitting the excitation curve to a step function as in Roush et al [33]. They used an arctangent function:

\[ Y = A + B \arctan\left(\frac{E - E_r}{\Gamma}\right) \]

Equation 5-1

where:
- \( Y \): the gamma yield.
- \( A, B \): Constants.
- \( E \): particles energy.
- \( E_r \): particles energy at the resonance point.
- \( \Gamma \): Resonance width.

Two resonances in the \(^{27}\text{Al}(p,\gamma)^{28}\text{Si}\) reaction and one in the \(^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}\) reaction will be discussed.

5.3.1 \(^{27}\text{Al}(p,\gamma)^{28}\text{Si}\)

An aluminium foil was used as a sample. In order to bombard it with a high number of protons, the sample was placed at the zero port (before the beam lines) of the tandem accelerator. A proton beam current of \(\sim 3 \mu\text{A}\) was obtained.

An Ortec® high-purity germanium (HPGe) gamma ray detector was used to collect gamma ray spectra and was placed directly behind the sample to maximise the solid angle and hence the gamma ray yield.
Induced gamma ray spectra were collected (see Figure 5-5) using different terminal voltages (corresponding to different beam energies). The data were acquired using OM_DAQ software. In each measurement the number of counts both under the peak corresponding to 1.77MeV and the Compton spectrum were measured (see the region of interest in the spectrum in Figure 5-5). From this was subtracted a background run (i.e. a run was taken when the beam was off) corrected to the live time of each run. The nett spectrum was normalised to the collected charge and plotted versus the corresponding terminal voltage to obtain two excitation curves (Figure 5-6 and Figure 5-7).

Two resonances were energy-scanned, corresponding to beam energies of 991.86keV and 1025.29keV respectively [71]. The excitation curves were fitted using Equation 5-1. Using this fit the two tandem terminal voltages corresponding to the two resonances are found to be:

<table>
<thead>
<tr>
<th>$V_{r1}$ (kV)</th>
<th>$V_{r2}$ (kV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>473.7±0.0</td>
<td>490.2±0.3</td>
</tr>
</tbody>
</table>
Figure 5-5: Two gamma-ray spectrum, one for the $^{27}$Al($p,\gamma$)$^{28}$Si reaction and the other is for background
**Figure 5-6**: First excitation curve for the $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ reaction

**Figure 5-7**: Second excitation curve for the $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ reaction
5.3.2 $^{19}\text{F}(p,\alpha)^{16}\text{O}$

Teflon™ or PTFE (Poly Tera Fluoro Ethlene) tape was used as a fluorine sample since it contains 76% fluorine by weight. It was placed in the vacuum chamber. A scintillation detector was used to pick up induced gamma rays. It was placed at 135° to the direction of the beam and calibrated using $^{60}\text{Co}$ and $^{137}\text{Cs}$ gamma sources. Higher gamma ray counts are expected compared to the case of HPGe detector since the scintillation detector is more efficient but it has poor energy resolution as it is shown in Figure 5-8. Gamma ray energies of 7.12, 6.92, 6.13MeV and their corresponding single and double escape peaks were considered in this study (see the region of interest in the spectra in Figure 5-8). An excitation curve was subsequently obtained in Figure 5-9 as for the $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ reaction above. Fitting this curve using Equation 5-1 gives terminal voltage resonance of $444.3\pm1.5$ kV corresponding to a beam energy of 935keV [72].

![Gamma ray spectrum collected when the beam was hitting the target (Teflon)](image)

![Gamma ray spectrum corresponding to background](image)

**Region of interest**

![Region of interest](image)

**Figure 5-8:** Two gamma-ray spectrum, one for the $^{19}\text{F}(p,\alpha)^{16}\text{O}$ reaction and the other is for background.
Figure 5-9: Excitation curve for the $^{19}\text{F}(p,\gamma)^{16}\text{O}$ reaction
5.4 The energy calibration of the machine

Table 5.1 summarises the four measured calibration points. The real terminal voltage column in the table was obtained taking into account that the protons energy obtained in a tandem accelerator is:

\[
\text{Real energy} = 2 \times \text{real terminal voltage} + 20\text{keV (extraction energy of the source)}
\]

Real terminal voltages versus nominal terminal voltages are plotted in Figure 5-10. A linear fit to the results gives the energy calibration of the tandem accelerator and was found to be:

\[
\text{Real terminal voltage} = (\text{Nominal terminal voltage} \times 1.0269(7)}
\]

Where the number in brackets refers to the error in the last digit. The line fit is remarkably very good makes this calibration reliable for any accurate work. This calibration was adopted for the whole work in this thesis.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Nominal terminal voltage (kV)</th>
<th>Beam energy (keV)</th>
<th>real terminal voltage (kV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{27}\text{Al}(p,\gamma)^{28}\text{Si})</td>
<td>473.7</td>
<td>991.86</td>
<td>485.9</td>
</tr>
<tr>
<td>(^{27}\text{Al}(p,\gamma)^{28}\text{Si})</td>
<td>490.2</td>
<td>1025.29</td>
<td>502.6</td>
</tr>
<tr>
<td>(^{7}\text{Li}(p,n)^{7}\text{Be threshold})</td>
<td>905.8</td>
<td>1880.42</td>
<td>930.2</td>
</tr>
<tr>
<td>(^{19}\text{F}(p,\alpha\gamma)^{16}\text{O})</td>
<td>444.3</td>
<td>935.00</td>
<td>457.5</td>
</tr>
</tbody>
</table>

Table 5.1: A summary of the four measured calibration points
Figure 5-10: Real terminal voltage versus nominal terminal voltage. The linear fit is constrained to pass through zero
Chapter Six: Nuclear Reaction Analysis and Backscattering Measurements for the Investigation of Lithium Intercalation into Thin Films of Vanadium Pentoxide $V_2O_5$

6.1 Introduction

6.1.1 Basic principle of batteries

Batteries are devices in daily use. Different kinds and sizes are needed depending on the application. For instance batteries smaller than a button are needed to power computer memory chips; medium sizes are required for laptops and mobile phones; large sizes are used to power electric cars.

A battery is a device that converts chemical energy directly into electrical energy when a chemical reaction occurs in the cell [73]. A typical electrochemical cell consists of two metal electrodes immersed into an aqueous solution (electrolyte). Reactions occur at the electrode-solution interface.

A simple electrochemical cell can be seen in Figure 6-1. It is made from copper and zinc metals together with solutions of their sulphates. Zinc loses electrons more easily than copper, so placing zinc and copper metals in solutions of their salts can cause electrons to flow through an external circuit from the zinc to the copper.

When a zinc atom gives two electrons, it becomes a positive ion and goes into the zinc sulphate solution as a positive ion, decreasing the mass of the zinc electrode. On the
copper side, the two electrons are received (via an external electrical circuit) by the copper sulphate solution causing a copper ion from the solution to be converted into copper atom which deposits on the copper electrode, increasing its mass. Oxidation-reduction reactions are simultaneously occurred in the electrochemical cell. The two reactions are typically written as:

At the anode: \( \text{Zn}_\text{(s)} \rightarrow \text{Zn}^{2+}_\text{(aq)} + 2e^- \)

At the cathode: \( \text{Cu}^{2+}_\text{(aq)} + 2e^- \rightarrow \text{Cu}_\text{(s)} \)

Figure 6-1: Basic electrochemical cell
6.1.2 Intercalation compounds and the rechargeable batteries

The need to develop energy sources that have high performance, a recharging capability, non-toxic content and small size has grown in tandem with the development of portable devices (e.g. laptops, mobile phones, rechargeable digital equipment...etc.).

Batteries using lithium have shown promising results [74] as well as their ability to be recharged. Lithium ion rechargeable battery operation is based on the migration of \( \text{Li}^+ \) ions between the cathode and the anode of the battery. The anode is either elemental lithium or a lithium-containing compound. It represents the source of ions and hence electrons. The cathode, which is the acceptor of ions, is a material which is able to accept \( \text{Li}^+ \) ions into its structure (intercalation compound).

For these rechargeable batteries, \( \text{Li} \) has the advantages of having both a small atomic mass (i.e. it has low density) and the highest electrochemical potential for a metal (i.e. the most electropositive metal in the electrochemical series). This property makes it a good reactant for a battery [75].

Figure 6-2 illustrates the operating principle of Li rechargeable battery through both discharging (left side) and charging (right side) processes respectively [76]. The basic working principle of this cell involves only the transfer of lithium ions between two simple insertion electrodes. In general, commercial lithium-ion batteries use either \( \text{Li} \) or a \( \text{Li} \) containing compound as the anode, \( \text{Li} \) intercalation compound (i.e. a host for \( \text{Li} \) ions) as the cathode and a lithium-ion containing conducting electrolyte. During the discharging route the \( \text{Li} \) ions in the anode material migrate through a separator towards the cathode. This process is accompanied by flow of electrons (electric current) in the load (it can be any electric portable device). Using an external power supply can charge the battery again. This drives \( \text{Li} \) ions back towards the anode.
A strong interest in vanadium pentoxide (V$_2$O$_5$) thin films as an intercalation compound has been introduced due to their extensive usage as cathode electrodes in rechargeable battery technology \[74\]. V$_2$O$_5$ electrodes allow easy insertion and extraction of the lithium ions during discharge and recharge processes respectively due to the V$_2$O$_5$ layered structure \[77\]. Vanadium pentoxide can be intercalated by lithium according to the reaction shown below:

\[
V_2O_5 + xLi^+ + xe^- = Li_xV_2O_5 \quad (x \leq 1)
\]

Figure 6-2: An outline of the basic working principle of a Li rechargeable battery throughout both discharging (left side) and charging (right side) processes respectively
6.1.3 Analytical energy loss techniques for studying intercalation compounds containing lithium

The Li content is of importance for the performance of rechargeable batteries. It is important to study Li depth profiles in the $V_2O_5$ to check if Li has been completely intercalated and if not where Li is located and to make sure whether it is homogeneous throughout the whole thickness or inhomogeneous. Different techniques have been applied to study and characterise Li distribution in rechargeable batteries. X-ray and UV induced photoelectron spectroscopy (XPS and UPS) are widely used to investigate Li intercalation into $V_2O_5$ thin films [78, 79].

Ion beam analysis techniques have been recommended recently as very good tools to investigate Li depth profiles in the intercalation compounds. Pruvost et al [43] have realised that the nuclear microprobe techniques are efficient tools to study intercalation compounds containing lithium. They offer non-destructive multi elemental detection devices. Berger et al [80] has performed the first elemental characterisation of Li intercalation into graphite, which can be used as a negative electrode in the Li-ion based batteries.

In this study depth profiles of Li uptake (in $V_2O_5$ thin films) were obtained via an energy loss technique using

- The $^7Li(p,\alpha)^4He$ reaction with $Q = +17.347$MeV by detecting the induced alpha particles.
- Simultaneous Backscattering measurements relying on the high elastic (non-Rutherford) cross section of protons on Li ions.

The novel University of Surrey IBA DataFurnace software [26] was used to obtain an elemental depth profile quickly and automatically taking into account the beam conditions (e.g. incident particle, incident beam energy, detection angle), the composition of the sample and the cross section of every reaction (BS and NRA), which can occur. It
can handle both techniques at the same time. Sample preparation is discussed, experimental arrangements are explained, IBA DataFurnace software is reviewed and the data analysis is demonstrated.

6.2 Sample preparation

Samples (see Figure 6-3) were prepared at the Surface Analysis Laboratory in the School of Engineering at the University of Surrey. They were $\text{V}_2\text{O}_5$ thin films (~400nm thick) prepared by a \textit{sol-gel technique} \cite{81} which involves the transition of a system from a liquid (the colloidal "sol") into a solid (the "gel") phase. Films were deposited on a conductive layer of fluorine-doped tin oxide ($\text{SnO}_2\cdot\text{F}$) on a glass substrate using the \textit{dip coating technique}, which is an established procedure for applying uniform thin films to flat substrates (i.e. a thin film deposition technique).

![Diagram](image)

\textbf{Figure 6-3:} $\text{V}_2\text{O}_5$ thin film deposited on a conductive layer of fluorine-doped tin oxide ($\text{SnO}_2\cdot\text{F}$) on a glass substrate
Li intercalation was carried out using a three-electrode cell [82], which is widely used for electrochemical measurements. It consists of three electrodes - a working electrode, a counter electrode, and a reference electrode - all immersed in an electrolyte (an electrically conductive solution). The group of the electrodes, the electrolyte, and the container holding them is the three-electrode cell. This setup can be used to investigate the kinetics and mechanism of the reaction occurring on the working electrode surface.

The first of the three electrodes is the working electrode. This is the electrode where the electrochemical reaction being investigated takes place. The second electrode is the reference electrode, which is used in measuring the working potential of the whole electrochemical cell (i.e. it is used as a reference point against which the potential of each of the other electrodes is compared). The counter electrode is used to make a connection to the electrolyte so that a current can be applied to the working electrode. However, the processes happening on the counter electrode are insignificant. The counter electrode is usually made of an inert material.

