Enhanced mass transport in liquid-saturated porous media due to surface shear

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Enhanced Mass Transport in Liquid-Saturated Porous Media Due to Surface Shear

by

David Jeremy Richardson

Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of

Doctor of Philosophy of Loughborough University

17 May 1999

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Barry Powell, 'Pip' Amos and Graham Moody built the experimental cells and probes

Steve Graver and Martin Kerry assisted generally in the lab and particularly with particle sizing and microscope work

Ian Sinclair helped with the initial design of the electronics

Terry Neale assisted with electrical matters including computer hardware

Paul Izzard provided IT support

Simon Brock introduced me to ray-tracing software and advised on the image processing involved in the particle sizing

Martin Bardsley provided the data shown in Figure 3.3.

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My parents for all their support and understanding especially during the period when I was writing up at home.
Abstract

The principal aim of this work was the development of a novel conductivity probe for measuring solids concentrations in slurries. The relevance of the thesis to this probe is that it requires rapid transport of aqueous electrolyte through a porous disc to an internal conductivity cell.

The bulk of the experimental work is concerned with the mass transfer of very dilute hydrochloric acid through beds of ballotini of varying diameter and with different surface shear rates. The concentration of HCl is monitored at fixed depths within the beds by means of electrical resistance measurements. Two types of cell are used, a cylindrical cell with radial flow across the surface which accelerates from the circumference towards the centre and a rectangular cell with uniform flow, both cells are only exposed to flow at the top surface.

At low surface shear rates a similar value is obtained for the diffusion coefficient of aqueous HCl to that in the literature. At higher crossflow rates, however, the rate of mass transport is enhanced by increasing surface shear and a model is developed with an 'induced velocity' term to account for this. The induced velocity decays exponentially moving away from the exposed surface and is correlated with surface shear. The induced velocity is larger for larger particles. The results from the rectangular cell are used to determine the relation between induced velocity and surface shear using a one-dimensional model. The relation is then used to predict the results from the cylindrical cell using a two-dimensional model where induced velocity is a function of both radial and axial position and there is radial as well as axial mass transfer of electrolyte.

Some results with prototype probes of three different diameters, using sintered polyethylene as the porous medium, are also reported. The induced velocity model is applied to mass transport within the probe to give information about the predicted response times for probes of different dimensions and compares favourably with the experimental results.
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<tr>
<td>$A$</td>
<td>Area</td>
<td>$(m^2)$</td>
</tr>
<tr>
<td>$A_r$</td>
<td>Fractional open area</td>
<td>(-)</td>
</tr>
<tr>
<td>$a_m$</td>
<td>Sorption retardation coefficient</td>
<td>(-)</td>
</tr>
<tr>
<td>$B$</td>
<td>Viscous flow permeability</td>
<td>$(m^2)$</td>
</tr>
<tr>
<td>$c$</td>
<td>Concentration</td>
<td>$(mol \cdot l^{-1})$</td>
</tr>
<tr>
<td>$C$</td>
<td>Non-dimensional concentration</td>
<td>(-)</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacitance</td>
<td>($F$)</td>
</tr>
<tr>
<td>$c_v$</td>
<td>Volume concentration</td>
<td>(-)</td>
</tr>
<tr>
<td>$d$</td>
<td>Diameter of sphere or Equivalent spherical diameter</td>
<td>$(m)$</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
<td>$(m^2 \cdot s^{-1})$</td>
</tr>
<tr>
<td>$D'$</td>
<td>Dispersion coefficient</td>
<td>$(m^2 \cdot s^{-1})$</td>
</tr>
<tr>
<td>$D_{ij}$</td>
<td>Dispersion tensor</td>
<td>$(m^2 \cdot s^{-1})$</td>
</tr>
<tr>
<td>$e$</td>
<td>Height of obstruction on rough surface</td>
<td>$(m)$</td>
</tr>
<tr>
<td>$E$</td>
<td>Percentage unextracted</td>
<td>(-)</td>
</tr>
<tr>
<td>$F$</td>
<td>Electrical formation factor</td>
<td>(-)</td>
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<tr>
<td>$F$</td>
<td>Faraday's Constant</td>
<td>$(96485 \ C \cdot mol^{-1})$</td>
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<tr>
<td>$g$</td>
<td>Acceleration due to gravity</td>
<td>$(9.81 \ \text{m} \cdot \text{s}^{-2})$</td>
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<tr>
<td>$H$</td>
<td>Hydraulic mean diameter</td>
<td>$(m)$</td>
</tr>
<tr>
<td>$h$</td>
<td>Height</td>
<td>$(m)$</td>
</tr>
<tr>
<td>$h'$</td>
<td>Equivalent head</td>
<td>$(m)$</td>
</tr>
<tr>
<td>$I$</td>
<td>Electric Current</td>
<td>($A$)</td>
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<td>Definition</td>
<td>Unit</td>
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<tr>
<td>--------</td>
<td>------------</td>
<td>------</td>
</tr>
<tr>
<td>$J$</td>
<td>Mass flux</td>
<td>(mol m(^2) s(^{-1}))</td>
</tr>
<tr>
<td>$K$</td>
<td>Constant</td>
<td>(-)</td>
</tr>
<tr>
<td>$K''$</td>
<td>Kozeny’s constant</td>
<td>(-)</td>
</tr>
<tr>
<td>$K_H$</td>
<td>Henry’s law constant</td>
<td>(-)</td>
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<tr>
<td>$K_m$</td>
<td>Ratio between adsorbed and dissolved concentrations</td>
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</tr>
<tr>
<td>$l$</td>
<td>Length</td>
<td>(m)</td>
</tr>
<tr>
<td>$L$</td>
<td>Inductance</td>
<td>(H)</td>
</tr>
<tr>
<td>$m$</td>
<td>Hydraulic radius</td>
<td>(m)</td>
</tr>
<tr>
<td>$M$</td>
<td>Molecular weight</td>
<td>(g mol(^{-1}))</td>
</tr>
<tr>
<td>$n$</td>
<td>Empirical exponent</td>
<td>(-)</td>
</tr>
<tr>
<td>$N_m$</td>
<td>MacMullin number (resistivity ratio)</td>
<td>(-)</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
<td>(Pa)</td>
</tr>
<tr>
<td>$Pe$</td>
<td>Peclet number</td>
<td>(-)</td>
</tr>
<tr>
<td>$q$</td>
<td>No. of ions</td>
<td>(-)</td>
</tr>
<tr>
<td>$Q$</td>
<td>Volume flow rate</td>
<td>(m(^3) s(^{-1}))</td>
</tr>
<tr>
<td>$Q$</td>
<td>Irreversible sink/source term</td>
<td>(s(^{-1}))</td>
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<tr>
<td>$r$</td>
<td>Radius or Radial coordinate</td>
<td>(m)</td>
</tr>
<tr>
<td>$r$</td>
<td>Harned’s calibration constant</td>
<td>(-)</td>
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<tr>
<td>$R$</td>
<td>Electrical Resistance</td>
<td>(Ω)</td>
</tr>
<tr>
<td>$R$</td>
<td>Non-dimensional radial co-ordinate</td>
<td>(-)</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
<td>(8.315 J K(^{-1}) mol(^{-1}))</td>
</tr>
<tr>
<td>$R$</td>
<td>Shear stress</td>
<td>(kg m(^{-1}) s(^{-2}))</td>
</tr>
<tr>
<td>$R_b$</td>
<td>Bias resistance</td>
<td>(Ω)</td>
</tr>
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# Nomenclature

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<thead>
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<th>Description</th>
<th>Unit</th>
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<tr>
<td>$R_f$</td>
<td>Retardation factor</td>
<td>(-)</td>
</tr>
<tr>
<td>$R_m$</td>
<td>Face retardation factor</td>
<td>(-)</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds Number</td>
<td>(-)</td>
</tr>
<tr>
<td>$s$</td>
<td>Surface concentration</td>
<td>(-)</td>
</tr>
<tr>
<td>$S$</td>
<td>Conductance</td>
<td>(S)</td>
</tr>
<tr>
<td>$S_s$</td>
<td>Specific storage term</td>
<td>(m⁻¹)</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>(s)</td>
</tr>
<tr>
<td>$T$</td>
<td>Non-dimensional time</td>
<td>(-)</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>(K)</td>
</tr>
<tr>
<td>$T_i$</td>
<td>Principal diffusion relaxation time</td>
<td>(s)</td>
</tr>
<tr>
<td>$u$</td>
<td>Induced velocity</td>
<td>(m s⁻¹)</td>
</tr>
<tr>
<td>$U$</td>
<td>Non-dimensional induced velocity</td>
<td>(-)</td>
</tr>
<tr>
<td>$u_c$</td>
<td>Superficial velocity</td>
<td>(m s⁻¹)</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage</td>
<td>(V)</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
<td>(m³)</td>
</tr>
<tr>
<td>$v_d$</td>
<td>Darcy velocity</td>
<td>(m s⁻¹)</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Measured voltage between electrodes</td>
<td>(V)</td>
</tr>
<tr>
<td>$V_s$</td>
<td>Supplied voltage</td>
<td>(V)</td>
</tr>
<tr>
<td>$x$</td>
<td>Spatial coordinate</td>
<td>(m)</td>
</tr>
<tr>
<td>$X$</td>
<td>Non-dimensional distance</td>
<td>(-)</td>
</tr>
<tr>
<td>$y_a$</td>
<td>Activity coefficient</td>
<td>(-)</td>
</tr>
<tr>
<td>$z$</td>
<td>Spatial coordinate (vertical)</td>
<td>(m)</td>
</tr>
<tr>
<td>$Z$</td>
<td>Impedance</td>
<td>(Ω)</td>
</tr>
<tr>
<td>$Z_i$</td>
<td>Valency</td>
<td>(-)</td>
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</tbody>
</table>
Greek Letters