In the case of Li intercalation into V<sub>2</sub>O<sub>5</sub>, the following reaction happens:

\[ \text{V}_2\text{O}_5 + x\text{Li}^+ + xe^- = \text{Li}_x\text{V}_2\text{O}_5 \quad (x \leq 1) \]

V<sub>2</sub>O<sub>5</sub> is the working electrode in the three-electrode cell arrangement. Li electrodes are used for the reference and counter electrodes. Figure 6-4 shows a schematic diagram of the three electrode cell used for the intercalation process of Li in V<sub>2</sub>O<sub>5</sub> thin films. A solution of 1:1 M LiClO<sub>4</sub>/propylene carbonate is used as the electrolyte. It is ideal in this set up as it is a good conductor and does not react with Li electrodes (Li is very active metal).

After intercalation, the sample is removed from the solution and cut into two pieces (parts A & B) for the ion beam analysis. Part A was in contact with the LiClO<sub>4</sub> solution (i.e. was subjected to the Li intercalation process). Part B was above the solution (i.e. was the non-intercalated part) and was considered in this study to check any Li diffusion either
along the interlayer (e.g. Li ions trapped in the underlayer) or across the surface (see Figure 6-3).

Figure 6-4: A schematic diagram of the three electrode cell used for the intercalation process of Li in V$_2$O$_5$ thin films
6.3 Experimental arrangements

Parts A, B were mounted separately in a vacuum chamber (~10\(^{-6}\) mbar) set at the end of the microbeam line. They were fixed to a sample holder using conductive double sided carbon adhesive tape to ensure a conductive path from the sample to the sample holder to enable a beam current measurement. The samples were viewed via a microscope located in a chamber port at 135\(^{\circ}\) to the beam and equipped with a camera that connected to a TV monitor. Each sample was bombarded by protons directed perpendicularly to the surface.

A 2MeV proton beam was chosen to both induce \(\alpha\) particles from the \(^7\text{Li}(p,\alpha)^4\text{He}\) reaction and to collect backscattered protons simultaneously. The reasons for choosing this energy are:

- For 2 MeV protons the cross section of \(^7\text{Li}(p,\alpha)^4\text{He}\) reaction is high.
- The fluorine is present as a dopant in the SnO\(_2\) layer. At 2MeV the cross section of the \(^19\text{F}(p,\alpha)^{16}\text{O}\) reaction cross section is very low as is shown in Figure 6-5 [22].
- Choosing this energy is also excellent for the study of the elastic scattering of protons on Li since the non-Rutherford cross section is \(~40\) times higher than the Rutherford scattering (see Figure 6-6)
- Figure 6-7 shows the alpha particle energy versus incident proton energy at \(\theta_{\text{lab}}=150^{\circ}\) and \(\theta_{\text{lab}}=165^{\circ}\) for the \(^7\text{Li}(p,\alpha)^4\text{He}\) and the \(^19\text{F}(p,\alpha)^{16}\text{O}\) reactions respectively [22]. At 2MeV a clear distinction can be made between the energies of the two peaks of alphas emitted at the surface of the sample. The proton energy falls as it is slowed down in the V\(_2\)O\(_5\) layer, the energy difference between the two peaks increases. The reason being that for the \(^7\text{Li}(p,\alpha)^4\text{He}\) reaction inverse kinematics are obtained below 2MeV whilst for the \(^19\text{F}(p,\alpha)^{16}\text{O}\) reaction normal kinematics are observed.

These reasons make 2MeV ideal for the investigation of lithium intercalation into V\(_2\)O\(_5\) thin film.
A broadbeam of ~4mm\(^2\) was used to minimise the beam damage to the samples. This was performed by opening the apertures (slits) in the microbeam line. The beam current was set to ~1.5 nA. Run times of ~1 hour were needed to obtain reasonable counting statistics from very small amount of Li present.

An Ortec\textsuperscript{®} silicon surface barrier (SSB) detector was used of 100mm\(^2\) active area and thick enough (400\(\mu\)m depletion layer) to stop ~8MeV alpha particles. Backscattered protons were detected simultaneously in the detector. It was placed at an angle of 165\(^\circ\) to the direction of the beam and at ~80mm from the sample. The signal produced by the detector is routed through a preamplifier, an amplifier and finally an analogue to digital converter (ADC) i.e. the heights of pulses from the detection system are converted into numeric form. Data were acquired and handled using OM_DAQ software [55]. Figure 6-8 shows a schematic diagram of the experimental arrangements in the in-vacuum chamber.
Figure 6-5: The differential cross-section versus proton energy of the $^7\text{Li}(p,\alpha)^4\text{He}$ and the $^{19}\text{F}(p,\alpha)^{16}\text{O}$ reactions at $\theta_{\text{lab}}=150^\circ$ and $\theta_{\text{lab}}=165^\circ$ respectively [22]

Figure 6-6: The elastic scattering cross-section relative to Rutherford cross-section plotted versus the proton energy scattered from $^7\text{Li}$ at 165° [22]
Figure 6-7: Alpha particles energies versus proton energies from both $^7$Li(p,α)$^4$He and $^{19}$F(p,α)$^{16}$O reactions at $\theta_{lab}=165^\circ$.

Figure 6-8: Schematic diagram of the experimental arrangements using the microbeam chamber.
6.4 MCA energy calibration procedures

To establish an accurate energy calibration, seven points of calibration were obtained using a triple alpha source and a 2 MeV proton beam bombarding a standard thin LiF (48.9$\mu$g/cm$^2$) sample deposited on Mylar$^\text{TM}$ ($\text{C}_{10}\text{O}_{4}\text{H}_8$). NRA and BS spectra were obtained simultaneously.

The spectrum in Figure 6-9 shows (from left to right):

- Backscattered proton spectra from Li, C, O and F respectively.
- The $^3\text{He}$ peak from the $^6\text{Li}(p,^3\text{He})^4\text{He}$ reaction which has a Q-value (+4.02 MeV). This is normally obscured by the backscatter spectrum if the sample contains heavy elements. However, the peak is clear here since the sample does not contain heavy elements.
- Three alpha peaks from a triple alpha source.
- Two alpha peaks from the $^7\text{Li}(p,\alpha)^4\text{He}$ and $^{19}\text{F}(p, \alpha)^1\text{O}$ reactions.

The triple alpha ($^{239}\text{Pu}$ / $^{241}\text{Am}$ / $^{244}\text{Cm}$) source was placed inside the vacuum chamber facing the surface barrier detector. This source predominantly emits alpha particles at three distinct energies of 5.155 MeV, 5.486 MeV and 5.805 MeV respectively. The channel number in the spectra corresponding to the centroid of each alpha peak was determined.

Alpha particles induced from the $^7\text{Li}(p,\alpha)^4\text{He}$ and $^{19}\text{F}(p, \alpha)^1\text{O}$ reactions were collected. Kinematics calculations (see chapter 2 and Equation 2-6) gave energy values of 7.534 MeV and 7.289 MeV for the alphas induced from the two reactions respectively at the surface of the LiF sample and at detection angle of 165°. The channel numbers related to the surface in each peak was located taking into account the inverse kinematics (i.e. as the beam energy decreases while penetrating in the sample, the energy of the resulting alpha particles increases) of the $^7\text{Li}(p,\alpha)^4\text{He}$ reaction and the normal kinematics of the $^{19}\text{F}(p, \alpha)^1\text{O}$ reaction (see Figure 6-10).
Another two points can be obtained at low energies to obtain accurate calibration. These points are due to the elastic backscattering peak from the Li and the F. The energy of backscattered protons at the surface of Li and F are found at detection angle of 165° using the tabulated Kinematic factor [22] or Equation 2-2 to be 1.173MeV and 1.682MeV respectively. The channel numbers corresponding to the BS edges were positioned in the spectra as is shown in Figure 6-9.

Table 6.1 summarises the channel numbers used for the calibration process and the corresponding energies. The multi-channel analyser calibration line was obtained subsequently in Figure 6-11.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Channel</th>
<th>E(MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Backscattered particles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BS (Li)</td>
<td>93</td>
<td>1.173</td>
</tr>
<tr>
<td>BS (F)</td>
<td>130</td>
<td>1.682</td>
</tr>
<tr>
<td>Triple alpha source</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>380</td>
<td>5.155</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>404</td>
<td>5.486</td>
</tr>
<tr>
<td>$^{244}$Cm</td>
<td>428</td>
<td>5.805</td>
</tr>
<tr>
<td>Nuclear reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{19}$F(p, $\alpha$)$^{16}$O</td>
<td>534</td>
<td>7.289</td>
</tr>
<tr>
<td>$^{7}$Li(p,$\alpha$)$^{4}$He</td>
<td>550</td>
<td>7.534</td>
</tr>
</tbody>
</table>

Table 6.1: Summary of the channel numbers used for the calibration process and the corresponding energies
Figure 6-9: NRA and BS spectra collected at the same time for the LiF thin film deposited on Mylar™. The triple alpha peaks from ($^{239}$Pu / $^{241}$Am / $^{244}$Cm) source are shown.
Figure 6-10: Two alpha peaks from the $^7\text{Li}(p,\alpha)^4\text{He}$ and the $^{19}\text{F}(p,\alpha)^{16}\text{O}$ reactions at $\theta_{\text{lab}}=165^\circ$.

Figure 6-11: Energy calibration of the multi channel analyser.
6.5 The Ion Beam Analysis DataFurnace software

The phrase *simulated annealing* derives from the physical process of heating and then slowly cooling down a substance to obtain a superior crystalline structure [83]. The annealing process consists of three stages: heating the substance to the desired temperature, holding it at that temperature, and finally cooling it down gradually to the room temperature or even less. The annealing process tends to align atoms or molecules on the crystal lattice sites (i.e. no defects) as shown in Figure 6-12. Metals for instance are normally subjected to an annealing process to make them less brittle and more workable. Sequences of times and temperatures are critical in the annealing process (called annealing or cooling schedules). The cooling rate should happen in many steps and has to occur over a fairly long time. Failure to do so may cause the final state of the system to be distorted.

![Figure 6-12: The annealing process tends to align atoms or molecules on the crystal lattice sites](image)

Simulated annealing [83] is a programming method that tries to simulate the physical process of annealing. Figure 6-13 shows a simple outline of the simulated annealing algorithm. Using this algorithm, different “hard” problems can be solved (including “annealing”). The main purpose of this algorithm is to find the minimum of an *objective function* that controls the investigating system. To understand this we can simplify the situation by going back to the annealing process. In the annealing process, from an
existing state \( i \) of the system with energy \( E_i \), another state \( j \) with energy \( E_j \) is produced by a random process, where the state \( i \) is slightly changed. If the energy decreases in the transition the system is taken to be in the new state \( j \). If the energy increases, then the transition has a certain probability given by the Boltzmann factor. That is the probability of accepting a transition is controlled by the following rules:

\[
P = \begin{cases} 
1 & \text{if } \Delta E < 0 \\
\exp(-\Delta E / k_B T) & \text{if } \Delta E > 0 
\end{cases}
\]

where \( T \) is the absolute temperature of the system, and \( k_B \) is the Boltzmann constant. If the original temperature of the system is set to be high enough, and if the cooling rate happens in many steps and occurs in fairly long times then at \( T = T_{\text{min}} \) the system is has to be in a state with minimum energy. The introduction of a non-zero probability if \( \Delta E > 0 \) allows the process to progress until obtained the global minima rather than trapped in a local minima.

\[\text{Figure 6-13: Simulated annealing algorithm outline}\]
In 1997, Nuno Barradas et al. [3] applied the simulated annealing algorithm to the analysis of Rutherford backscattering data. Their analogy to simulated annealing considers [26]:

- The state of the system is defined as the possible structure of the sample (i.e. number of layers, layer thickness and stoichiometry).
- A state transition is defined as the production of a new structure derived from the previously calculated one by randomly changing the depth profiles by some amount.
- The probability $P$ of accepting a transition depends on the related change in the chi squared ($\chi^2$)

$$P = \begin{cases} 
1 & \text{if } \Delta \chi^2 < 0 \\
\exp(-\Delta \chi^2 / T) & \text{if } \Delta \chi^2 > 0 
\end{cases}$$

where $\Delta \chi^2$ is the change in the $\chi^2$ due to the transition and $T$ is a control parameter.

WiNDF (Figure 6-14) is a Windows® interface to the NDF (Nuno’s DataFurnace) code. It is an advanced data analysis tool which solves the inverse problem for MeV ion beam analysis data (i.e. “given the spectrum, what is the depth profile?”). It can handle RBS, EBS (non-RBS), ERD, and non-resonant NRA.

In the fitting process many test elemental depth profiles are generated, and a calculation is made of the chi-squared difference between the spectrum simulated from the current test profile and the real spectrum to be fitted. Thus, for one fit many thousands of spectra may be simulated. The algorithm is able to increase or reduce the number, stoichiometry and thicknesses of individual layers in the test profiles, completely independently of the analyst.
The main specifications of DataFurnace are,

- It can handle RBS, EBS (non-RBS), ERD, and non-resonant NRA data simultaneously.
- It can simulate spectrum before fitting to check the energy calibration and to validate the software parameters.
- It fits the spectrum given only the experimental conditions and the knowledge of the elements in the sample.
- It supports wide variety of data formats.
- Graphical output with a variety of spectral manipulation and display options is provided.
- Straggling and pile up corrections are supported.

Figure 6-14: Windows® interface to the IBA DataFurnace software
6.6 Demonstrating DataFurnace fitting with a known uniform LiF sample

To validate the use of NRA measurements to study Li depth profiles intercalated into V$_2$O$_5$ sample, a preliminary study was performed using a standard thin layer of lithium fluoride (LiF) (48.9µg/cm$^2$) deposited on Mylar™. The Li concentration is considered to be uniform across the whole depth of this sample. Lithium is identified by detecting alpha particles induced from the $^7$Li(p,$\alpha$)$^4$He reaction. This reaction is ideal for Li detection since $^7$Li constitutes ~92% abundance of the natural lithium and the reaction has a high Q-value (+17.347MeV). The use of $^6$Li(p,$^3$He)$^4$He or $^6$Li(p,$^4$He)$^3$He reactions is not widely used due to the low abundance of $^6$Li compared with $^7$Li. The whole spectrum collected from this sample was discussed previously in the calibration process. Figure 6-10 above shows the energy spectrum of the alpha peak where the sensitivity of the Li detection is a maximum at the surface and drops deeper into the sample. This is due to the drop in the reaction cross section as the proton beam energy reduces whilst penetrating the sample.

The $^7$Li(p,$\alpha$)$^4$He reaction cross section versus proton beam energies were obtained using Experimental Nuclear Reaction Data (EXFOR) [46], which is hosted by the International Atomic Energy Agency (IAEA). It contains most of the available experimental nuclear cross-sections relevant to the Ion Beam Analysis techniques (more than 16,300 experiments).

Similar to the case of BS, the energy scale in the NRA spectra can be translated into depth information. The IBA DataFurnace BS software was modified initially to incorporate NRA data in the study of depth profiles of deuterium diffusion in polymer films via the D($^3$He,p)$\alpha$ reaction [84]. It can now handle both NRA data for any reaction and RBS data at the same time.
Figure 6-15 shows the best fit to the backscattering spectrum from the LiF film and the substrate (Mylar™), where the non-Rutherford effects of the carbon, oxygen, lithium and fluorine were taken into account. Two fits for the alpha peaks corresponding to the $^7\text{Li}(p,\alpha)^4\text{He}$ and the $^{19}\text{F}(p,\alpha)^{16}\text{O}$ reactions are also displayed. The yield of the alpha peak corresponding to the $^{19}\text{F}(p,\alpha)^{16}\text{O}$ reaction is lower than that of the $^7\text{Li}(p,\alpha)^4\text{He}$ due to the differences in the cross sections of both reactions. The best structure of LiF and the Mylar™ substrate (relative concentration versus depth) has been obtained and are shown in Figure 6-16. Li depth profiles were evaluated from the BS and NRA measurements simultaneously taking into account the fact that for ~2000keV incident protons the non-Rutherford scattering cross section is ~40 times higher than the Rutherford one for Li [22].

By doing this preliminary study on LiF standard, the different components of the IBA DataFurnace software (e.g. geometry files, structure files, calibration, etc...) were verified and established to investigate Li depth profiles after intercalation in V$_2$O$_5$ thin films.
Figure 6-15: NRA and BS spectra collected at the same time for the LiF thin film deposited on Mylar™. The best fit for both NRA and BS data is shown.
6.7 Verifying the thickness of $V_2O_5$ and SnO$_2$ layers by means of BS measurements

To confirm the thickness of $V_2O_5$ and SnO$_2$ layers in the sample, BS measurements were carried out using a 2MeV proton beam in a sample as deposited (i.e. not exposed to Li intercalation process). Figure 6-17 shows the BS spectrum of this sample. The channel number in the spectrum represents the energy scale which can be translated (using our calibration- see Figure 6-11) into a depth scale. The Sn peak is more dominant than V since the BS cross section is higher for heavy elements. The Sn peak presents at the high energy end of the backscatter spectrum, despite the fact that Sn is deeper in the sample as it is the heaviest element in the sample. The width of each peak is related to the thickness of the corresponding element in the sample. This can be determined by calculating the energy loss of protons in the different layers of the sample using the tabulated stopping powers and ranges of ions in matter or by using the simulation package SRIM software [25]. This can be performed much more easily by using special software. Different BS simulation and fit packages have been developed such as SIMNRA [85] and ALEGRIA [86]. The IBA DataFurnace software (discussed in section 6.5) written by Barradas et al. [3] is a novel code routinely used at Surrey that can quickly, accurately and automatically
extract depth profiles from ion beam analysis data. It was first devised to handle BS data. This has been extended to include NRA [84]. The BS spectrum in Figure 6-17 was fitted by the IBA DataFurnace taking into account the non-Rutherford effects for O (in the whole sample) and Si (in the substrate). Non-Rutherford data were obtained using SigmaCalc software. This software is hosted by The Nuclear Data Section of the International Atomic Energy Agency (IAEA) [24]. The best structure (the depth profile obtained from the best fit) of V$_2$O$_5$ and SnO$_2$ was subsequently obtained in Figure 6-18. The energy calibration was corrected by IBA DataFurnace to include the energy loss of the detected particles in the dead layer of the detector (40µg/cm² of Au), and also to take into account any possibility that the nuclear collisions in the active layer of a Si detector do not contribute to the formation of the electron-hole pairs [87].

Figure 6-17: Backscattering spectrum of V$_2$O$_5$\SnO$_2$\glass substrate sample
Figure 6-18: V$_2$O$_5$, SnO$_2$ and glass absolute (atomic %) concentration profiles of V$_2$O$_5$|SnO$_2$|glass sample

6.8 Investigating Li depth profiles in V$_2$O$_5$ thin films after intercalation process

The part that had been subjected to the intercalation process (Part A) was bombarded with protons to study the Li content across the sample. Both NRA and BS spectra were collected simultaneously using OM_DAQ data acquisition system. The alpha peak from the $^7$Li(p,$\alpha$)$^4$He reaction is shown in the spectrum (Figure 6-19) while the alpha peak due to the presence of F is negligible and does not overlap with the one corresponding to Li. This made the analysis easier (no peak interference was observed). The backscatter spectrum of the whole sample was collected. The peak corresponding to the protons backscattered from the vanadium does not appear as it is buried under the one corresponding to Sn. The peak corresponding to the backscattered protons from Li is clear since the non-Rutherford effect is high enough to make it apparent at the top of the backscatter spectrum. This peak is ideal to inform the Li depth profile in addition to considering the alpha peak corresponding to the $^7$Li(p,$\alpha$)$^4$He reaction.
Data were analysed, again using the IBA DataFurnace software. Different necessary components of the software (e.g. the structure files, the geometry files, batch file, calibration, etc) were obtained from the previous NRA and BS investigation on the standard LiF sample and the non-intercalated V₂O₅ sample respectively. Non-Rutherford effects of Li were taken into account in the software to consider Li depth profiles using backscattering data in addition to NRA. Figure 6-19 shows the collected spectra and the best fit for NRA and BS data. The peak corresponding to the backscattered protons on Li is fitted as well as the alpha peak corresponding to the \(^7\)Li (p,α)\(^4\)He reaction. The rest of the backscatter spectrum corresponding to V, Sn and the substrate is fitted as well.

The Li depth profiles obtained from simultaneous fitting of both BS and NRA data are shown in Figure 6-20. This presents the relative concentration of Li compared with other components of the sample versus depth. It implies that Li has intercalated across the V₂O₅ thin layer. With the exception of the surface where high Li content is observed, the Li distribution seems to be homogeneous across the V₂O₅ thin film. Some Li was detected at the SnO₂*F/glass interface.
Figure 6-19: BS and NRA best fit obtained for Part A

Figure 6-20: Li depth profiles obtained from both NRA and BS data for Part A
Part B, which was not in contact with LiClO₄ solution (i.e. has not been subjected to the intercalation process), has been studied in similar way to Part A. The detection discriminator level was set high enough to eliminate the signals from elastically scattered particles, to minimise the background. This has been performed to reduce the backscattering spectra from the substrate but not from Sn or V (i.e. the peaks corresponding to them are not eliminated). Doing so has increased the sensitivity of detecting the alpha particles from Li with low concentration (i.e. has reduced the detection system dead time). This procedure was repeated in the case of Part (A) to make a comparable study between the two cases. An alpha peak corresponding to the $^7\text{Li}(p,\alpha)^4\text{He}$ reaction is shown, implies that part (B) has Li content. Figure 6-21 shows alpha peaks due to the $^7\text{Li}(p,\alpha)^4\text{He}$ reaction in both Part (A) and (B) respectively. This finding provides evidence of a Li diffusion to the part that had not been subjected to the intercalation process. To find out how the diffusion has occurred, a new study using IBA DataFurnace was established.

![Figure 6-21: Two alpha peaks from the $^7\text{Li}(p,\alpha)^4\text{He}$ reaction in both Part (A) and (B) respectively](image)

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DataFurnace has the advantage of being able to deal with a situation where severe low level discrimination is used. The program can make a rough guess at the shape of the spectrum it can not see. Figure 6-22 shows the spectrum collected where the backscattered protons from the substrate were eliminated, and its estimated fit. The fit includes Sn and V peaks. The alpha peak corresponding to the \(^7\text{Li}(p,\alpha)^4\text{He}\) reaction is zoomed in to be shown and has been fitted by the software too.

NRA data implies that diffusion has occurred in Part B across the width of the electrode surface (i.e. across the V\(_2\)O\(_5\) thin film) as is seen in Figure 6-24. Depth profiles were obtained using NRA data only since the BS spectrum has been rejected by setting the MCA discriminator to be high. Figure 6-20 and Figure 6-23 show similar behaviour of the Li content. This is expected since both cases are dealing with the same sample (Part A). This implies that Li depth profiles can be obtained from either NRA (using \(^7\text{Li}(p,\alpha)^4\text{He}\) reaction) or the combination between NRA and BS using the IBA DataFurnace with good agreement.
Figure 6-22: BS estimated fit (for the discriminated part) and NRA best fit obtained for the Part A
Figure 6-23: Li depth profiles obtained from NRA data for Part A

Figure 6-24: Li depth profiles obtained from NRA data for Part B
6.9 Overall conclusions and discussion

It has been shown that lithium depth profiles after intercalation into V\textsubscript{2}O\textsubscript{5} thin films can be determined using ion beam analysis techniques (IBA). NRA and BS measurements were carried out simultaneously.

The IBA DataFurnace software has been tested on a uniform LiF sample deposited on Mylar\textsuperscript{™} to validate its use to investigate Li depth profiles using the \(^7\text{Li}(p,\alpha)^4\text{He}\) reaction. This was followed by a BS study of non-intercalated sample of V\textsubscript{2}O\textsubscript{5} deposited on conductive layer of SnO\textsubscript{2}*F on glass substrate to verify the thicknesses of its components. The part that had been subjected to the intercalation process was investigated using both NRA and BS techniques. The Li depth profile implies a homogeneous distribution of Li across the V\textsubscript{2}O\textsubscript{5} thin film. A rise in the Li content was observed at the surface and on the interface between the substrate and the conductive layer of SnO\textsubscript{2}*F.

Lithium was also observed in the part that had not been subjected to the intercalation process (the part which was above the electrolyte). Analysis has shown that this is due to diffusion within the V\textsubscript{2}O\textsubscript{5} layer.

This study represents the first application of using both NRA and BS measurements at the same time to investigate the Li distribution in V\textsubscript{2}O\textsubscript{5} thin films using the novel IBA DataFurnace software. This study could make a contribution towards the development of rechargeable micro-batteries.
Chapter Seven: External Beam Scanning Micro-PIXE Studies of Cementitious Materials

7.1 Introduction

7.1.1 Basic Definitions

_Cement_ is a powdered material with adhesive properties, which chemically hardens when mixed with water on drying to form a _neat paste_. The most common type of cement is _Ordinary Portland Cement_ (OPC), which is made of a mixture of oxides (CaO, SiO₂, Al₂O₃, Fe₂O₃ and others) in specific proportions and subject to special heat treatment. If OPC is mixed, in a specific proportion, with another cement component chosen to give it a specific required property then the resulting cement is called _a blended cement_. For instance, _Pulverised Fuel Ash_ (PFA), which is produced as a result of coal burning in power stations, can be mixed with OPC in certain proportions to give the cement high performance and resistance to chloride ingress [88].

If aggregate (a mixture of sand and stones) is mixed with paste (as 75% volume filler), then the dense material formed is called _concrete_ or _mortar_, depending on the size of the aggregate, whether it is coarse (>10mm) or finely ground respectively. The ratio between cement and aggregate must be chosen carefully to obtain the desired strength. Concrete is usually used in bridges and buildings as it both forms a very hard mixture [89] and is cheaper. Steel rods (_rebars_) are often inserted inside the concrete, (e.g. in buttresses in buildings and bridges) to form what is called _reinforced concrete_.

Water is the most significant ingredient of concrete. It allows the concrete to be both semi-liquid (and therefore easily handleable) and to react with the cement powder to set it and make it harden after drying. The water to cement ratio (w/c) plays a crucial rule in determining the strength of concrete and its permeability to water (and hence to the
penetration of any dissolving ions such as chlorides or sulphates) and it should be chosen carefully.