\( \alpha \)  
Sorption retardation factor  
(-)

\( \alpha_r \)  
Viscosity correction factor  
(-)

\( \delta \)  
Constrictivity  
(-)

\( \varepsilon \)  
Porosity  
(-)

\( \varepsilon \)  
Dielectric permittivity  
\((J^{-1} \text{ C}^2 \text{ m}^{-1})\)

\( \kappa \)  
Electrical Conductivity  
\((\text{S m}^{-1})\)

\( \kappa \)  
Reciprocal of Debye length  
\((\text{m}^{-1})\)

\( \Gamma \)  
Source term  
\((\text{mol l}^{-1} \text{s}^{-1})\)

\( \gamma_w \)  
Wall shear  
\((\text{s}^{-1})\)

\( \lambda \)  
Ratio of solute diameter to pore diameter  
(-)

\( \lambda^\theta \)  
Limiting equivalent conductivity  
\((\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})\)

\( \Lambda_D \)  
Diffusivity ratio  
(-)

\( \lambda_m \)  
Species decay term  
\((\text{s}^{-1})\)

\( \mu \)  
Viscosity  
\((\text{kg m}^{-1} \text{s}^{-1})\)

\( \nu \)  
Pore water velocity  
\((\text{m s}^{-1})\)

\( \nu \)  
No. of ions formed from 1 mole of electrolyte  
(-)

\( \theta \)  
Angle  
(-)

\( \rho \)  
Density  
\((\text{kg m}^{-3})\)

\( \sigma \)  
Specific surface  
\((\text{m}^{-1})\)

\( \tau \)  
Tortuosity factor  
(-)

\( \tau_s \)  
Mean survival time.  
\((\text{s})\)
### Nomenclature

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<thead>
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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>(\omega)</td>
<td>Angular frequency</td>
<td>((s^{-1}))</td>
</tr>
<tr>
<td>(\psi)</td>
<td>Electric potential</td>
<td>((V))</td>
</tr>
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</table>
1. Introduction

1.1 General Overview

This thesis is about mass transport in liquid-saturated porous media and, specifically, the effect of surface shear on the rate of mass transport. The type of system under consideration is a porous medium which is open to liquid at one surface and sealed at all other surfaces, hence there is no bulk flow within the pores. Flow of liquid across the surface is smooth to prevent any effects caused by oscillating or fluctuating flow.

![Diagram of the types of flow configuration used for the experiments described in Chapters 3 and 4.](image)

**Fig. 1.1** Diagram of the types of flow configuration used for the experiments described in Chapters 3 and 4.

The diagram above shows the three types of flow used, the striped arrows represent accelerating flow while the other arrows represent a constant flow rate, the shaded
areas are the liquid-saturated porous media and the solid lines are sealed surfaces. For the two types of cell the porous medium was packed ballotini, and for the probe it was sintered high density polythene known as Vyon, supplied by Porvair.

Results are presented for each of these configurations with the diffusing species being HCl in each case and with surface shears up to approximately $40 \text{ s}^{-1}$ for the cell experiments and up to over $1000 \text{ s}^{-1}$ for the probes. Experiments were performed using different sizes of ballotini in the range 100 to 1000 micron. The results demonstrate that the rate of mass transport increases with increasing surface shear and the effect is greater for beds composed of larger beads.

This increase in mass transport is modelled by introducing a velocity term to the diffusion equation. The velocity decreases exponentially moving away from the surface into the porous medium and is termed the induced velocity. Results from the rectangular cell are used to determine the relation between surface shear, bed depth and induced velocity thus allowing the results for the cylindrical cell and the probe to be predicted. The induced velocity is not a bulk fluid velocity but is a way of modelling the increase of mass transport, over and above Fickian diffusion, caused by mixing due to eddies and miroturbulence induced in the pore spaces adjacent to the bed surface.

1.2 Relevance and Applications

The particular reason for starting this study was to improve the design of a novel conductivity probe for measuring solids concentrations in slurries and dispersions. The main advantage of this probe over previous conductivity methods is that it automatically compensates for any change in the conductivity of the liquid phase in which the solid is dispersed. The response time of the probe to any change in the conductivity of the liquid phase is dependent on the rate of transport of ions within a saturated porous disc (the white discs in Fig. 1.2 below). A detailed description of the probes is given in Chapter 3. In order to improve the response time a study of the rate of diffusion of electrolytes in porous media depending on porous media properties and surface shear was necessary.
Transport of ions in porous media is also important in other areas, for example the confinement of nuclear waste, the diffusion of chloride ions in concrete and any ionic pollutants in groundwater. It is acknowledged that these systems are generally more complex than the experimental systems described here but it is useful to study individual effects in isolation to understand what part they will play in more complex situations.

1.3 Chapter by Chapter Summary

Chapter 2

The literature review starts off by briefly reviewing methods of measuring dispersed solids concentration in solid-liquid systems. The use of electrical measurements is then examined in a little more detail. The next main section, following a brief introduction to diffusion and diffusion coefficients in general, deals with diffusion in porous media and how it has been related to medium properties such as porosity and tortuosity. This is followed by a summary of some experimental methods for studying diffusion in porous media. The use of models based on convective-dispersion equations to describe various processes is then reviewed. Finally, there are two short

Fig. 1.2 3D visualisation of the conductivity probes (refer to Chapter 3 for further details of the probes).
sections, of relevance to experiments carried out using ballotini, on the properties of the glass water interface and on sphere packings.

Chapter 3
Chapter 3 deals with the design and construction of the conductivity probes including the electrical circuitry, physical dimensions and the properties of the porous section. The experimental method for experiments designed to study mass transport within the probe is also described.

Chapter 4
This chapter is concerned with the other experiments, these were carried out using beds of glass beads in perspex cells with series of electrodes at different bed depths. Two different types of cell with different flow configurations and five different sizes of ballotini were used. The design of the cells, electrical circuits, flow circuits, a computer program used for data acquisition, the size distributions of the ballotini and the experimental method are all described.

Chapter 5
The modelling chapter describes a finite difference model for the experiments described in the two preceding chapters. Firstly, a one dimensional model based on Fick's law, with a diffusion coefficient adjusted to allow for the tortuosity of the porous medium, is introduced to describe experiments where the effect of surface shear is negligible. A similar model using radial co-ordinates is used to model probe experiments at low flow rates. The induced velocity model is then developed and applied to a two dimensional model for the cylindrical cell which also includes radial as well as axial diffusion. Finally the model is applied to the probes at higher shear rates.

Chapter 6
In Chapter 6 the experimental results for the probes and the cells are presented and compared with the models from Chapter 5. The modelling is discussed in the light of the results and suggestions are made for improvements and future work.
Chapter 7

The conclusions which can be drawn from this work are summarised.
2. Literature Review

2.1 Techniques for measuring the concentration of dispersed solids

A variety of techniques have been used for the measurement of the concentration of solids dispersed in a liquid continuous phase. Many of these techniques may also be used for measuring the dispersed phase in emulsions e.g. oil in water. For dilute systems optical methods may sometimes be used but many systems are optically opaque necessitating the use of other techniques. Williams et al. have published a comprehensive review covering techniques for measurement of phase concentration, flux and particle size in opaque, sedimenting systems which they divided into five main areas-

- External radiation
- Emitted radiation
- Electrical properties
- Physical properties
- Direct methods

For concentration measurement, which is the area of particular interest here, there are a number of advantages in using electrical measurements, in particular conductance measurement-

1) The measuring circuit is simple and cheap.
2) Measurements can easily be automated at regular intervals or could even be continuous.
3) Safety is not an issue (very low currents are used).
4) Provided that the conductivities of the solid and the liquid phase are significantly different measurements can be made over virtually the entire concentration range (0-100%).
None of the other methods offer all of these advantages: radiation methods tend to be much more expensive and some such as X-rays have associated safety hazards, physical property measurements, such as pressure and density, do not give high accuracy and direct methods such as sampling tend to be time consuming and may disturb the process.

In recent years there have been a lot of developments in tomographic imaging techniques and some of these, including electrical resistance tomography, are now in use industrially. Tomography can give concentration measurements but tends to be very expensive and the details of creating tomographic images are not within the scope of this thesis.

2.2 Electrical measurements of two-phase, solid - aqueous electrolyte systems

2.2.1 General principles

Resistances of electrolytes are generally obtained from AC measurements because using DC there are problems due to polarisation resistance at the electrodes. Using AC there are complications because the resistance cannot be found simply from Ohm's law since for alternating currents:

\[ V = IZ \]  

(2.1)

where \( V \) is voltage, \( I \) is current and \( Z \) is impedance, which as well as a resistive part also has capacitive and inductive contributions. Depending on the conditions used and the accuracy required the effect of capacitance and inductance can usually be made negligible by choosing an appropriate frequency for the AC supply. Assuming the cell can be modelled as a series circuit (which is generally considered to be the most reasonable physical approximation for a simple system consisting of an electrolyte between two electrodes) the following equation applies:

\[ I = \frac{V}{\sqrt{R^2+(\omega L-1/\omega C)^2}} \]  

(2.2)
where, $V$ is applied voltage, $R$ is Resistance, $\omega$ is angular frequency (frequency multiplied by $2\pi$), $L$ is inductance and $C$ is capacitance.

For this circuit $I = \frac{V}{R}$ when $\omega = \frac{1}{\sqrt{LC}}$. In practise there is often a wide range of frequencies over which the impedance and resistance are approximately equal. In general the main effect apart from resistance in the electrolyte is capacitance due to the electric double layer which forms at the surface of the electrodes. For example Conca and Wright\cite{16} used a frequency of 1kHz for their set up but they found that any frequency from 600 to 7000Hz would have been appropriate. This conclusion was reached by monitoring the total impedance and the phase angle whilst varying the frequency, a technique known as electrical impedance spectroscopy. Capacitance measurements can be used to determine solids concentrations but they are somewhat more complex and are not suitable for a highly conducting continuous phase\cite{7},\cite{8}.

2.2.2 Measurement of concentration of dispersed solids
Electrical measurements on suspensions of solids in electrolyte solutions for the determination of solids concentration have been used previously by a number of authors. Fixed arrays of electrodes on the sides of the container have been used to study solids concentration with depth during sedimentation\cite{8},\cite{9}. A variety of relations between the mixed (solid-liquid) and the continuous (liquid phase) have been suggested, the best known theoretical equation is probably that due to Maxwell\cite{10}:

$$\frac{\kappa_m}{\kappa_c} = \frac{1+2\beta c_v}{1-\beta c_v} \quad (2.3)$$

where-

$$\beta = \frac{\kappa_d-\kappa_c}{\kappa_c+2\kappa} \quad (2.4)$$

$\kappa$ is conductivity, $c_v$ volume concentration of solids and the subscripts $m$, $c$ and $d$ refer to the mixed, continuous and dispersed phases respectively. When the conductivity of the dispersed phase is negligible, $\beta$ is 0.5 and-
Maxwell's equation was derived for dilute suspensions ($c_r < 0.1$) of mono-sized spheres but has been found to give a good approximation over a wider range of concentrations and particle shapes. Another relationship has been suggested by Bruggeman\cite{11} which leads to-

$$\frac{k_m}{k_c} = \frac{1-c_r}{1+0.5c_r}$$ \hspace{1cm} (2.5)

When the conductivity of the dispersed phase is zero, this equation is the same as the first two terms of Equation (2.5) expanded as a power series. De La Rue and Tobias\cite{12} compared the effectiveness of the two equations for fitting their data and concluded that, other than for mono-sized spheres, Bruggeman's equation gave a better fit whilst for uniform spheres the data fell between the two theoretical curves.

A conductivity probe\cite{13} for measuring local solids concentrations in slurry systems has been developed by Nasr-el-Din and co-workers. The probe consists of 4 electrodes, 2 field electrodes and 2 sensor electrodes, the separation of the sensor electrodes being just one millimetre. The probe was calibrated for voltage across the sensor probes against solids concentration of non-conducting solids. (This type of arrangement with separate injection and sensor electrodes is normally used in electrical resistance tomography but in that case there is a large array of electrodes and readings are taken between each combination of electrodes within a plane.)

Concentrations can be determined by simply measuring the current between the field electrodes but the results would be dependent on the flow rate past the probe because the polarisation resistance at the electrode surface is flow rate dependent. Using this method calibration with flow rate would be needed but the problem is eliminated by using a separate sensor circuit. The experimental results showed that the variation in measured voltage with fluid velocity was indeed insignificant. Two factors were identified which did effect the voltage, these were temperature and the chemical composition of the conducting fluid. The measured potential was found to increase with temperature by about 2% per °C in the range 8 to 25 °C.
In a more recent paper\cite{14} Holdich and Sinclair suggest the use of Equation (2.6) with an empirical exponent $n$, determined by calibration. Solids concentration is then given by-

$$c_v = 1 - \left(\frac{c_e}{c_f}\right)^\frac{1}{n}$$

(2.7)

In their paper the concentration in the feed to a crossflow filtration rig was measured by measuring the conductivity of the filtrate and the conductivity of the feed simultaneously, thus eliminating any error due to changes in temperature or electrolyte concentration. The same equation was used by Butt in his study of sedimenting systems\cite{15} who reported values for $n$ varying from 1.33 for ballotini to 2.10 for Kaolin. The same equation is also used in reservoir modelling where it is known as Archie's law\cite{16}.

The impedance of suspensions of highly conductive particles has been studied by Sonneveld et al.\cite{17}, they found strong dependence on the frequency of the voltage source although their readings did reach a high frequency limit. They also discussed the implications of flocculation or chain formation in their suspensions.

2.2.3 Porous media containing electrolyte solutions

A porous medium containing electrolyte can be considered to be similar to a concentrated dispersion. Electrical measurements for this type of system can also be taken to give information about the structure of the porous medium and the rate of diffusion of electrolyte through the medium. Electrical measurements have been used to study the migration of chloride in concrete and the transport of ionic species in soil. The use of this type of technique is mentioned again in the following section about diffusion.
2.3 Diffusion

2.3.1 Introduction to diffusion

Diffusion is the process whereby mass transport occurs along the direction of negative concentration gradient. Hence in a closed system the concentration of each species present will eventually be constant throughout in the absence of any disturbing forces.

The rate of diffusion of a species under set conditions is given by the diffusion coefficient $D$ where-

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

(2.8)

This is known as Fick's first law, $c$ refers to concentration, $J$ is mass flux, and $x$ is a spatial co-ordinate. Fick's second law may then be derived-

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

(2.9)

$D$ is here treated as being a constant with concentration for a given system and temperature but, in fact, the diffusion coefficient for aqueous electrolytes does vary somewhat with concentration.

There is a large body of literature concerning the mathematics of diffusional processes. The approach taken is largely dependent on the geometry and boundary conditions for the particular system under consideration. The relevant approaches for the set-up used in this thesis are considered again in Chapter 5.

Analytical solutions have been obtained for diffusion into or out of bodies of various regular shapes where diffusion occurs at all the surfaces but other systems generally have to be treated numerically. Another approach which can be fruitful is to treat an object where diffusion occurs at only one face as semi-infinite. This will give accurate results at least until the concentration at the closed end of the object begins to change.

The solution to Fick's second law for diffusion into a semi-infinite slab is-
\[ c(x,t) = c_0 \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{D}t} \right) \right] \]  

(2.10)

2.3.2 Measurement of diffusion coefficients

There are numerous methods for determining diffusion coefficients in liquid systems and these are discussed in some detail by Tyrrell and Harris\textsuperscript{[18]}. One of the most common is the diaphragm method as used by Stokes\textsuperscript{[19],[20]} and, with various alterations, by many others. In this technique there are two chambers, initially containing different concentrations of the diffusing species, which are separated by a diaphragm. The two cells are generally stirred to ensure 'perfect mixing' within the cells whilst the pores of the diaphragm have to be small enough to prevent any hydrodynamic flow within the membrane. In some cases the stirring speed has been reported to have an effect on the results produced by this method but Mills\textsuperscript{[21]} found that using a cell of the Stokes design this effect was not observed. For dilute electrolyte solutions (below approximately 0.05M) surface effects within the diaphragm can also interfere with the results.

Conductimetric methods are generally considered to give the most accurate results for the diffusion coefficients of ions in solution. The Harned technique\textsuperscript{[22]} has given the most accurate results for dilute electrolyte solutions (Harned is also the author of a comprehensive review concerning diffusion of electrolytes\textsuperscript{[23]} covering both theory and experimental work). This technique involves the use of a cell of height 'h' with 2 pairs of electrodes at a distance of h/6 from either end of the cell. This positioning of the electrodes is essential if the diffusion coefficient is to be calculated as it allows the equation required to be simplified. The diffusing electrolyte is introduced to the bottom of the cell and if a low concentration is used the differential diffusion coefficient is obtained from the equation-

\[ D = -\left( \frac{h}{2} \right)^2 \cdot \frac{d\ln(c_e - c_t)}{dt} \]  

(2.11)

where \( \kappa_b \) and \( \kappa_t \) are the conductivities between the bottom and the top electrodes respectively, \( r \) is a calibration constant allowing for different cell constants for the two electrode pairs and \( t \) is time. This equation applies only to restricted diffusion so
measurements are only taken after enough time has elapsed for the concentration to begin to change at the ends of the cell. The cell must be kept at a constant temperature and free from vibration to prevent any disturbances which will increase the apparent rate of diffusion. This technique can be used to measure diffusion coefficients in porous media as well as in bulk solution as demonstrated by Leaist\cite{24}. Leaist has also used the Harned technique to determine the first accurate diffusion coefficients for aqueous hydrofluoric acid and aqueous potassium fluoride\cite{25}.

\[ \text{Electrodes} \]
\[ \text{Salt Cup} \]

\[ h/6 \]
\[ h \]
\[ h/6 \]

Fig. 2.1 Simplified diagram of Harned's apparatus; the more concentrated electrolyte solution is placed in the 'salt cup' which is then slid into position at the start of an experiment.