### 7.1.2 Concrete deterioration

Concrete structures (e.g. bridges, tunnels and buildings) cost enormous amounts of money. They are built with the intention of them lasting for a very long time (e.g. in the UK the bridges should have a life time of ~120 years). There are many factors affecting the durability of concrete. The basic causes of damage and deterioration of concrete include accidental loading, chemical reactions, corrosion of embedded metals, temperature changes,...etc [90]. Chloride and sulphate ingress from the surrounding environment is often the cause of adverse chemical reactions.

#### 7.1.2.1 Chloride attack

Corrosion of steel in concrete is the major deterioration factor affecting the durability of reinforced concrete. Billion of dollars are spent every year around the world to repair reinforced concrete in highway bridges [73].

Steel in reinforced concrete is protected by a thin (~10nm) layer of oxide formed by high pH (~13-13.8) of concrete pore water due to the presence of calcium, potassium and sodium hydroxides. This means that steel should remain effectively insulated and hence have a negligible corrosion rate for many years. However if it is subject to chloride attack, which lessens the alkalinity, it can lose this protection. It has been demonstrated that the presence of chloride ions in reinforced concrete is one of the major factors behind the occurrence of steel corrosion [91]. De-icing salts and marine environments are the main sources of chlorides. When the chloride exceeds a critical concentration (typically ~0.4 % by weight of the cement), the corrosion starts to occur in the presence of water and oxygen according to the following chemical mechanism [92]:
\[ \text{Fe}^{++} + \text{Cl}^- \rightarrow \text{FeCl}_2 \]
\[ \text{FeCl}_2 + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{HCl} \]

\( \text{Fe(OH)}_2 \) (Ferrous Hydroxide) can be further oxidised in the presence of oxygen to form \( \text{Fe(OH)}_3 \) (Ferric Hydroxide) followed by the formation of the rust.

\[ 4\text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 \]
\[ 2\text{Fe(OH)}_3 \rightarrow 2\text{Fe}_2\text{O}.3\text{H}_2\text{O} \text{(Rust)} + 4\text{H}_2\text{O} \]

The characterisation of chloride diffusion is normally governed by Fick's second law [93, 94], which assumes that the concentration gradient is the only driving force of the penetration of chloride into concrete. However, more complicated models have been introduced to include some other factors affecting the chloride penetration [95].

Different methods have been established to give the concrete high resistance to chloride penetration. These include using intense concrete with a low w/c ratio, covering the exposed part of concrete by protective layer of resin, covering the rebars with a thin metallic layer (e.g. zinc) and finally by means of cathodic protection [96]. Using a PFA\(\text{OPC}\) blend can also inhibit chloride penetration into concrete.

7.1.2.2 Sulphate attack

The presence of sulphate salts (e.g. \( \text{CaSO}_4 \), \( \text{K}_2\text{SO}_4 \), \( \text{Na}_2\text{SO}_4 \), and \( \text{MgSO}_4 \)) either in the ground or mixing water or in saline environments affects the durability of concrete. The sulphate attack mechanism [97, 98] involves a chemical reaction between the free calcium hydroxide (\( \text{Ca(OH)}_2 \)) in the paste and the sulphate to form calcium sulphate (gypsum). The gypsum combines with hydrated calcium aluminate to form calcium sulphaaluminate (ettringite). Both gypsum and ettringite have bigger volumes than the reactant materials resulting in cracking and breakdown in the concrete structure. The inhibition of sulphate attack can be obtained (as in the case of chloride attack) by using dense high quality concrete with low water/cement ratio and by using special cement blends.
7.1.3 Decontamination of cementitious materials

7.1.3.1 Electrochemical chloride extraction

As the presence of chlorides can lead to corrosion in reinforced concrete structures, in chloride contaminated structures, it is very important to have methods to decrease the corrosion attack on the reinforcing steel. Electrochemical chloride extraction (ECE) methods for removing chloride ions, and hence forcing them to move out of the concrete systems, have been established [99]. They are based on the migration of the chloride in the concrete specimen in the presence of an electric field. Both electrochemical chloride extraction (ECE) and cathodic protection (CP) are based on the same idea. The difference is that CP is usually permanently installed in the structure and operates at low current densities. In the case of ECE, it is a temporary treatment procedure that is applied to a contaminated structure. High current densities are required to perform the treatment and 4-8 weeks are typically needed.

Figure 7-1 shows a simple diagram of an ECE set up. The anode is the electrode to which negatively charged chloride ions migrate when an electric voltage is applied across the concrete. At the anode, ECE can generate the following reactions [100]:

\[ 2\text{H}_2\text{O} \rightarrow 4e^- + \text{O}_2 + 4\text{H}^+ \]
\[ 2\text{Cl}^- \rightarrow 2e^- + \text{Cl}_2(g) \]

By contrast at the cathode, to which positively charged ions migrate, two possible reactions can occur:

\[ 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 4\text{OH}^- \]
\[ \text{H}_2\text{O} + e^- \rightarrow \text{H} + \text{OH}^- \]

The first set of reactions shows that chloride ions are oxidised to form chlorine gas at the anode. The second set shows a pH increase due to the production of hydroxide ions at the cathode, which has a positive effect on corrosion prevention.
7.1.3.2 Electro-Kinetic radioactive heavy metals extraction

Concrete is widely used to form shields against radiation in nuclear reactors since it is a very good absorber of penetrating radiations and has reasonable set up cost [101]. During nuclear reactor operation, large quantities of radioactive products build up in the shielding structure making it a source of radiation contamination. Because of that any reactor has a service life that has to be taken into account. Therefore it is very important to find a way to decontaminate these structures in order to dispose of them in a conventional way. The decontamination of a nuclear reactor is called decommissioning.

The decommissioning [102] of a nuclear reactor involves several actions at several stages to allow it to be safely removed from service (when necessary) and to reduce any residual radioactivity to a level that makes it safe for the public and the environment. The decommissioning process takes a long time- of the order of several years. To accelerate this procedure, electro-kinetic methods have been devised [103]. Similar to the case of the chloride extraction method mentioned above, a DC electric field is applied across the contaminated concrete to transport the heavy element contaminants from the concrete.
pores to a collector placed at the concrete surface. Figure 7-2 shows an outline of a typical decontamination cell [104]. The cementitious material is sandwiched between two chambers containing cathode and anode electrodes respectively both being immersed in electrolyte solutions.

Figure 7-2: An outline of a typical electro-kinetic decontamination cell
The study of the content of cementitious materials is an important issue since it can provide extremely useful information regarding the cause or causes of failure of concrete. Chemical analysis methods have been used to investigate qualitative and quantitative measurements of the concrete contents [105]. These tests involve crushing the concrete sample to a fine dust and subjecting it to traditional wet chemical methods. It is obvious that wet chemical methods are both destructive procedures and expensive. Non-destructive, modern and faster techniques have been devised [106] including X-ray fluorescence [107], Atomic spectrophotometry and Scanning electron microscopy. Electro-chemical analytical techniques have also been developed [108].

An in-vacuum micro-PIXE technique was used for the first time at Surrey University to study diffusion of chloride into paste cement [109] demonstrating its potential to be a powerful tool to monitor the presence of chloride in concrete.

This report describes external beam scanning micro-PIXE technique that has been developed to study cementitious materials. There are many reasons for choosing this technique [110]. The most important ones are that PIXE is a non-destructive method and sensitive to elemental concentration levels as low as ppm (part per million by weight). In air the samples can be large ones with dimensions of several cm.

A proton beam spot size of ~50 microns can be obtained. Magnetic beam scanning across a circular area of 3mm diameter can be achieved. Larger distances are covered by moving the sample in 3mm steps, doing a scan at each step. NO sample preparation (other than cutting a flat surface) is necessary. The spatial distribution of all elements heavier than aluminium is given simultaneously in only 1 - 5 minutes.
This technique has been applied in this thesis to study of:

- Chloride diffusion in laboratory prepared mortar samples.
- Sulphate diffusion in laboratory prepared concrete samples.
- Chloride and sulphate diffusion in samples taken from concrete blocks exposed to sea water for ~30 years.
- Electrochemical chloride extraction from cement paste.
- The investigation of heavy metal distribution in both mortars and bricks, before and after extraction techniques (in conjunction with simultaneous BS measurements).
7.2 Experimental arrangements

The experimental arrangements near the beam exit window are shown in Figure 7-3. The proton beam is brought into air through a copper nozzle of 3mm internal diameter covered by a Kapton™ foil 8 microns thick. Samples are placed with their front faces at a distance of a few millimetres from the exit window on an XYZ traversing stage. They can be aligned and viewed on a TV monitor (Figure 7-7). A 2.5MeV proton beam is used to induce characteristic X-rays from the samples. SRIM simulations [25] imply that protons of energy ~2.3MeV reach the sample after suffering energy loss in the exit window (8 microns Kapton™) and ~5mm of air. A proton beam spot of 50-60 microns is typically obtained. This can be raster scanned over the sample in two directions resulting in a circular scanning area (due to the shape of the exit window) of 3mm diameter. Samples can be traversed vertically or horizontally in 3mm steps across the beam from one edge to another. At each step they are raster scanned by the proton beam to obtain the required elemental profiles across the whole sample.

A lithium drifted silicon detector (Si(Li)) with an area of 80mm² collimated with a conical aperture, to enable He gas flow towards the sample, is used to collect PIXE spectra. The detector is calibrated using characteristic X-rays induced from Cu, Si, and Fe foils. It is placed at an angle of 135° to the direction of the beam and its front face is ~20mm from the target. The signal produced in the detector is amplified and routed into an analogue to digital converter (ADC). The Oxford Microbeam Ltd data acquisition system [55] (OM_DAQ) is then used to read the ADC, correlate the signal with the raster (x,y) position of the beam and display the 2-D data in addition to the collection of the PIXE spectra (see Figure 7-4).

A silicon surface barrier detector (SSB) of 50mm² active area is used to pick up backscattered (BS) protons from the sample simultaneously with PIXE to allow both beam charge measurements and the characterisation of the local matrix composition. It is placed at an angle of 135° to the direction of the beam and its front face is ~15mm from the target. It is equipped with a nozzle that allows a He gas stream between the detector
and the sample. Standard electronics (preamplifier, amplifier and ADC) are connected to the SSB detector to enable the collection of the backscatter spectra. OM_DAQ is used to acquire the BS spectra at the same time as the PIXE. The energy calibration of the SSB detectors is achieved by bombarding different known target materials with the beam and collecting the corresponding BS spectra. Pure foils of Si, Fe and Cu were used as targets. Kinematics calculations (see Equation 2-2 in chapter 1) have been made to allow calibration of the charged particle detector taking into account the energy loss before and after the collision with the target sample.

Beam intensity is monitored by detecting the protons backscattered from a chopper (see chapter 3) located upstream in the evacuated section of the beam line. Beam current measurements are made with an in-vacuum Faraday cup before and after each run and the time of the run is also noted.

Induced characteristic X-rays and backscattered protons from the samples are detected, spectra are collected and 2-D maps of each of the elements in the samples are obtained.

Figure 7-3: Experimental arrangements near the beam exit window

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Figure 7-4: An outline of the Oxford microbeam Ltd data acquisition system (OM-DAQ)

To establish optimum experimental conditions for data taking using the external microbeam line, several advanced procedures have to be performed each time data is collected. These include:

7.2.1 Checking the uniformity of X-ray detection within the scan area

The X-ray detector has, in front of it, a thick polyethylene cylindrical nozzle with a conical end. This both cuts down light ingress to the detector and allows the flow of helium between the detector and the sample. It also, however, acts as a collimator (see Figure 7-5).

To ensure that the detector collects X-rays in a uniform way across the scanned sample, a run is taken on a homogeneous iron foil placed perpendicular to the beam and a 2-D map...
of Fe X-ray intensity is obtained. The sample position along the beam direction (the Z-axis) is then adjusted (using an XYZ stage traversing table) and new measurements are taken. This procedure is repeated several times in order to obtain the most uniform map as shown in Figure 7-5. The numbers refer to the Z-position of the sample relative to the beam exit nozzle. It is clear that the position numbered (3) is the best at a distance of about 5mm from the exit window. An iron profile is shown at this position in Figure 7-6 obtained by summing up the counts vertically in each pixel of the Fe X-ray map and then dividing the resulting number by the number of these pixels. A flat profile is obtained. This implies that the X-ray detection efficiency across the scanned area is uniform.

Figure 7-5: Adjusting the distance between uniform iron sample and the beam exit nozzle to obtain the best uniform elemental mapping. Numbers refer to the Z-position of the sample relative to the beam exit nozzle.
7.2.2 Focusing the beam and positioning the scan area on the sample using the optical system

After the sample is correctly positioned, the traversing table is fixed in this position. To allow subsequent accurate alignment, the optical system is used (see Figure 7-7). This consists of an alignable laser, a mirror and a microscope equipped with a camera connected to a TV monitor. A scintillator (a substance in which molecules, ionised by high energy charged particles, fluoresces in the visible part of the electromagnetic spectrum) is placed at the distance decided from the previous stage (see 7.2.1 above).

When the beam is brought into air, it passes through the exit foil (8 microns thick Kapton™). It then passes through 5mm of air. It undergoes both energy loss and straggling in both these two media and its smaller size at the scintillator is ~50 microns.
The focussing magnets in the external beam (see Figure 3-7) are optimised to give the smallest beam focus at the scintillator as viewed on the TV monitor.

A laser beam is positioned at the same place as the proton (unscanned) focussed beam spot by adjusting the laser tube orientation. The laser is then fixed at this position and can be used subsequently to align the samples, since they do not usually have the ability to scintillate when bombarded by the beam. Before removing the scintillator, the beam is scanned across it to determine the scan area. This is monitored on the TV screen, via the microscope and the camera. Vertical and horizontal line cursors can be set to show the limits of the scan area. The beam spot is set to be in the middle of the scan area by adjusting the exit nozzle vertically and horizontally. The scan area is circular since the exit window shape is circular. The scan size is set using a scanning amplifier controlled by a computer and the Oxford Microbeam Ltd data acquisition system (OM_DAO).

Figure 7-7: The optical system used for the samples positioning in the external beam
7.2.3 Demonstrating the influence of the helium gas between the sample and both PIXE and BS detectors

In PIXE measurements the low energy X-rays are attenuated whilst passing through the air towards the detector. The presence of argon in the air produces a characteristic Kα X-ray peak in the PIXE spectra, which can be used as a good monitor of the beam current. Using He gas flow between the sample and the detector reduces the attenuation effects of the air. Figure 7-8 shows the transmission of X-rays [111] through 1Bar pressure of He gas and air respectively over 2cm distance. It is clear that using He gas has a positive effect on the detection of soft X-rays. Figure 7-9 demonstrates this using a sample of concrete. The argon X-ray peak has been reduced, the total number of counts of the whole spectrum has increased and the soft X-ray detection efficiency has improved.

The presence of the air in external microbeam measurements also causes the beam to undergo energy loss and straggling and therefore affects the resulting BS spectrum. Figure 7-10 shows SRIM simulations of the energy loss of 2MeV protons in both He and air. Energy loss is about 10 times greater in air than in He. The corresponding energy straggling is also greater. Two backscattering spectra for a concrete sample, collected with and without He gas flow, are shown in Figure 7-11. Three main features can be observed, first the shift in the whole spectrum towards low energies when the He gas is not flowing due to the greater energy loss. A massive peak due to nitrogen appears in the spectrum when air is dominant since it constitutes ~75% of the air. It obvious that it decreases when He gas is used. The residual peak represents a measurement of any remaining air. The third main aspect is the intense backscattering peak of the He when it is flowing. This peak can be used for beam current monitoring and energy calibration.
Figure 7-8: The X-ray transmission through 2cm of He gas and air respectively (1bar pressure at room temperature)

Figure 7-9: Two X-ray spectra of a concrete sample collected without and with He gas between the detector and the sample for the same beam charge
Figure 7-10: The energy loss of 2MeV backscattered protons in air and in He gas

Figure 7-11: The influence of the presence and absence of the He gas atmosphere between the sample and the charged particle detector on the backscattering spectrum
7.2.4 Energy calibration of both PIXE and BS detectors

The energy calibration of both PIXE and RBS detectors is achieved by bombarding different known target materials with the beam and collecting the corresponding PIXE/RBS spectra. Pure foils of Si, Fe and Cu were used as targets. Their characteristic X-rays are used to calibrate the X-ray detector (Si(Li) detector). Kinematics calculations (see Equation 2-2 in chapter 1) have been made to allow calibration of the charged particle detector taking into account the energy loss before and after the collision with the target sample.

7.3 Data recording procedure (the list mode option)

Data acquisition software was used in the list mode option where every event read by the system is stored sequentially in a binary file as a list of \((E, X, Y)\) triplets, where \(E\) is the X-ray or RBS energy, \(X\) and \(Y\) are the positions of the beam spot. The file can be played back after the run to generate new maps from selected regions of the scan. This is ideal in the study of mortar/concrete systems. This will be shown later.
7.4 Preliminary studies of diffusion of chloride in cement paste/mortar

7.4.1 Preliminary study to assess the capability of external micro-PIXE to detect chloride in cement

7.4.1.1 Sample preparation

To establish the possibility of detecting chloride Kα X-rays in cementitious materials using the external beam, standard samples of cement paste (a mix of water and cement) containing sodium chloride were made. The mass ratio between the water and the cement was chosen to be W/C=0.4. Samples were made containing known concentrations of chloride. The chlorine content was 0%, 0.5%, 1.5% and 2% respectively of the mass of the whole mix of the cement paste. Samples were cured in sealed containers.

7.4.1.2 Experimental and results

Using a 2.5 MeV proton beam from the accelerator, each sample was raster scanned to induce characteristic X-rays from the elements present. The resulting induced X-rays were collected using the Si(Li) detector. The energy spectra of the samples are shown overlaid in Figure 7-12. The spectra were normalised to the Ca counts. The number of counts in the Cl X-ray peak is directly proportional to the concentration of the chloride. This was proved by measuring the number of counts in the chlorine peak and normalising it to that of the Ca peak in each spectrum, since the Ca content is the same in each sample. CaO constitutes ~60% by mass of the whole sample (i.e. Ca is a matrix element). These ratios were plotted versus the chloride concentrations. A separate normalisation of Cl X-ray counts was obtained, this time relative to the chopper reading. A linear fit is obtained in both normalisation methods (Figure 7-13). Excellent agreement between the two normalisation techniques is obtained. This implies that external micro-PIXE technique is capable of detecting the presence of the chloride in cementitious materials at a level of ~0.5% by weight. Two different normalisation methods can be applied,
• One is internal to the Ca counts
• The other is external to the chopper readings.

This conclusion encouraged us to do more investigation by moving on to study chloride diffusion in mortars.

Figure 7-12: Four overlaid X-ray spectra of cement paste samples containing chloride of 0%, 0.5%, 1.5% and 2% by the total mass
Figure 7-13: Normalised chloride counts (using both internal and external normalisation methods) versus the chloride content of each sample. The linear fit is constrained to pass through zero

7.4.2 Preliminary study of chloride diffusion profiles into cylindrical OPC\PFA blended mortar

7.4.2.1 Sample preparation

A cement combination containing 70% OPC and 30% PFA by mass was used. The water and aggregate ratios to cement were W/C=0.4 and A/C=4.5/1 respectively. These were mixed together using a special blender for about 60 seconds. The mix was cast into plastic cylindrical tubes, 60mm diameter and 100mm height. Entrained air bubbles were removed by vibrating the mortar mix using a mechanical vibrator. The mortar sample was let to cure for a month. It was taken out of the plastic container and left over two months in 5% by mass of Cl\ solution to study the diffusion ingress of Cl into it. Subsequently it was cut in a transverse direction (see Figure 7-14) to study the chloride diffusion profile in the exposed cross section. Beam scanned areas are shown in the same figure from the centre towards the edge.
Figure 7-14: Mortar sample emersion in the chloride solution. The sample cutting procedure and the scanned areas are shown.
7.4.2.2 Experimental and results

A photograph of the mortar cement sample, with beam scan areas highlighted, is displayed in Figure 7-15. The top row of Figure 7-16 shows 256×256 pixel² elemental maps of Ca from this sample obtained by moving it to different positions in a sequence of 3mm steps across the beam. The other two rows show the Cl and Si maps respectively. The dark coloured regions in the Si maps display where the aggregates are. It is clear from the maps that Cl is to be found in the main paste where it is rich in Ca since ~60% of the OPC cement has CaO.

To obtain Cl profiles, the following procedures are performed. From the Ca maps, the areas that rich in Ca are selected to generate new Cl maps corresponding to the same selected areas. The areas that are excluded (i.e. the non-Ca areas) correspond mainly to Si (i.e. where aggregate is located) (see Figure 7-17). Subsequently a new X-ray spectrum is generated as shown in Figure 7-18. The number of Cl counts in each region in the new Cl maps is determined, by calculating the counts under the Cl X-ray peak in the new spectrum, and divided by the selected area (i.e. the number of pixels in the area). This is corrected by the ratio of real time to live time of the run and normalised to the beam chopper readout. The resulting number is associated with the scan position. Doing this in each scan across the sample will result in the profile of Cl diffusion as is shown in Figure 7-19. Absolute concentration profiles can be obtained, (compare ref [109]), by reference to one containing a known uniform chloride concentration.
Figure 7-15: A photograph of the mortar cement sample after being cut parallel to the ingress direction. The beam scan areas are highlighted as circles starting from the edge towards the centre.

Figure 7-16: The top row shows 256×256 pixel² elemental maps of Ca from the mortar sample obtained by moving it to different positions in a sequence of 3mm steps across the beam. The other rows show the Cl and Si maps respectively.
Figure 7-17: Area selection from the elemental maps

Figure 7-18: The generation of new X-ray spectrum corresponds to the new selected maps
The experimental profiles were fitted to Fickian diffusion profile in cylinder [94]:

\[
\frac{C}{C_0} = 1 - \frac{2}{\alpha} \sum_{\alpha_1}^{\infty} \frac{\exp(-D \alpha_n^2 t) J_0(\alpha_n r)}{\alpha_n J_1(a \alpha_n^2)}
\]

where,
- \(C\): Concentration of the diffusing molecule.
- \(C_0\): The surface concentration of the diffusing molecule.
- \(D\): Diffusion coefficient.
- \(a\): The radius of the cylinder. (here it is 50mm)
- \(t\): The exposure time. (here it is two months)
- \(r\): The radial distance from the centre
- \(J_0\): Bessel function of the first kind of order zero
- \(J_1\): Bessel function of the first kind of the first order
- \(\alpha_n\): The roots of \(J_0(\alpha_n) = 0\)

A diffusion coefficient, \(D=(1.93\pm0.42)\times10^{-9}\) cm²/sec was obtained by fitting the data using Microsoft® EXCEL. These preliminary results gave us the confidence to continue to a more detailed investigation.

![Figure 7-19: The experimental chloride diffusion profiles in the cylindrical mortar cement sample. The experimental data were fitted to Fickian diffusion in cylinder](image)

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7.5 Diffusion of Sulphate into Concrete

7.5.1 Study of sulphate diffusion profiles in samples prepared and exposed to sulphate solution in the lab

7.5.1.1 Sample preparation

Samples were prepared at the Federal Institute for Materials Research and Testing (BAM) in Berlin, Germany. There were three concrete samples each representing a cross section through concrete cubes of 100×100×100 mm³. They were:

- Sample (1): concrete with w/c = 0.80; 32 mm maximum aggregate size, cement content 170 kg/m³.
- Sample (2): concrete with w/c = 0.71; 32 mm maximum aggregate size, cement content 210 kg/m³.
- Sample (3): ready mixed repaired concrete with w/c = 0.5

The cubes were submerged in a sodium sulphate Na₂SO₄ solution (29g/l) for 10 months. Afterwards they were sliced across the ingress direction to allow beam scans at successive points along the ingress direction to obtain sulphur diffusion profiles. A cross section of one sample and the scanned areas along the sulphate ingress direction are shown in Figure 7-20.

7.5.1.2 Experimental and results

The samples were raster scanned by the proton beam in steps of 3mm each. Induced characteristic X-rays were collected for each scan using the Si(Li) detector. An X-ray spectrum is shown in Figure 7-21. Peaks from sulphur and all other elements heavier than aluminium present in the sample are shown. Elemental maps were extracted simultaneously by association windows around the peaks in the spectra with the 2-D scan
position using special software (OM-DAQ). Figure 7-22 displays the Ca, S and Si maps for a randomly selected run. It is noticeable from the maps that the sulphur is present in the Ca-rich areas. Offline, as the data were stored in the list mode option, areas in the maps were selected to include the Ca, a constituent of the cement paste, in which sulphate diffusion occurs, and to exclude high Si concentrations (Si being highly concentrated in the aggregate). New X-ray spectra corresponding to the new maps were generated. The sulphur counts were determined in each run and normalised to both

- the Ca counts
- and to the selected area and the chopper reading

i.e. both internal (to the spectrum) and external normalisation methods were used. The resulting values were plotted versus scan position (distance from the ingress face to the middle point of each scan) to obtain sulphur diffusion profiles. Figure 7-23 shows the sulphur diffusion profile of the second sample. An excellent agreement between the two normalisation methods is obtained for the diffusion profile of sulphur.

Figure 7-20: A concrete sample (100×65×25 mm³) and the beam scanned areas in the micro-PIXE measurements (yellow circles) of 3mm diameter each. The sulphate ingress direction is shown. The yellow rectangle is the scanned area in the micro-XRF measurements
Figure 7-21: An X-ray energy spectrum collected for a concrete sample exposed to sodium sulphate solution

Figure 7-22: Ca, S and Si maps for a typical run
Figure 7-23: Sulphur diffusion profile using normalisation methods both to the selected Ca area and chopper and to the Ca counts respectively.

7.5.1.3 A Comparison study between PIXE and XRF

In order to validate the sulphate diffusion profiles obtained by PIXE with another method, an independent measurement was performed for the same sample (sample 2) using scanning micro X-ray fluorescence spectroscopy (µ-XRF) technique (see chapter 2). The scanning micro-XRF experiments were performed at the Federal Institute for Materials Research and Testing (BAM) in Berlin, Germany by staff there. Figure 7-24 shows an outline of the scanning micro-XRF instrument. It consists of:

- A source of X-Rays used to irradiate the sample (an X-ray tube emits intense narrow X-ray beams).
- A sample holder that can be automatically controlled to enable movement in two dimensions, in known steps, to allow the X-ray beam to be scanned across the whole sample.
• An X-ray detection system to detect the emitted fluorescent X-Rays (The fluorescent or characteristic X-rays are measured at 45° to the incident X-ray beam using a lithium drifted silicon Si(Li) X-ray detector). This is followed by digital signal processing to enable the collection of both X-ray spectra and elemental maps.