The work of Carey et al. on ionic diffusion\cite{26} shows how the variation of $D$ with concentration should be taken into account when large changes in concentration are involved. They carried out one dimensional diffusion experiments with aqueous copper sulphate, at high concentrations, using absorbance of monochromatic visible light for the concentration measurements. In their model they used a diffusion coefficient which was a function of electrolyte concentration (the function used was a fit to previously published experimental data).
Thus Fick's second law became:

\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D'(c) \frac{\partial c}{\partial x} \right] \]  

(2.12)

where \( D'(c) \) is the volume-fixed mutual diffusion coefficient as a function of concentration.

This equation was solved numerically using a Crank-Nicolson approximation. The model predicts asymmetric diffusion profiles and less diffusion than a Fickian model which uses the value of \( D \) for infinite dilution in an error function solution to the diffusion equation. The experimental results were more like the Non-Fickian than the Fickian model predictions but the departure from Fickian behaviour was larger than predicted. The authors considered that the discrepancy could be due to inaccuracies in the available data for \( D(c) \), which was supposed to allow for any density or viscosity effects, or alternatively an effective interfacial tension between the 'two' fluids, or some other unmodelled process could have been the cause.

### 2.3.3 Effective Diffusion Coefficients

One way of dealing with diffusion in porous media is to use a diffusion coefficient modified by some type of hindrance factor which can be related to the structure of the porous media. The most common structural property to consider is the porosity. Neale and Nader\(^{27}\) used a model of a porous medium made of spheres in which each sphere is considered to be surrounded by a void the shape of a spherical shell which is in turn surrounded by an external porous mass. They defined the diffusivity factor \( \Lambda_D \) as the 'Effective diffusivity within the porous medium divided by the absolute diffusivity in the unobstructed fluid' and calculated it to be \( 2\varepsilon/(3-\varepsilon) \) where \( \varepsilon \) is the porosity. This result is independent of the size distribution of the spheres and applies to electrical conductivity as well as diffusivity. They compared their equation with previously reported experimental results which were mainly electrical conductivity results and obtained satisfactory agreement. A number of other authors have suggested relations between diffusivity factor and porosity and some of these are shown in the table below.
## Table 2.1 Table of suggested relations between diffusivity factor and porosity.

<table>
<thead>
<tr>
<th>Diffusivity Factor</th>
<th>Author(s)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\varepsilon/(3-\varepsilon)$</td>
<td>Neale and Nader\textsuperscript{[23]}</td>
<td>Derived for medium composed of spheres, independent of size distribution.</td>
</tr>
<tr>
<td>$\varepsilon[1-(1-\varepsilon)/2]$</td>
<td>Prager\textsuperscript{[28]}</td>
<td>Considered a model of an idealised bed of spheres in which the centres are randomly situated and the spheres are not restricted to non-overlapping locations.</td>
</tr>
<tr>
<td>$\varepsilon/[1-1/2(1n\varepsilon)]$</td>
<td>Weissberg\textsuperscript{[29]}</td>
<td>Based on Prager’s work, this is an upper bound.</td>
</tr>
<tr>
<td>$\varepsilon/2$</td>
<td>Wheeler\textsuperscript{[30]}</td>
<td>Applies for porosities up to approx. 0.3.</td>
</tr>
<tr>
<td>$\varepsilon^{3/2}$</td>
<td>Marshall\textsuperscript{[31]}</td>
<td>Model consists of layers of randomly distributed pores.</td>
</tr>
<tr>
<td>$\varepsilon^{4/3}$</td>
<td>Millington\textsuperscript{[32]}</td>
<td>Derived for isotropic porous media, pores assumed to be approximately spherical.</td>
</tr>
<tr>
<td>$(\varepsilon/(2-\varepsilon))^2$</td>
<td>Mackie and Meares\textsuperscript{[33]}</td>
<td>Used a ‘site-jumping’ model in a simple cubic lattice.</td>
</tr>
<tr>
<td>$\varepsilon/\tau$</td>
<td>MacMullin\textsuperscript{[40]} and others</td>
<td>$\tau$ is a tortuosity factor.</td>
</tr>
<tr>
<td>$\varepsilon\delta/\tau^{-2}$</td>
<td>Van Brakel and Heertjes\textsuperscript{[34]}</td>
<td>$\delta$ is constrictivity and $\tau'$ is a different tortuosity factor. For homogeneous, isotropic packings of round particles, $\delta/\tau^{-2}$ is approximately 0.57.</td>
</tr>
</tbody>
</table>

All the relations tabulated above are specifically stated to apply to diffusion in porous media. Further relations can be found listed elsewhere\textsuperscript{[35]} which are primarily aimed at describing electrical conductivity but by analogy may be considered to apply to diffusional transport.
Apart from the values due to Mackie and Meares (and Wheeler for porosities above 0.3) those models which are solely dependent on porosity all give very similar curves. From the available experimental data it is not possible to say, with certainty, which is the most accurate. This is demonstrated in Figure 2.2 below.

![Graph showing predicted variations of diffusivity factor with porosity.](image)

**Fig. 2.2** Graph showing predicted variations of diffusivity factor with porosity.

Clearly the diffusivity factor will not depend solely on porosity, however, because porous media can have vastly different structures whilst having the same porosity. For example, it is not realistic to expect the same diffusional behaviour through a medium consisting of straight through cylindrical pores as for a highly disordered medium of the same porosity which is likely to include dead-end pores. The simplest approach to allowing for such variations in structure is to introduce a tortuosity term, $\tau$. Having said this, the approach using just porosity can be very useful, particularly for systems of relatively regular particles.

Tortuosity is generally considered to be a measure of the ratio of the average path length to traverse a porous medium (staying within the pore space) to the thickness of the medium. For the purposes of this discussion tortuosity will be regarded as an experimentally measured characteristic property of a porous medium. It should be noted, however, that exact definitions for tortuosity and a tortuosity tensor have been
given by researchers working on mathematical descriptions of porous media\cite{34}.

Van Brakel and Heertjes\cite{32} introduce an additional constrictivity term which means that their tortuosity will not be the same as the tortuosity of MacMullin. The constrictivity is defined in terms of the ratio of the maximum and minimum pore cross-sectional area of a pore space segment. For well defined packings $\delta$ and $\tau'$ can be calculated and $\delta$ can be measured independently by mercury porosimetry.

### 2.3.4 Experimental work in porous media

#### 2.3.4.1 Conductivity ratios and diffusion

Taffinder and Batchelor\cite{37} were concerned with the measurement of effective diffusivities in solidified wastes. In this area the aim is to minimise effective diffusivities in order to prevent contaminants from diffusing out of the solidified waste into the environment. They found conductivity measurements to be a convenient and quick way of determining effective diffusivities in Portland cement. They made extensive use of the diffusivity factor which they call the 'MacMullin Number' $N_m$ and also equate with the conductivity ratio-

$$N_m = \frac{\kappa_p}{\kappa_s} = \frac{D_m}{D_e} = \frac{1}{\epsilon} \quad (2.13)$$

where, $\kappa_p$ is conductivity of pore water, $\kappa_s$ conductivity of porous medium and pore water, $D_m$, Molecular diffusivity in water and $D_e$, Effective diffusivity

The diffusivity factor was obtained by measuring the conductivity of a sample of cement and then expressing the pore water and measuring its conductivity. These results were checked by carrying out measurements of the diffusivity of lithium bromide solution through samples of cement using a traditional two chamber method and the results were in approximate agreement. There are a number of other papers in this area\cite{38},\cite{39},\cite{40},\cite{41} which all suggest that the MacMullin number, also commonly known as the Formation Factor when determined from conductivity measurements, can be linked to the porosity empirically by the equation-
where \( p \) and \( q \) are empirical factors which depend on the substance making up the porous medium. This can be fitted fairly well to their own data but the authors say that there is no evidence for general applicability and more data is required. They also found a correlation between bulk density and MacMullin number. The results showed that the MacMullin number could be considerably lowered by increasing the water to cement ratio \( i.e. \) effective diffusivity increased with increasing porosity, as one would expect.

MacMullin\(^{[42]}\) had previously suggested the following relationship-

\[
m^2 = KB \frac{R}{R_0}
\]  

(2.15)

where \( m \) is hydraulic radius, \( K \) a constant, \( B \) viscous flow permeability and \( R/R_0 \) is the resistivity ratio \( i.e. \) Taffinder and Batchelor's 'MacMullin Number'

The viscous flow permeability is an experimentally determined parameter for characterising porous media and is given by the equation known as Darcy's law-

\[
B = -\frac{u \mu l}{\Delta P}
\]  

(2.16)

Where \( u \) is superficial velocity, \( \mu \) the viscosity of the fluid passing through the porous medium, \( l \) is the sample thickness and \( \Delta P \) is the pressure drop across the sample. \( B \) is independent of the fluid used, depending only on the properties of the bed.

Using a large amount of available data for a variety of porous media, a graph was plotted of log \( m \) against log \( B(R/R_0) \) which gave a straight line and \( K \) was determined as 3.666±0.098.

The work of Torquato and Kim\(^{[43]}\) is highly theoretical but shows that it may be possible to link diffusivity factor to porosity and permeability. They were working on the relation between permeability \( B \) and other properties of porous media and they give the following 3 relations for porous media with perfectly absorbing walls \( i.e. \)
trap boundaries).

\[ B \leq D\tau_s \]  
(2.17)

\[ B \leq D^{T_j}_{F} \]  
(2.18)

\[ B \leq D^{\xi}_F \]  
(2.19)

where \( D \) is the diffusion coefficient in fluid region, \( \tau \) 'Mean survival time associated with steady-state diffusion of reactants in fluid region’, \( F \) the electrical formation factor (i.e. as MacMullin number above) and \( T_j \) is the principal (largest) diffusion relaxation time associated with the time dependent trapping problem.

For pore walls which are partially reflecting, these inequalities need to be adjusted to take into account the surface rate constant. Equations (1) and (2) can be rigorously proved whereas (3) is not strictly true, as theoretical counter examples can be found, but it tends to give a sharper bound. If an accurate relation between permeability and effective diffusivity were available this would enable good predictions to be made for the rate of diffusion in various porous media based on permeability data.

2.3.4.2 Diffusion in packed beds

Schofield and Dakshinamurti\(^{44}\) studied diffusion in various packed beds. In their method they used a container, the lower half of which was occupied by a porous medium saturated with potassium bromide solution. Either potassium nitrate or ammonium nitrate solution at the same concentration as the potassium bromide was added carefully to fill the container. (These particular solutions were chosen because the ionic mobilities of bromide and nitrate and of ammonium and potassium are very similar so the system could be considered to have a single diffusion coefficient for cations and anions.) After allowing 1-2 days for diffusion to take place the solution above the porous medium was drawn off and the quantity of bromide and/or ammonium contained therein was determined volumetrically. The following equation,
due to Einstein\cite{45}, was used-

\[ \sqrt{\frac{n}{2}} \cdot \frac{q}{c_p A} = \sqrt{2Dt} = \Delta \bar{X} \]  

(2.20)

where \( q \) is the number of ions which diffuse across a plane of area \( A \) in time \( t \), \( \Delta \bar{X} \) is the root mean square displacement of an individual ion and \( c_p \) is the concentration at the boundary given by-

\[ c_B = \frac{\varepsilon \cdot c_0}{1 + \varepsilon} \]  

(2.21)

where \( c_0 \) is the initial concentration of KBr within the channels of the porous medium and \( \varepsilon \) is defined as the fraction of the total cross section taken up by channels \( i.e. \) the porosity. \( c_B \) and hence \( \varepsilon \) were determined using a known value of \( D \). The porous media used were glass beads, sand, bentonite, Rothamsted subsoil clay and kaolin. The results with glass beads showed good agreement with the theory of Neale and Nader\cite{47}.

Leaist\cite{22} used Hamed's conductimetric technique, which had previously been used to study diffusion in bulk solutions, to study diffusion through packed beds of spheres. In his first experiment, he studied the diffusion of HCl through a packed column of glass beads of diameter 0.30 ± 0.01 mm. After injecting HCl into the bottom of the cell it was left for a day for any unwanted temperature disturbances or lateral concentration gradients to decay before the conductance measurements were begun. Measurements were taken over 4 days and the diffusion coefficient, \( D \) was found to remain constant (within 0.3%). Further experiments were carried out using beads of cation exchange resin. Allowing for the different size of these beads, diffusion was found to occur more quickly than through the column of glass beads, this was attributed to the porous nature of the beads themselves.

Leaist defined tortuosity \( \tau \) by the equation

\[ \tau = \frac{D_{aw}(c_p)}{D(c)} \]  

(2.22)

where \( D_{aw} \) and \( D \) are the diffusion coefficients of electrolyte in water and in the packed
bed and $c_{aq}$ and $c$ are the molar concentrations of electrolyte in the pore solution and in the column as a whole. The measured tortuosity was found to be $1.45 \pm 0.01$ and independent of the acid used for hydrochloric, sulphuric and nitric acids. This paper mentions the possibility of different rates of diffusion at the glass-water interface but suggests that this will have little effect in his experiment because of the low specific area of the beads used.

Another experimental study of diffusion of electrolytes was carried out by Jahnke and Radke\cite{46} who used caesium chloride diffusing into a Montmorillonite clay gel. They considered that, in general, the transport rate in porous media is modified relative to that expected in bulk solution by two phenomena, the tortuosity of the porous media and adsorption which. They accounted for the latter by using a sorption retardation coefficient $\alpha$ which is related to the porosity, $\varepsilon$ and the Henry's law constant $K_H$, in the Henry's law region by-

$$a = 1 + \frac{(1-\varepsilon)K_H}{\varepsilon}$$

(2.23)

**Fig. 2.3** Schematic of Jahnke and Radke's\cite{46} radially perfused cell. Not shown is an exit line within the cell used to eliminate trapped air.
The experimental method involved pumping the stock solution of CsCl across the top of the porous sample and around a closed loop (see Fig. 2.3). The concentration of the solution was monitored during the experiment then at the end of the experiment the Montmorillonite gel was sliced into thin sections in order to obtain a concentration profile. This allowed simultaneous determination of the effective diffusion and the sorption retardation coefficients. Jahnke and Radke concluded that there was strong evidence for surface diffusion increasing the diffusion rate in their experiment. They also considered in detail the validity of using a one dimensional diffusion equation to describe what took place in their experiments and concluded that it was valid under the conditions used.

Webster and Taylor\(^{47}\) carried out experiments in a wave tank. They measured the rate of transport of sodium chloride out of a sediment at the bottom of the tank for three different grain sizes of sediment with and without waves. They found the rate of dispersion increased with waves by over a thousand fold for a grain size of 3.5 mm whilst for 0.8 mm grains there was no effect. They modelled this in terms of ‘rotational dispersion’ induced by the fluctuating pressure gradients caused by the wave motion.

### 2.3.4.3 Extraction

Another area in which rate of diffusion is very important is extraction. Piret\(^{48}\) studied the extraction of aqueous solutions of KCl, NaCl, K\(_2\)CrO\(_4\), CuSO\(_4\) and acetic acid from single capillaries, tubes containing beds of glass beads and porous alumina spheres. The transfer mechanism was verified as diffusional. For the tubes containing no beads log-log graphs of percentage of electrolyte extracted against time were straight lines of gradient 0.5 as predicted by the Liebhafsky equation:

\[
E = 100 - 200 \sqrt{\frac{\pi D t}{\delta}}
\]  

which is an approximation, valid up to 50% extraction, to the exact solution:

\[
E = \frac{400}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp\left(-\frac{(2n-1)^2 \pi^2 D t}{4 \delta^2}\right)
\]  

22
where, $E$ is the percentage unextracted, $D$ the diffusion coefficient, $t$ time and $l$ the tube length.

The ratio of diffusivity in the packed bed to diffusivity in the unpacked tube was the same for all the electrolytes. The glass spheres were of diameter $0.15 \pm 0.02$ mm and gave a packing porosity of $0.394 \pm 0.5\%$. The tortuosity (referred to in this paper as 'pore-shape factor') was found to be $1.46 \pm 0.04$, in excellent agreement with Leaist’s tortuosity value from his diffusion experiments. A similar equation was derived for extraction from porous spheres and was applied to the extractions from alumina.

Osburn and Katz\textsuperscript{49} previously studied the effect of structure on extractions from porous media, they produced theoretical extraction curves for 7 different types of structure-

1) Uniform Porous Solid
2) Capillaries perpendicular to face
3) Capillaries at an angle to face
4) Capillaries leading from reservoir
5) Wedge shaped solid
6) 2 different capillary sizes
7) 2 different sample thicknesses

Their experimental work was done on the extraction of oil from Soybean flakes. The extraction curves obtained were similar to the theoretical ones where there were two different diffusion coefficients (i.e. structures 6 and 7) and a method was developed for determining these two coefficients. In this case the diffusion coefficient was found to vary with the thickness of the flakes but this was attributed to differences in structure due to the finer crushing.

2.3.4.4 Ion-Exchange
Lewnard Petersen and Radke\textsuperscript{50} developed a theory concerning the diffusion of $H^+$ and $OH^-$ in adsorptive, porous solids and tested it by measuring the uptake of acid and
base into γ-alumina pellets which showed good agreement with the theory. For a linear adsorption isotherm and $D = 1$, their equation simplifies to-

$$\frac{\partial C(x,T)}{\partial T} = \nabla^2 C(x,T)$$  \hspace{1cm} (2.26)

where $C(x,T)$ is dimensionless concentration, $T$ is dimensionless time and $x$ is the $x$ co-ordinate. In all other cases the resulting equation can not be solved analytically but numerical methods must be used.