**Figure 7-24: An outline of the scanning micro-XRF instrument**

The instrument is capable of measuring areas of 70×60mm² (yellow rectangle in Figure 7-20). Elemental maps in this area can be obtained (Figure 7-25). These maps can be used subsequently to obtain elemental profiles based on their colour intensity. Very good agreement between the two independent experimental techniques of both micro-XRF and micro-PIXE is obtained and shown in Figure 7-26 for the diffusion profile of sulphur.
Figure 7-25: Elemental maps of S, Ca, Si (top raw) using micro-XRF technique. They are all overlapped in the bottom map.

Figure 7-26: Sulphur diffusion profile using both Micro-XRF and Micro-PIXE techniques.
7.5.1.4 The influence of the W/C ratio on the sulphate ingress

The influence of the W/C ratio on the sulphate ingress was investigated using the external micro-PIXE technique on the three samples. It is clear from the sulphur profiles in Figure 7-27 that the first sample, where W/C=0.8, has poor resistance to sulphate attack. The third one (W/C=0.5) has the strongest resistance and the second one lies in between. It is clear that reducing the W/C ratio has increased the resistance to sulphate attack.

Figure 7-27: Investigating the influence of the W/C ratio to the sulphate resistance using external micro-PIXE
7.5.2 Studying both sulphate and chloride diffusion profiles from core samples taken from a massive concrete block exposed to a saline environment for ~30 years

7.5.2.1 A comparison study between PIXE and XRF

A cylindrical core of 100mm diameter was taken from a 30-year-old massive reinforced concrete block located in the sea off Bergen in Norway. The structure was constructed in 1977 using OPC cement. The maximum aggregate size is ~50 mm and the estimated water to cement ratio is 0.4. The core was cut into quarters perpendicular to the circle surface. One quarter was smoothed perpendicular to the ingress direction to allow beam scanning of the sample along the chloride and sulphate ingress direction in order to obtain diffusion profiles. The same quarter was also subjected to a scanning micro-XRF study (see section 7.5.1.3) in BAM, Germany.

A comparison of Cl and S profiles from the two techniques was obtained by plotting:

- **For XRF:**
  a) A lateral sum (i.e. parallel to the ingress surface) of both raw Cl and S X-ray fluorescent yields as a function of depth. This is obtained by summing up the counts in the maps vertically in each pixel to produce a plot of counts versus distance horizontally.
  b) The ratios of both Cl and S counts to the Ca counts as a function of depth.

- **For PIXE:**
  a) Cl per unit area of Ca and S per unit area of Ca (both normalised to the chopper readings) as a function of depth.
  b) The ratios of both Cl and S counts to the Ca counts as a function of depth.
For XRF the effect of (a) is to sum Cl and S counts over the same large area (50×1mm²) at different depths. This averages out the chlorine and sulphur concentrations over the different areas of cement paste at each pixel within the area. It is directly comparable with the PIXE (a) data processing procedure, where for a small area (3mm diameter) the chlorine and sulphur counts per unit area of paste is determined.

The PIXE (a) and XRF (a) data processing results are compared for chlorine and sulphur in Figure 7-28 and Figure 7-29. The PIXE (b) and XRF (b) data processing results are compared for chlorine and sulphur in Figure 7-30 and Figure 7-31.
Figure 7-28: Chlorine diffusion profiles obtained from micro-PIXE (red) and micro-XRF (blue) data each normalised to the Ca counts

Figure 7-29: Sulphur diffusion profiles obtained from micro-PIXE (red) and micro-XRF (blue) data each normalised to the Ca counts
Figure 7-30: Chlorine diffusion profiles obtained from both micro-PIXE data (red) normalised to the Ca area and to the chopper reading and from the raw data of the micro-XRF (blue)

Figure 7-31: Sulphur diffusion profiles obtained from both micro-PIXE data (red) normalised to the Ca area and to the chopper reading and from the raw data of the micro-XRF (blue)
The diffusion coefficients of both Cl and S were calculated for each technique and for each normalisation method. The mathematical model used for the study of both chloride and sulphate diffusion on concrete was based on the particular solution of Fick's second law of diffusion corresponding to the case of an “infinite source diffusion” (see chapter 3). In other words, the experimental data were fitted to Fickian diffusion from an infinite source into plain matrix taking into account a constant surface concentration of the diffusing molecules or atoms (see chapter 4 and Equation 4-4). The equation is:

\[ C(x, t) = C_0 \times \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \]

Where \( C(x, t) \) is the concentration of the diffusant at the distance \( x \) from the exposed edge after \( t \) seconds. \( C_0 \) is the constant concentration at the surface. \( D \) is the diffusion coefficient and \( \text{erfc} \) is the complementary error function.

The fitting of the experimental diffusion profiles, obtained at a diffusion time of 30 years, allowed the determination of the diffusion coefficient. The fitting process was performed using Mathcad™ 2001 professional software. The diffusion coefficients obtained from various normalisation methods mentioned above are tabulated below (Table 7.1 and Table 7.2).
### Table 7.1: Diffusion coefficients for S and Cl obtained by applying both micro-PIXE and micro-XRF techniques. Normalisation to Ca counts in each technique is performed.

<table>
<thead>
<tr>
<th></th>
<th>PIXE (Norm to Ca)</th>
<th>XRF (Norm to Ca)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>( D=(6.4\pm2.6)\times10^{-10} \text{cm}^2/\text{sec} )</td>
<td>( D=(8.4\pm3.5)\times10^{-10} \text{cm}^2/\text{sec} )</td>
</tr>
<tr>
<td>S</td>
<td>( D=(10.9\pm4.1)\times10^{-10} \text{cm}^2/\text{sec} )</td>
<td>( D=(9.2\pm1.0)\times10^{-10} \text{cm}^2/\text{sec} )</td>
</tr>
</tbody>
</table>

### Table 7.2: Diffusion coefficients for S and Cl obtained by applying both micro-PIXE and micro-XRF techniques. Normalisation to the area and chopper is performed in the PIXE technique. Only raw data is taking into account in the XRF technique.

<table>
<thead>
<tr>
<th></th>
<th>PIXE (Norm to area and chopper)</th>
<th>XRF (Raw data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>( D=(11.2\pm5.0)\times10^{-10} \text{cm}^2/\text{sec} )</td>
<td>( D=(11.4\pm4.2)\times10^{-10} \text{cm}^2/\text{sec} )</td>
</tr>
<tr>
<td>S</td>
<td>( D=(16.7\pm5.4)\times10^{-10} \text{cm}^2/\text{sec} )</td>
<td>( D=(11.4\pm1.5)\times10^{-10} \text{cm}^2/\text{sec} )</td>
</tr>
</tbody>
</table>
We can conclude from the tables:

i) There is excellent agreement between Cl and S diffusion coefficients from both PIXE and XRF techniques when we compare Cl/Ca and S/Ca ratios.

ii) There is excellent agreement between Cl diffusion coefficients obtained from PIXE data by normalising them to the chopper and the paste cement area and from the raw data of Cl profiles using the micro-XRF technique; the corresponding coefficients for S differ.

iii) The diffusion coefficients from i) are always lower than from ii). However, all values of the Cl diffusion coefficients are compatible within error bars as are the S values.

iv) The weighted mean values are:

   for the Cl diffusion coefficient, \((8.3 \pm 1.7) \times 10^{-10} \text{cm}^2/\text{sec}\)
   for the S diffusion coefficient, \((10.1 \pm 0.8) \times 10^{-10} \text{cm}^2/\text{sec}\)

Using method i) – internal normalisation to Ca – only statistical errors are present as both Cl and Ca counts derive from the same spectrum. Using method ii), there are also systematic errors in the data due to the different areas of Ca associated with each data point and this is reflected in the increased error bars associated with the fits.

Hence the comparison to the Ca counts should be the method of choice when trying to determine Diffusion Coefficients from a limited amount of data. As we saw in our comparison of the two techniques (section 7.5.1.3), where we had a large number of data points, both methods gave identical profiles.

The number of points was limited here as this sample was only one of many in a much wider study of concrete blocks from the sea off Bergen.
7.5.2.2 Comparing small core chlorine and sulphur profiles with large core profiles

In testing existing reinforced concrete structures for chloride ingress there is an existing British standard method (BS EN 14629) [105], which includes taking a core diameter of 30 mm to 50 mm, depending on the maximum aggregate size. For the determination of the chloride profiles, the cores are cut into 1mm thick slices and ground to obtain fine powder. They are stored in plastic bags. The bag contents are then chemically analysed for chloride content and hence the chloride ingress profile is obtained.

As an alternative we are suggesting the possibility of taking a small core (18mm diameter) and analysing the elemental concentration of chlorine (and matrix elements such as Ca, S and Si) as a function of depth using the external beam scanning micro-PIXE technique.

To test the feasibility of this we want to compare results from a small core taken from a sample with a chloride and sulphate depth profiles determined from a large sample.

A cylindrical core of 100mm diameter and ~100mm length was taken from a separate 30-year old in-sea concrete block. It was then subjected to different cutting processes,

1. A smaller core (18mm diameter) was taken from the large core using a wet diamond core drill, model Unitec, Inc END 1521 P CS. (see Figure 7-32-A).

2. A flat surface was obtained by cutting the large core along the cylindrical axis (see Figure 7-32-B).
Figure 7-32: concrete core samples preparation
Three sets of measurements were performed:

1. Beam scanning on the small core (i.e. scanning on a curved surface).
2. Beam scanning on the previous small core but after being carefully flattened using an abrading tool perpendicular to the ingress direction.
3. Beam scanning on the cut face of the large core.

The normalisation was performed to the Ca counts (i.e. internal normalisation). The chlorine and sulphur diffusion profiles obtained in both Figure 7-33 and Figure 7-34 are clearly dissimilar for the case where the sample flattening was not performed (i.e. scanning across the curved surface). This confirms the fact that the beam has to scan across a flat surface.
Figure 7-33: Chloride diffusion profiles of the small concrete core, the small concrete core after flattening and a cut face of the large concrete core

Figure 7-34: Sulphur diffusion profiles of the small concrete core, the small concrete core after flattening and a cut face of the large concrete core
If we compare the scan on the flattened small core with the large core scan we obtain both Figure 7-35 and Figure 7-36. One reason for the difference in the profiles may be the cutting method used for the large core where water-cooled circular saw was used. The cutting direction was opposite to the direction of chlorine and sulphur ingress. Also the saw itself was not changed (or washed) between samples.

Given the uncertainties inherit in these shortcomings of the large sample cutting process, the agreement is good.
Figure 7-35: Chlorine diffusion profiles of the small concrete core after flattening and the cut face of a large concrete core.

Figure 7-36: Sulphur diffusion profiles of the small concrete core after flattening and the cut face of a large concrete core.
7.6 Decontamination of cementitious materials by means of electrochemical extraction methods

7.6.1 Electrochemical chloride extraction from cement past samples

7.6.1.1 Sample preparation

Samples were prepared at the Institute of Construction Sciences “Eduardo Torroja”, CSIC, in Madrid, Spain. Two sets of cement-paste samples were prepared to investigate the influence of the addition of microsilica to OPC on the chloride extraction process. Each sample is (30×20×20 mm³); one is made from 100% OPC and the other from a cement combination containing typically 90% OPC and 10% microsilica by mass (labelled here as MS). The microsilica (or silica fume) is a mineral addition that improves the corrosion protection and strength of concrete by reducing the permeability of the cement paste [112].

Each set consists of three samples, one pure paste, and the other two containing 2% of Cl⁻ by mass of these; one is used as a reference material and the other subjected to an electrochemical migration cell designed to extract chloride ions.

The electrochemical chloride extraction (ECE) process was performed at CSIC. The migration cell is similar to the one described in sections 7.1.3.1 and 7.1.3.2 (see Figure 7-2). The paste specimen, 30mm long, is sandwiched between the cathode and the anode electrodes of the cell. The electrodes are connected to a DC power supply. A typical DC voltage (normally ~ 60V) is applied between the cathode and the anode for a period of one month. During treatment, the negatively charged chloride ions are displaced toward the positively charged anode and trapped in the anodic electrolyte. Afterwards, the samples are taken from the cell. One face is manually smoothed with emery paper, perpendicular to the diffusion direction, in order to have a flat surface for proton beam scanning.
7.6.1.2 Experimental procedures and results

Each sample was cut at CSIC into three pieces. These were held together with an encircling band of cellotape™. The joins are shown at the top and the bottom of the middle red arrow in Figure 7-37.

A joined sample was placed on a traversing table in air and bombarded by the proton beam, inducing element-characteristic X-ray production. Samples were moved in steps of 3mm. They were raster scanned over a 3mm diameter circular area at each step with the proton beam as shown in Figure 7-37. 10 circular scan areas were required on each sample since the length of each sample is 30mm. A time of 5 min was sufficient for each scan to detect the induced characteristic X-rays. Backscattered protons were detected simultaneously, using a silicon surface barrier detector, to monitor both the collected charge and the main matrix composition. A He gas flow was arranged between the sample and each of the Si(Li) and the charged particle detector. Chopper readings were registered for normalisation purposes.