Mackie and Meares\textsuperscript{17} also combined theory and experiment in their work on diffusion in ion exchange membranes. Using an idealised model of a cation-exchange membrane they derived an integrated rate equation for the flux of cations through the membrane which applied to steady state diffusion for both 1:1 electrolytes and for salts with a divalent cation. They tested the theory using 5 different electrolytes and a membrane which was as far as possible similar to their idealised membrane. The results showed reasonable agreement particularly in the middle of the concentration range used and the deviations could be explained in terms of the approximations made.

\subsection*{2.3.4.5 Effect of ratio of solute diameter to pore diameter}

When the radius of the diffusing species is not negligible in comparison to pore diameters there is additional hindrance to diffusion due to frictional and size-exclusion effects.

Cady and Williams\textsuperscript{31} studied molecular diffusion into water saturated wood. They carried out an extensive series of experiments using refractometry to monitor concentrations. Diffusion was found to be hindered mainly by a mechanical blocking effect and the diffusion coefficient, $D$ was found to be independent of the length of sample. They used the following equation to determine the 'Fractional Open Area', $A_f$ of the wood samples-

$$D_wA_f = D_s(1 + 2.4\lambda)(1 + \alpha_f)$$  \hspace{1cm} (2.27)

where $D_s$ is the diffusion coefficient of the substance in water, $D_s$ is the diffusion
coefficient of the substance within the porous solid, $\lambda$ is the ratio of radius of the diffusing species to radius of the pore through which diffusion is taking place and $\alpha$, is a correction factor for changed viscosity.

The Dumanski\textsuperscript{[52]} equation-

$$A_f = \frac{1}{1+(1-\epsilon)^{2\lambda}}$$  \hspace{1cm} (2.28)

where $\epsilon$ is the porosity, defined in this paper as 'The ratio of the density of the porous solid to the density of the solid material forming the structure', was found to be an accurate approximation. They distinguished three types of diffusion which they labelled *Hindered Diffusion, Free Diffusion* and *Stirred Diffusion*.

Satterfield *et al.*\textsuperscript{[53]} studied diffusion in fine pores where the pore diameter is of a similar order of magnitude to the diffusing particles. Diffusion measurements were made for a variety of organic molecules and of aqueous sodium chloride diffusing into porous silica-alumina catalyst beads. At equilibrium, the solute concentration was found to be the same within and outside the pores for solute molecules with diameters up to half the pore diameter. With non-adsorbing solutes, the logarithm of the ratio of effective to bulk diffusivities decreased linearly with increasing ratio of solute diameter to pore diameter the equation for the best fit being-

$$\log_{10} \Lambda_D = -0.37 - 2.0\lambda$$  \hspace{1cm} (2.29)

Where adsorption did occur the effective diffusivity was decreased further. Deen\textsuperscript{[54]} presents previously published data which also shows a rapid drop in diffusivity with increasing solute size and discusses the theoretical explanation for this in some depth.
Matsuyama, Teramoto and Suzuki give the following equation relating the diffusion coefficient in a single pore, $D_H$, to the corresponding value in bulk solution, $D$:

$$\frac{D_H}{D} = \frac{3}{4} \cdot \pi \sqrt{2} (1 - \lambda)^{-5/2} \left[ 1 - \frac{73}{60} (1 - \lambda) + \frac{77293}{50400} (1 - \lambda)^2 \right] - 22.5083 - 5.6117\lambda - 0.3363\lambda^2 - 1.216\lambda^3 + 1.647\lambda^4$$

(2.30)

where $\lambda$ is the ratio of solute to pore diameter as previously.

2.4 Convective-dispersive transport in porous media

2.4.1 Additional factors supplementing diffusion

In general transport of ions in porous media is not restricted to diffusion, a number of other important processes can occur. These include hydrodynamically induced dispersion, adsorption at pore walls and chemical reactions which either produce the dispersing species or consume it.

When there is flow through the porous medium dispersion of solute is increased by several mechanisms. Within a single pore there exists a velocity profile with fluid flowing fastest at the centre of the pore and being stationary at the pore wall. Thus solute in the centre tends to be 'swept' rapidly along leaving behind solute closer to pore walls. The second group of mechanisms occurs when there are diverging flow
streams in which case the rate of transport through separate pores with different shapes and sizes may vary a great deal. Dispersion is also enhanced if there is any turbulence in the flow which increases the amount of fluid mixing. Frequently this is accounted for in transport equations by redefining the diffusion coefficient \((D)\) as a dispersion coefficient \((D')\) which takes into account these additional mechanisms. Different values for dispersion coefficient must often be used parallel and perpendicular to the direction of flow\(^{56}\).

Selim and Amacher\(^{57}\) give the following general one-dimensional convective-dispersive equation:

\[
\frac{\partial c}{\partial t} + \frac{\partial}{\partial x} \left( v \frac{\partial c}{\partial x} \right) = D \frac{\partial^2 c}{\partial x^2} - \frac{Q}{v} \tag{2.31}
\]

where \(Q\) is an irreversible sink/source term, \(v\) is pore water velocity, \(s\) is the surface concentration of adsorbed solute (mass of adsorbed solute per mass of solid matrix) and \(\rho\) is solid density. Many authors have used numerical approaches to solve equations similar to this one which can only be solved analytically under strictly limited conditions. Brenner\(^{58}\) has published a solution accounting for advection and dispersion across the upper surface for beds of finite length. His solution is an infinite series which under most conditions tends to converge rather slowly and is expressed in terms of Peclet number, \(Pe\). Peclet number is defined as

\[
Pe = \frac{vL}{D} \tag{2.32}
\]

where \(v\) is velocity, \(L\) is a characteristic length and \(D\) is the diffusion coefficient. For low Peclet number mixing is mainly due to pure diffusion whereas for high Peclet number dispersion due to fluid velocity dominates over any molecular diffusion taking place.

### 2.4.2 Filter cake washing

Filter cake washing is one process where there is simultaneous flow through a porous medium and diffusional transport. One of the models used is the ‘Blind Side Channel’ model of Han and Bixler\(^{59}\). In this model the filter cake is considered to consist of
straight through pores with dead end side channels containing filtrate. The contaminant being washed out diffuses into the flow channels and is then swept through the cake by the flow. Both rectangular and wedge shaped side channels were considered and wedge shaped channels were found to be better for modelling a cake composed of spherical particles. The differential equations derived were solved numerically giving good agreement with experimental results obtained using simple beds of particles such as glass beads. The most important variable in the model is the length of the side channels and the values predicted by the model agreed well with the results of calculations based on the pendular ring model for residual liquid in centrifuged beds. Han extended the model for the washing of cakes where the individual particles are themselves porous[60]. In this case washing is slower because the majority of the residual liquid is in the pores within particles rather than in the interstices and so diffusion is much slower because of the tortuous nature of the pores.

More recently the multiphase transport equations have been successfully applied to filter cake washing by Wakeman[61]. Cake thickness, saturation and permeability were found to be the most important parameters. This work is based on multiphase models derived from a spatial averaging theorem. In this type of modelling, the medium being modelled is divided up into ‘representative elementary volumes’ (as described, for example, by Bear[62]) which must be large relative to individual pores but small relative to the scale on which any macroscopic effects occur. A volume averaging process is then used. Quintard and Whitaker[63] have reviewed much of the work in this area.

2.4.3 Transport in soil and rock formations

Under certain circumstances natural convection due to density differences can be an important factor in describing transport in porous media, for example in the transport of volatile contaminants through soils[64],[65],[66]. Falta et al give the following equation as an estimate of the velocity of a parcel of fluid of density $\rho_0$ through a stagnant fluid of density $\rho_\infty$ which could be used to estimate the significance of density driven convective flow in any system-
where $v_d$ is the Darcy velocity ($\text{m s}^{-1}$), $B$ is permeability ($\text{m}^2$), $\mu$ is dynamic viscosity ($\text{N s m}^{-2}$) = 0.001 for water, $g$ is acceleration due to gravity ($\text{m s}^{-2}$), $\rho_0$ is the density of parcel of fluid moving with velocity $v_d$ and $\rho_\infty$ is the density of bulk fluid ($\text{kg m}^3$).

Mendoza and Frind$^{[66]}$ also point out that the amount of convective flow increases with increasing permeability. This group of papers are all about similar systems where an organic liquid is initially contained in a localised area near the surface of the ground, some distance above the water table. The transport of the contaminant is then modelled taking into consideration diffusion and convection. This involves considering the partitioning between phases and the calculation of the convective flow due to the organic vapour being more dense than air. These models can give useful information such as how much of the contaminant will end up in the water (which may be a water supply) and how much will diffuse into the atmosphere as gas. They all use the concept of equivalent head which is defined by Mendoza and Frind$^{[66]}$ as

$$h^* = \frac{P}{\rho_0 g} + z$$

where, $h^*$ is equivalent head, $P$ is fluid pressure relative to atmospheric pressure, $\rho_0$ is density of uncontaminated soil gas, $g$ is gravitational constant and $z$ is height above water table.