Elemental maps corresponding to each scan area were obtained subsequently. The bottom part of Figure 7-37 shows the elemental maps of the Ca, Si and Cl for a typical run. Ca and Si are constituents of the paste.

Figure 7-38 shows four overlaid X-ray spectra, two of them from a sample subjected to the electrochemical process, at positions near the cathodic and anodic regions. It is clear that the Cl⁻ yield is higher for the position next to the anodic region than that next to cathodic region. By contrast, the K⁺ content is higher near the cathodic region. The X-ray peak just next to the Si peak corresponds to the Ca Kα escape peak [113]. This is due to the photoelectric effect in the detector in which an incident X-ray photon (from Ca here) ionises a Si atom in the crystal in the detector and causes secondary electron emission and a Si Kα X-ray emission. This may escape from the detector. If escape occurs a pulse is recorded equivalent to that produced by an X-ray photon of energy (E₀-Eₚ), where E₀ and Eₛᵢ are the energies of the incident initial photon and the Si Kα X-ray respectively.
(i.e. in our case $E_i=3.69\text{keV}$ and $E_{is}=1.74\text{keV}$ so the Ca $K_{a}$ escape peak has an energy of $1.95\text{keV}$).

Figure 7-37: (Top) A paste sample and the beam scanned areas (yellow circles) of 3mm diameter each. The chloride extraction direction is shown. (Bottom) Ca, Cl and Si maps for a typical run
Figure 7-38: Four overlaid X-ray spectra. Two for paste samples with either no chloride or containing 2% by weight. Two are from areas near either the cathode or anode from an initially 2% chloride-containing sample that has been subjected to a chloride extraction process.
The variation in chloride quantity in the treated specimens across the samples was measured. This was obtained, as mentioned above, by measuring the number of counts under the Cl peak in each new spectrum generated after selecting areas from the Ca maps. The selected areas were chosen to be strips each 1mm wide (i.e. each Ca area was divided into three strips). Doing this enables more detailed profiles. The counts in the Cl peak were divided by the corresponding Ca area and then normalised to the chopper reading. Chloride profiles were obtained by plotting the resulting normalised value versus the corresponding distance from the exposed edge (Figure 7-39 and Figure 7-40). This was repeated for K and Ca to study their profiles before and after treatment (Figure 7-41 to Figure 7-44).

The Y-axis (the normalised counts) in the chloride profiles was translated into absolute concentrations (% of the whole mass) by reference to samples that contain 2% by weight added chloride. Measurements were performed at several points on these samples. These were averaged and the average value is plotted as a line in the graph of the chloride diffusion profile. This is shown with error bars for both OPC and MS samples in Figure 7-39 and Figure 7-40 respectively. A similar line for a pure paste sample (i.e. no chloride added) is also shown. Looking at Figure 7-39, the sample join positions (at distances of ~10 and 20 mm from the anodic region) are clearly visible in the OPC sample (reduced counts).
Figure 7-39: Chloride profiles for OPC before and after chloride extraction

Figure 7-40: Chloride profiles for MS before and after chloride extraction
Figure 7-41: K profiles for OPC before and after chloride extraction

Figure 7-42: K profiles for MS before and after chloride extraction
Figure 7-43: Ca profiles for OPC before and after chloride extraction

Figure 7-44: Ca profiles for MS before and after chloride extraction
• Conclusions

About 75% of the initial chloride was removed from the MS sample whilst only ~25% is removed in the case of OPC indicating that the chloride extraction is easier in the case of MS than that for OPC. K⁺ ions from the samples accumulate near the cathodic region as is shown in the K profiles in Figure 7-41 and Figure 7-42. The K⁺ accumulation rate is roughly similar in the two cases. Figure 7-43 and Figure 7-44 show no major change has occurred in the Ca²⁺ content in both cases, OPC and MS.

This study has shown that using microsilica as an addition to the OPC cement has the advantage that the chloride contamination in its structure can be easily removed electrochemically. This advantage is accompanied by the fact that adding microsilica to the OPC reduces the penetration of chlorides into the concrete and therefore delays the start of corrosion [112].
7.6.2 Heavy element decontamination of bricks and mortars using an electro-kinetic technique

7.6.2.1 Sample preparation

Two sets of cylindrical samples were prepared at the Institute of Construction Sciences “Eduardo Torroja”, CSIC, in Madrid, Spain. The first series involved cylindrical mortar specimens 75mm diameter and 15mm in height. They were exposed at both circular ends to a solution of Cs\(^+\), Sr\(^{2+}\), Co\(^{2+}\), Cd\(^{2+}\) and Cu\(^{2+}\), in the form of their chloride salts for 1 month. These heavy elements are normally associated with nuclear reactors. The second series were brick cylindrical specimens of 75mm diameter and 30mm height exposed in the same way as the mortars.

Each set contains two samples; one is used as a reference and the other subjected to a decontamination process. To decontaminate these specimens a migration cell was used by CSIC, as described in Chapter (3). The cylinders were sandwiched between the two chambers where the cathode (graphite) and anode (titanium) were placed. Both chambers were filled with distilled water (see Figure 7-45). A DC voltage was applied (60V) between the cathode and the anode for a period of 1 month. Samples were then left to be cured and finally were sectioned vertically to study the heavy element distribution across them following the extraction process.
Figure 7-45: Schematic diagram of the electro-kinetic decontamination cell
7.6.2.2 Experimental procedures and results

- **X-ray spectra**

Two X-ray detectors were used. The first was the normal lithium drifted silicon detector (Si(Li)) with an area of 80\,mm$^2$ and having good efficiency for detecting X-rays of energies up to 20\,keV. The second was a cadmium telluride detector (CdTe), which is capable of detecting higher X-ray energies (up to 100\,keV) from heavy elements with 100% efficiency (see chapter 3). They were each placed at an angle of 135° to the direction of the beam and their front faces were 20\,mm from the target. The CdTe detector calibration was performed using a variable X-ray source (VEX), in which primary gamma rays from an $^{241}$Am source excite Cu, Rb, Mo, Ag, Ba and Tb targets to emit their characteristic X-rays. An X-ray spectrum for the calibration of CdTe detector is shown in Figure 7-46. A funny filter (consisting of an aluminium absorber disk with several small central holes) was placed in front of the Si(Li) detector to minimise the dead time caused by the high count rate from the main light element matrix to increase the detection sensitivity of high X-ray energies.

![Figure 7-46](image_url)

**Figure 7-46:** $K_\alpha$ and $K_\beta$ X-ray peaks from VEX source used for the calibration of the CdTe detector
Overlaid PIXE spectra from mortar and brick before and after extraction at a distance of 3mm and 6mm respectively, from the end that had been attached to the anode, collected by Si(Li) and CdTe detectors are shown in Figure 7-47, Figure 7-48, Figure 7-49 and Figure 7-50. The X-ray peaks labelled in black are for the matrix elements in each sample while the red ones are for the pollutants (heavy elements and chlorine). All four figures are normalised for the same beam charge.
Figure 7-47: Overlaid PIXE spectra for two mortar samples before and after extraction at a distance of 3mm from the top edge, collected by the Si(Li) detector.

Figure 7-48: Overlaid PIXE spectra for two mortar samples before and after extraction at a distance of 3mm from the top edge, collected by the CdTe detector.
Figure 7-49: Overlaid PIXE spectra for two brick samples before and after extraction at a distance of 6mm from the top edge, collected by the Si(Li) detector.

Figure 7-50: Overlaid PIXE spectra for two brick samples before and after extraction at a distance of 6mm from the top edge, collected by the CdTe detector.
The main conclusion from these spectra is that:

1) Elements (Cl, Sr, Cd, Cs) diffuse into brick at a much higher rate than into mortar.
2) The fraction of these elements extracted is much higher for brick than for mortar.

This is due to the higher porosity of brick (20-40%) [114].

Other observations are,

- Looking at the Cd Kα lines from bricks and mortars using both Si(Li) and CdTe detectors, it is clear that the count rate is much higher in the case of the CdTe detector. Its efficiency is much higher for the detection of Kα lines from heavy elements, making it very necessary for this work.
- For Cs the Kα X-ray peak using the CdTe detector is much clearer than the L-lines using the Si(Li) detector, which is all that detector can pick up.
- Conversely, in the Sr case, the Kα peak is clear in the brick samples using both detectors; this is not the case in the mortars using the CdTe detector as its Kα X-ray peak is masked by the low energy background spectrum. It is only the high concentration levels of Sr in the brick that makes its Kα peak to background ratio high enough to be visible in the spectra obtained by CdTe detector. Hence the two detectors are complementary.
- The Kα X-ray peak of Co overlaps the Kβ of Fe. The Co Kβ X-ray peak is much clearer.
Backscattering spectra

Backscatter spectra were collected for the whole scan using a silicon surface barrier detector at the same time as the PIXE spectra, for both bricks and mortars, before and after treatment. They are shown in Figure 7-51 and Figure 7-52 respectively. They were obtained with a helium gas flow between the charged particle detector and the sample, giving an intense He peak, which is used to calibrate the spectra. The nitrogen peak in each spectrum is due to the residual air, which has ~75% nitrogen, between the sample and the BS detector. The Cs edge is labelled in each spectrum since it is the heaviest element present in the samples. It is clear that the whole spectrum yield has decreased after the electro-kinetic process. This is noticed clearly in both Figure 7-51 and Figure 7-52 in the right part of the spectrum where heavy element backscatters occur. This is due to the reduction of heavy elements after extraction. The other observation is that the concentration (i.e. the diffusion rate) of the heavy elements is higher in the case of bricks than for mortars when exposed to the heavy element chloride solution. The extraction rate is higher as well (leading to a lower remaining heavy element concentration). This supports the main conclusion from the PIXE spectra.
Figure 7-51: Backscattering spectra collected for a mortar sample before and after the treatment.

Figure 7-52: Backscattering spectra collected for a brick sample before and after the treatment.
- **Elemental 2-D maps from X-ray spectra**

Figure 7-53 shows the scanned areas on a mortar sample, before extraction, from one edge to the other. The distributions of the elements in the samples were 2-D mapped. 2-D maps of selected elements (Ca, Si, Cs and Cd) for a typical run are shown in the same figure. As in the case of chloride and sulphate diffusion in concrete (sections 7.4 and 7.5 above), the diffusant heavy elements are mainly located in the main paste (i.e. regions that are rich in Ca).

![Scan areas in the sample and 2-D maps of selected elements in a typical scan on a mortar sample before extraction of diffused elements](image)

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**Figure 7-53: Scan areas in the sample and 2-D maps of selected elements in a typical scan on a mortar sample before extraction of diffused elements**
Elemental profiles

Once again, OM_DAQ software was used to collect the data in the list mode option. For the mortars, before and after extraction, the selected areas were set to include the region that is rich in Ca. For the brick samples where is no cement paste or specific aggregate, the composition is quite uniform and the area selected was the whole scan. Corresponding PIXE spectra were generated simultaneously and then analysed using the Windows® based software package DAN32 [55]. Elemental profiles were obtained and plotted in Figure 7-54 and Figure 7-55. Co profiles were obtained using its K_β X-ray rather than K_α to avoid the overlapping of Co K_α and the Fe K_β lines in the X-ray spectra. Cd and Cs profiles were extracted via their K_α lines using the CdTe detector since its efficiency is 100% for detecting K_α X-rays from heavy elements. The Sr profiles were extracted using the Si(Li) detector for the case of mortars and CdTe detector for the case of bricks. This is because the K_α line of Sr was clear only in the case of bricks using the CdTe detector.
Figure 7-54: Elemental profiles of the pollutants before and after extraction process in the mortar samples
Figure 7-55: Elemental profiles of the pollutants before and after extraction process in the brick samples
• **Conclusion**

It is clear that the Cs binding in both cases, mortars and bricks, is weak so it is easy to extract it. This is partially true also in the Sr case. The Cadmium and Copper profiles in the mortar sample imply that they bind more than Cs and Sr. They are accumulated near the cathodic region. More electro-kinetic process time is required. In contrast, the chloride ions are driven towards the anodic region. They are easily extracted from brick sample, not quite so easily from mortar.

**7.7 Overall conclusions and discussion**

An external scanning micro-PIXE technique has been developed to investigate cementitious materials. This technique has been applied to the study of:

1. Chloride and sulphate diffusion in laboratory prepared mortar samples.
2. Chloride and sulphate diffusion in samples taken from a concrete block built in the sea.
3. The electrochemical chloride extraction from cement paste.
4. The investigation of the heavy metal distributions in mortar and brick in conjunction with simultaneous RBS measurements, before and after an electro-kinetic extraction technique.