Mendoza and Frind then use the following two equations: Fluid continuity equation-

$$\frac{1}{r} \frac{\partial}{\partial r} \left[ r B^* \rho_0 g \frac{\partial h^*}{\partial r} \right] + \frac{1}{r} \frac{\partial}{\partial z} \left[ r B^* B_{zz} \frac{\partial h^*}{\partial z} \right] \left( \frac{\partial h^*}{\partial z} + \frac{\rho_0}{\rho_0 - 1} \right) + Q = S \frac{\partial h^*}{\partial t}$$

Mass continuity equation-

$$\frac{1}{r} \frac{\partial}{\partial r} \left[ r e_g D_{rr}^* \frac{\partial c}{\partial r} \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[ r e_g D_{rz}^* \frac{\partial c}{\partial z} \right] + \frac{1}{r} \frac{\partial}{\partial z} \left[ r e_g D_{zz}^* \frac{\partial c}{\partial z} \right]$$

$$+ \frac{1}{r} \frac{\partial}{\partial z} \left[ r e_g D_{zz}^* \frac{\partial c}{\partial z} \right] - e_g v_r \frac{\partial c}{\partial r} - e_g v_z \frac{\partial c}{\partial z} = R_f \frac{\partial}{\partial t} (e_g c)$$

where, $r$ is radial co-ordinate, $z$ is vertical co-ordinate, $B_{zz}$ is intrinsic permeability, $B^*$
is relative permeability, \( \rho \) is fluid density, \( \mu \) is viscosity of the gas mixture, \( S_g \) is the specific storage term, \( Q \) is the vaporisation source term, \( c \) is molar concentration, \( \varepsilon_g \) is gas filled porosity, \( R_j \) is the retardation factor, \( D_{ij} \) is the dispersion tensor and \( v \) is the interstitial velocity which has radial and axial components as follows-

\[
v_r = -\frac{1}{\varepsilon_g} B^* B_{rr} \frac{\rho g}{\mu} \frac{\partial \rho^*}{\partial r}
\]

\[
v_z = -\frac{1}{\varepsilon_g} B^* B_{zz} \frac{\rho g}{\mu} \left[ \frac{\partial h^*}{\partial z} + \frac{\rho}{\rho_0} - 1 \right]
\]

The numerical solution of these two coupled continuity equations is then found using finite difference methods. The work done by the other two sets of authors is quite similar, the obvious difference being that they use Cartesian co-ordinates. They all conclude that for dense vapours in permeable soils density driven advection can be the dominating transport mechanism.

In a recent paper Gioia\(^{(67)}\) has studied the emission from a bed of porous rock tuff (ground and sieved to create 2 - 4 mm sized particles) of organic volatiles such as benzene which are initially dissolved in tetradecane (which is very involatile and considered to be immobile during the release process). He extended his model from a previous paper\(^{(68)}\) to account for the emission of \( n \) volatiles rather than just one. The experimental work was carried out in a cell open to the atmosphere at the top and the bottom and for benzene the predominating release mechanism was found to be convective while for less volatile contaminants diffusion from the top surface was more significant. The measurements taken were the flow rate from the bottom of the cell, measured using a soap film flow meter, the concentrations of the different volatiles in the gas leaving the bed and the height (\( h \)) of the liquid fronts of the different contaminants when these were visible. A one dimensional model was used. First of all the gas concentration profile was determined both in the zone above and below \( h \), this allows the determination of the diffusive flux from the top of the bed and the overall density of the gas phase. The density regulated the natural convection velocity through the bed and hence the flow leaving the bottom of the bed which
could be compared with the experimental values. The main equation arrived at was as follows-

\[ \sum_{i=1}^{n} \left( M_i - M_0 \right) c_{i,e}^{*} \left( \frac{1}{\sum_{i=1}^{n} x_{i0}} \left[ h_i \left( 1 - \exp \left( \frac{-\Delta p_i}{D_i} \right) \right) + \frac{D_i}{u} \right] + \frac{1}{\sum_{j=j_{min}}^{n} \sum_{i=1}^{n} x_{i0}} \left( h_{j-1} - h_j \right) \right) = \frac{\Delta p_i}{g} \]

(2.39)

where, \( c_{i,e}^{*} \) is gas phase concentration of \( i \) in equilibrium with the initial liquid concentration \( x_{i0} \), \( D_i \) is gas phase effective diffusivity of \( i \) in the packed bed, \( M \) is molecular weight, \( u \) is superficial velocity, \( x_{i0} \) is mole fraction of \( i \) in the initial liquid mixture, \( \Delta p_i \) is total pressure drop across the system, \( h \) is moving boundary position from the top of the bed; the subscripts are \( a \) for air, \( i \) for any volatile and \( j_{min} \) is the index of the most volatile component which, at time \( t \), is still in the bed.

Morel-Seytoux and Billica\(^{1691.1701} \) have done some related work on a numerical model for predicting infiltration of rain water. They used a two phase approach so as to fully allow for effects due to the air initially in the pore spaces which is displaced by the infiltrating rain water. The need for using a two phase approach is demonstrated by their results. Chrysikopoulos\(^{1711} \) dealt with transport of non-aqueous pollutants in saturated porous media, analytical solutions using Laplace and Fourier transforms for sources with rectangular, elliptical or circular geometries are given in his paper.

Berkowitz and Scher\(^{1721} \) were concerned with flow in complex porous media where so called 'Anomalous Dispersion' can occur, they were critical of using a time dependent diffusion coefficient to tackle this problem and advocated the use of a 'multiple trapping model' which is based on the concept of regions of mobile and immobile water. This concept is frequently used for example by Lafolie and Hayot\(^{1731} \) whose model applies to double porosity aggregates where there is flow through the macropores with immobilised water in the micropores. Transport in the macropores is modelled by a convection-dispersion equation whilst transport inside the aggregates is considered purely diffusive. The two different models can either be coupled directly such that the concentration at the periphery of the porous blocks is equal to the concentration in the flowing fluid or, more realistically, there is a thin liquid film surrounding the particles which solute must diffuse through. In a system of
approximately monosized ballotini only the first model would be necessary-

\[ R_m \frac{\partial c_m}{\partial t} = \frac{\partial}{\partial z} \left( D_m^* \frac{\partial c_m}{\partial z} - \nu_m c_m \right) + \Gamma - \lambda_m c_m \]  

(2.40)

where, \( R_m \) is the face retardation factor \( (R_m = \varepsilon + \sigma k_m) \), \( \sigma \) is the surface to volume ratio of the macropores, \( k_m \) is the ratio between adsorbed and dissolved concentrations, \( c_m \) is pore concentration, \( t \) is time, \( z \) is depth, \( D_m^* \) is hydrodynamic dispersivity, \( \varepsilon \) is porosity, \( \Gamma \) is a source term accounting for solute exchange between the mobile and immobile phases, \( \lambda_m \) is the decay constant for the diffusing species and \( \nu_m \) is mean pore water velocity.

For zero velocity, negligible adsorption, uniform porosity and no decay of the solute, the dispersivity is equal to the diffusion coefficient \( (D_m) \) and this reduces to

\[ \frac{\partial c_m}{\partial t} = D_m \frac{\partial^2 c_m}{\partial z^2} \]  

(2.41)

as expected for Fickian diffusion.

They also introduce block geometry functions which allow for the shape of the aggregates and then go on to solve their equations numerically. In a second paper they went on to consider the effect of aggregate size distribution as predicted by the model.

Another area where density effects are important is the intrusion of sea water into aquifers at coastal boundaries, some of the modelling goes mathematically beyond the scope of this thesis\(^{74,75}\). Earlier, simpler models, however, use the abrupt interface approximation which ignores ionic diffusion across the boundary between salt and freshwater but can give adequate results on the macroscopic scale.

Generally the systems modelled have flow through the system and a lot of effort goes into allowing for the dual porosity of systems such as soil and into understanding transport in the unsaturated zone but neither of these features are expected to be relevant to our conductivity probes or experiments with glass beads. The parts of the models that are relevant to non-adsorbing porous media with relatively uniform pore sizes tend to be based simply on Fickian diffusion imposed on the fluid velocity as shown above for the model of Lafolie and Hayot.
2.5 Effect of solid-liquid interface on transport of aqueous ions

The importance of surface effects in the overall rate of mass transport is highly dependent on the specific surface area per unit volume of the medium under consideration as well as the surface properties. The two materials of main interest here are Vyon (polythene) from which the porous sections of the conductivity probes are constructed and lead glass, since the beads used in all the other experiments were made of this type of glass. Polythene is inert to acids and alkalis\(^{76}\) so should not react with dilute HCl. The properties of glass are discussed below after a general introduction to the electric double layer.