Two data normalisation methods have been used, one (internal to the X-ray spectrum) to the Ca counts in the spectrum (the main constituent of cement paste is calcium) and the other (external to the X-ray spectrum) to the Ca area and the beam intensity monitor (the beam chopper). Excellent agreement has been obtained. Both methods have been compared to an independent analysis of the same sample using scanning micro-XRF. Once again, excellent agreement has been found.
As an alternative to the British standard method (BS EN 14629) [105] of measuring chlorine profiles in existing concrete structures, a technique using a small cylindrical core has been developed. When the core is abraded to produce a flat surface, good results have been obtained when compared to analysis of the whole sample. The external scanning micro-PIXE technique appears to be viable and in addition to the chlorine profile the matrix element composition is given and matrix element profiles are measured enabling the correlation, in principle, between chlorine diffusion and the matrix to be found. The technique could be further developed to investigate the possibility of providing a realistic alternative to the present BS method for the analysis of large number of samples.

The application of external scanning micro-PIXE technique to the investigation of chloride electrochemical extraction from cement paste samples has been developed. Chloride profiles have been obtained for two cement paste samples, one made from 100% OPC and the other from 10% microsilica and 90% OPC, initially containing a known amount of chloride, after they were subjected to an electrochemical extraction process. The Cl profiles imply that electrochemical extraction of chloride is easier in the second case where the microsilica is added. K⁺ accumulation near the cathode region was noticed during the extraction process while no change in the Ca content was observed following the electrochemical process.

The study of diffused heavy element distributions in mortars and bricks before and after electro-kinetic extraction methodology has been investigated. Samples (brick and mortar), contaminated by diffusion with heavy metals and chloride, were subjected to an electro-kinetic extraction methodology to decontaminate them. Two X-ray detectors were used; one a Si(Li) detector and the other a CdTe detector that has 100% detection efficiency for high energy Kα X-rays from heavy elements. The high porosity of brick enables easy heavy metal and chloride diffusion and extraction, as has been shown by the elemental profiles. The Cs and Sr profiles in mortars have shown that they are easily extracted whereas longer extraction times are required for the cations Co²⁺, Cd²⁺ and Cu²⁺ and the Cl⁻ anion.
Chapter Eight: Summary and Overall
Conclusions

Ion beam analysis techniques have been developed to investigate diffusion in materials using both in-vacuum and in-air MeV proton beams.

Initially the energy of the Tandetron™ accelerator at the University of Surrey Ion Beam Centre was calibrated. Four energy points of calibration were established. The first one was obtained by detecting near-threshold neutrons from the $^7$Li(p,n)$^7$Be reaction. The other three were known resonant reactions - two resonances in the $^{27}$Al(p,$\gamma$)$^{28}$Si reaction and one in the $^{19}$F(p,$\alpha$$\gamma$)$^{16}$O reaction. The true terminal voltage was found to be:

$$V_t = \text{Nominal terminal voltage} \times 1.0269(7)$$

with the beam energy related to the terminal voltage by the relation:

$$E = eV_e + (q + 1)eV_t$$

Where $V_e$ is the extraction voltage in the source, $e$ the electron charge and $q$ is the charge status of the exit beam particles.

Two main investigations are described in this thesis. The first involves the measurement of lithium profiles following intercalation into vanadium pentoxide ($V_2O_5$) thin films. This was achieved using a beam energy-loss technique in-vacuum. Both nuclear reaction analysis (NRA) and backscattering spectrometry (BS) techniques were utilised to perform this study. The $^7$Li(p,$\alpha$)$^4$He reaction was chosen to profile the Li, due to its high Q-value ($Q = +17.347$ MeV) and its fairly high cross-section, in a model $V_2O_5$SnO2/Glass substrate triple-layered thin film following a Li intercalation process. A broad beam of protons was used to minimise sample damage. A 2MeV proton energy was preferred to maximise the cross-section of the $^7$Li(p,$\alpha$)$^4$He reaction, to minimise the $^{19}$F(p,$\alpha$)$^{16}$O reaction cross section and to maximise the proton scattering cross-section on Li.
The novel University of Surrey IBA DataFurnace software was used to analyse both NRA and BS data automatically and to rapidly obtain the elemental depth profiles. It is based on a simulated annealing algorithm. This software was initially devised to analyse backscattering data. It has subsequently been extended to include ERD and NRA data. The code had already been tested on NRA data using the $^7\text{He}^3\text{He},p)\alpha$ reaction. Here it was examined again using a thin LiF standard sample deposited on Mylar™ to demonstrate its ability to fit NRA data obtained from the $^7\text{Li}(p,\alpha)^4\text{He}$ reaction. This was performed in addition to fitting simultaneous backscattering protons from the LiF and from the substrate. This procedure was extremely useful to determine and establish the software essential components e.g. the experimental geometry and the sample structure files. Non-Rutherford cross-sections for proton scattering on light elements were included.

An independent run was performed on a model $\text{V}_2\text{O}_3\text{SnO}_2\text{Glass}$ substrate triple-layered thin film not subjected to Li intercalation in order to study the proton backscattering from the sample in the absence of any nuclear reactions. This run was required to predict the backscattering experimental geometry and the sample geometry file.

After testing the software on pure NRA and then on pure BS data, it was ready to use for both simultaneously. The IBA DataFurnace software has the ability to do this.

Two parts of a $\text{V}_2\text{O}_3\text{SnO}_2\text{Glass}$ substrate triple-layered thin film have been analysed, one which had been in contact with the electrolyte used in a three-electrode cell (i.e. this part had been subjected to the intercalation process) and the other part which had been above the electrolyte (i.e. this part had not been subjected to the intercalation process). This was studied to investigate vertical Li diffusion either along the interlayer or across the surface.
On the intercalated part, two independent data sets were taken:

- A set where both BS and NRA data were recorded.
- A set where the ADC (analogue to digital converter) discriminator threshold was raised so that only high energy BS and NRA data were recorded.

On the non-intercalated part one data set was taken with ADC discriminator threshold was raised so that only high energy BS and NRA data were recorded. The runs with the ADC threshold raised were taken to reduce system dead time and to maximise the sensitivity to alpha particles from the $^7\text{Li}(p,\alpha)^4\text{He}$ reaction form very low Li concentrations present (particularly important for the non-intercalated part).

Good agreement was obtained for the first part using either NRA and BS techniques or NRA alone. The Li profile in the first part shows a moderate homogeneous distribution except near the surface. Some Li content in the SnO$_2$/glass interface was detected. The Li profile in the second part implies diffusion across the sample surface i.e. across the V$_2$O$_5$ layer.

This study was performed to make a contribution towards the development of rechargeable thin-film lithium batteries that can be used as miniature power supplies for small electronic devices.

The other major task described in this thesis was the development of an in-air scanning micro-PIXE technique and its use in the investigation of diffusion in cementitious materials. Two main applications related to cementitious materials were investigated. These were the study of the diffusion of chloride and/or sulphate in concrete from a saline environment and the study of the electrochemical extraction of both chloride and heavy elements from cementitious materials.

A preliminary study was performed on cement paste samples made with different known amounts of chloride to establish the ability of the external scanning micro-PIXE technique to detect the chloride presence. The induced characteristic X-rays were collected using a Si(Li) detector. Excellent results were obtained by plotting the chloride
normalised counts from each sample versus the corresponding chloride contents. A linear plot was obtained. Two kinds of data normalisation were performed, one internal to the calcium area and the X-ray spectrum, to the Ca counts and the other external to the X-ray spectrum chopper reading. Excellent agreement between the two normalisation methods was obtained.

The results obtained in the paste case gave us encouragement to study chloride diffusion into cement-mortars. Cylindrical mortar samples were made in order to study the chloride diffusion into its perimeter. A sample was submerged in a solution that contains 5% chloride ions by weight for two months. Subsequently it was cut parallel to the ingress direction and the exposed surface raster scanned near its perimeter by a 2.5 MeV external proton microbeam over a circular area of 3 mm diameter. The sample was then moved in steps of 3 mm from the sample edge towards its centre. Each time the induced characteristic X-rays were collected and corresponding elemental maps were generated.

The Cl diffusion profiles were obtained by measuring the number of counts under the Cl peak in each new spectrum generated from the original one after selecting areas from the maps that are rich in Ca. This procedure includes the cement paste, where the Cl diffusion occurs, and excludes the aggregate. Cl counts per unit area were normalised to the chopper reading. This is repeated for each run and plotted versus the distance between the centre of each scan area and the exposed edge.

The studying of sulphate diffusion in concrete samples made in different water/cement ratios was investigated using the external scanning micro-PIXE technique. Cubic concrete samples were submerged in Na$_2$SO$_4$ for 10 months. Samples were then sliced across the ingress direction to study sulphate diffusion. They were raster scanned by the beam in steps of 3 mm each as mentioned above. The induced X-rays were collected and the spectra and the elemental maps were generated. The areas in the maps that are rich of Ca were selected since the sulphate diffusion occurs in the cement paste, which is rich in Ca. Then two normalisation methods, to the Ca counts and to the Ca selected area and the chopper reading were applied and excellent agreement was obtained. The influence of the
water/cement ratio on the resistance to sulphate ingress was investigated with the conclusion that the lower the ratio the more the resistance to sulphate attack. An independent study on one sample using the scanning micro-XRF technique has shown excellent agreement with the sulphur diffusion profiles measured with the micro-PIXE.

Chloride and Sulphate diffusion profiles were studied in a concrete block that had been in the sea for ~30 years. An 18 mm core was taken from this block to test the feasibility of using the scanning micro-PIXE procedure instead of the existing British standard method (BS EN 14629) where cores of 30-50mm diameter are recommended (i.e. we want to compare results from a small core taken from a sample with chloride and sulphate depth profiles determined from a large sample). Good agreement was obtained when the side of the core was abraded so that scans could be taken on a flat surface.

Both scanning micro-XRF and external micro-PIXE techniques were compared in studying chloride and sulphate diffusion profiles into a 100mm diameter core taken from another concrete block that had been in the sea for 30-years. A comparison study was performed on the chloride and sulphur profiles by

- firstly using the scanning micro-XRF technique and plotting the lateral sum in the Cl and S elemental maps (i.e. parallel to the ingress surface) of both raw Cl and S X-ray fluorescent yields and the ratios of Cl/Ca, S/Ca as a function of depth
- secondly using the external scanning micro-PIXE technique by plotting both the ratios of Cl/Ca, S/Ca and Cl per unit area of Ca, S per unit area of Ca as a function of depth for 3mm diameter scans.

Excellent agreement was obtained between the two techniques when normalising the data to the Ca counts in each one. This agreement was also observed when comparing the profiles obtained by micro-XRF raw data and the profiles obtained by normalising the data in micro-PIXE technique to the selected Ca area and the chopper counts.
This study has shown excellent agreement between both scanning micro-PIXE and micro-XRF techniques. Each provide a non-destructive tool for investigating elemental distributions in cementitious materials.

Electrochemical extraction of both chloride and heavy elements from cementitious materials has been investigated.

- Firstly, chloride extraction from cement paste samples has been examined. Two cement paste samples were prepared, one with 100% OPC cement and the other made from 90% OPC and 10% microsilica. 2% by weight of chloride was added to these samples. They were subjected to an electrochemical process in a migration cell, where the samples were sandwiched between cathode and anode electrodes, to release the chloride from them. In air micro-PIXE measurements were then performed to study the Cl profiles before and after the extraction method. The Cl profiles from the samples imply that Cl extraction is much easier in the case where 10% of microsilica is added.

- Secondly, the concentrations of heavy pollutant elements in mortar and brick before and after electro-kinetic extraction methodology were investigated. The heavy elements were diffused into the samples from a solution of their chloride salts. They are Cs⁺, Sr²⁺, Co²⁺, Cd²⁺ and Cu²⁺, heavy elements normally associated with nuclear reactors. The samples (brick and mortar) were subsequently subjected to an electro-kinetic extraction methodology to decontaminate them of heavy elements. Two X-ray detectors were used, one a Si(Li) detector and the other a CdTe detector that has 100% K X-ray detection efficiency for heavy elements. In the case of brick, heavy element profiles show high initial concentrations and very low concentrations after extraction due to its high porosity. For mortar, their initial concentrations are lower. The Cs and Sr seemed to be easier to extract than other cations (Co, Cd, Cu) where more extraction time is required. The chloride is extracted to the anode as expected. Simultaneous proton backscattering measurements were performed, result of which add extra weight to the conclusions from micro-PIXE.
Overall the use of the in-air scanning micro-PIXE technique is ideal for the investigation of diffusion in cementitious materials. It is a non-destructive and multi-elemental technique. It can be accompanied by other IBA techniques (backscattering here) simultaneously to give more information about the sample. It is flexible in terms of sample preparation, where the sample can be placed in air just opposite the beam exit window regardless of the size and the shape of the sample. The only sample preparation is needed is to ensure that the beam scans across a flat surface. Event by event data collection can be performed to produce data that can be replayed off line to produce new elemental maps and their corresponding spectra, selected for specific regions of the maps.

The work in Li intercalation in V$_2$O$_5$ was done in collaboration with Prof. J E Castle and Dr. David Alamarguy in the School of Engineering at the University of Surrey. The application of the external scanning micro-PIXE technique to diffusion in cementitious materials was done in collaboration with colleagues in the Federal Institute for Materials Research and Testing (BAM) in Berlin, Germany and the Institute of Construction Sciences “Eduardo Torroja”, CSIC, in Madrid, Spain. This work is going to be published soon. Other work related to the use of ion beam analysis techniques in studying diffusion in materials has led to these published articles,


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