*Fig. 2.5 The electric double layer (adapted from Shaw\(^{77}\)).*

If there is any surface charge on the solid an electric double layer will be formed\(^{77}\). The electric double layer consists of a charge at the solid surface which is balanced by an excess of oppositely charged ions in the solution adjacent to the surface. At the surface a number of counter ions are strongly adsorbed forming the 'Stern Layer' beyond this layer which has a typical thickness of \(5 \times 10^{-10}\) m, the potential eventually decays to zero in the bulk solution. After a sharp initial decline in the Stern layer, the
electric potential \( (\psi) \) decreases exponentially moving away from the interface into the bulk solution.

\[
\psi = \psi_0 \exp(-\kappa x)
\]  
\((2.42)\)

\(1/\kappa\) is referred to as the Debye length which is characteristic of the size of the electric double layer and is given by-

\[
\frac{1}{\kappa} = \left[ \frac{F^2}{\varepsilon \kappa T} \sum_i z_i^2 c_{\infty} \right]^{-\frac{1}{2}}
\]  
\((2.43)\)

where, \( F \) is Faraday's constant, \( \varepsilon \) is the dielectric permittivity and \( z_i \) and \( c_{\infty} \) are the valence and bulk solution concentration, respectively of electrolyte species \( i \).

For low electrolyte concentrations and/or small pores the Debye length may approach the pore radius in which case the whole of the contents of the pore are part of the double layer. If however the pore radius is much larger than the Debye length then any effect on diffusion due to the double layer will be negligible. At the simplest level, higher conductivity in the double layer region is to be expected because there is a higher concentration of ions there.

The effect of the double layer on the conductivity of saturated porous media has been discussed by Revil and Glover\(^{(78)}\) with particular reference to a quartz electrolyte system. A non-linear relation between the effective conductivity of the saturated medium and the electrolyte conductivity is predicted but the deviation from linearity is not large over relatively small concentration ranges such as those used in our experiments.

Leaist\(^{(24)}\) measured diffusion coefficients by AC electrical resistance measurements for HCl (at concentrations of 0.001 - 0.1 M) in columns of glass beads to a quoted precision of approximately \( \pm 0.4\% \). These experiments were done using Pyrex spheres of diameter 300 \( \mu \)m and the author state that the low specific surface area of the beads rules out significant complications due to surface effects. Pyrex glass is less durable than lead glass and the beads used in the experiments described in Chapter 3 are of a similar diameter, nevertheless a brief review of the properties of the glass-aqueous
solution interface follows.

Gosman, Liukkonen and Passiniemi\[79\] reported a surface layer of thickness as large as 30 μm for 10⁻³ M aqueous sodium chloride solution on Pyrex glass. They found that the diffusion rate in capillaries was increased by surface diffusion. The surface diffusion coefficient was found to be 1.75 times greater than the bulk diffusion coefficient and this was attributed to the surface diffusion being restricted to two dimensions as well as to the properties of the surface layer. No details of the relation between the magnitude of the effect on diffusion and electrolyte concentration is given, however it is stated that the effect is not observed at 'higher concentrations'. By carrying out diffusion measurements in capillaries of two different radii they determined the thickness of the layer in which surface diffusion took place as 25 μm. This compared with a thickness of 29 μm for the surface film measured by dipping experiments. The surface layer measured here was considered to be equivalent to the Nernst diffusion layer which is typically of the order 10 - 100 μm\[80\]. This is clearly not the same as the Debye length which would be approximately 0.1 μm for a 10⁻⁵ M aqueous solution of a 1:1 electrolyte. The Nernst layer is considered to be the layer in which the motion of ions is purely diffusive with no convective part as long as the flow of liquid past the surface is laminar.

Diffusion at the glass-solution interface was investigated by Mysels and MacBain\[81\], they studied diffusion of aqueous potassium chloride through a fritted glass disc. Two concentrations of solution were used, approximately 0.1 M and 0.0005 M. The ratio of the conductances at the two concentrations was found to be significantly different (5 - 10%) in a cell containing a fritted glass disc between the electrodes compared with a standard cell. The difference was such that the more dilute solution was, relatively, a better conductor with the fritted disc present. This was attributed to surface conductance which would make a larger contribution to the total conductance at lower concentrations. With the dilute solution the fritted glass did not reach an equilibrium state for many hours. Again the lower of these two concentrations is over an order of magnitude below the concentration range used in this thesis.

Bares\[82\] has taken electrical resistance measurements for packed beds of glass beads.
with no interstitial liquid. Both DC and AC resistance was found to increase approximately linearly with increasing particle size in the range 100 - 900 µm. Measurements were taken at 27 °C and 46% relative humidity giving a minimum AC resistance of more than 10⁷ Ω. Hence the type of system described in Chapter 4 (a packed bed saturated with electrolyte so that the overall bed resistance is of the order of 10³ Ω) would not be expected to be influenced by particle size in the same way.

Fricke and Curtis[831] measured the surface conductance for suspensions of small glass beads (approx. 1µm) in dilute electrolyte solution giving a surface conductivity of the order of 10⁻⁹ Ω⁻¹ per particle in a 0.002 M solution of KCl. They also observed that the conductivity of dilute solutions increased on the addition of glass beads which had been given an extended washing with distilled water.

Ermakova et al.[841] studied aqueous electrolytes in porous glasses with pore radii up to 160 nm. In HCl solutions an increase in surface conductance was found and was partly attributed to protonic conductance of undissociated surface silanol (SiOH) groups. The number of undissociated silanol groups increase with decreasing pH. Again the pore size is considerably less than the bead size for the experiments reported in the following chapters.

Glass does react with water[85] and with dilute acid albeit very slowly. The first stage in the reaction is the substitution of sodium ions at the glass surface by H⁺(aq) ions. Lead glass is relatively durable, for example in sulphuric acid it is over twice as durable as soda-lime[86]. The rate of dissolution of vitreous silica at room temperature is of the order of 10⁻¹² cm s⁻¹. As is the case for surface diffusion, the significance of this effect will depend strongly on the surface area of glass involved since the reaction can only take place at the surface.

To emphasise the limited influence of surface effects on the overall conductivity and diffusion measurements for the experiments described in Chapter 4 it is worth calculating the percentage of the pore solution that lies within the double layer as defined by the Debye length in Equation 2.43. For a packed bed of spherical particles of diameter 100 µm and a porosity of 0.38 assuming point contact between spheres and an electrolyte concentration of 0.002 Mol l⁻¹, 0.2% of the solution is within the
most experiments were performed using larger particles so the percentage would be even less.

2.6 Packing of Spheres

In this thesis a large number of experiments are described which involve the use of packed beds of approximately mono-sized ballotini. Real packings of particles will, inevitably, have a degree of randomness but will have a high-level of similarity to a regular packing of the same porosity. Porosities for regular close packings vary from 0.476 with a co-ordination number of 6 for simple cubic packing to 0.260, co-ordination number 12, for rhombohedral (also known as hexagonal close-packed) which is the closest possible packing. Intermediate between these two extremes is the orthorhombic case giving a porosity of 0.395 and co-ordination number 8 which is close to the values which are normally reported for experimental packings of mono-sized spheres, for example Gray1871 lists values varying from 0.369 to 0.409.

Goodling and Khader1881 found an average co-ordination number of 8.1 and porosity of 0.39 for their randomly packed beds and concluded that a regular orthorhombic structure could be used to model transport properties in such beds. The closeness of packing depends on the method of deposition. It has been suggested that when packing is relatively slow, horizontal layers will tend to be packed hexagonally with

Fig. 2.6 Unit cells for regular sphere packings, from left to right, simple cubic, ortho-rhombic and hexagonal close packed.
the horizontal displacement between layers being random, this approach was used by Frevel and Kressley\cite{89} to give a model for sphere packings with porosities between 0.260 and 0.395.

Mayer and Stowe\cite{190} who, like Frevel and Kressley were working in the field of mercury porosimetry, suggested an alternative model. In this model the unit cell, each side of which is a rhombus, can be described by a single acute angle $\theta$. This model will give a porosity of any value between 0.260 and 0.476 and the porosity varies uniformly with $\theta$ in all three spatial dimensions. Another approach used for example by Chan and Ng\cite{191} is to divide the porous medium into tessellating tetrahedra each of which contains one pore space, this gives a co-ordination number of six, however, which is a little low in comparison with much of the data reported elsewhere.

Another factor to consider in relation to sphere packings is the wall effect\cite{192}. At the container wall, the theoretical porosity is one since only point contacts with the wall are possible. Moving away from the wall, the porosity oscillates about its mean value; the period of oscillation is equal to the particle diameter and the amplitude rapidly decays nearly reaching zero within five particle diameters. The effect of container shape and wall roughness on sphere packings has been discussed in more detail by Graton and Fraser\cite{193}.
2.7 Summary

The literature reviewed here sets the scene for the experimental and modelling chapters that follow. Electrical resistance measurements are used to determine electrolyte concentrations as described in Section 2.2.

The bulk of the experimental work is carried out using experimental cells where there is flow across the surface of a bed of glass beads saturated with a dilute solution of HCl but no flow through the bed, as shown in Figure 1.1. There is a lack of published literature available about systems with exactly this type of flow configuration at significant surface shear rates, so these experiments themselves are novel. The experimental method and apparatus is based partly on the work of Leaist\(^{24}\) and Jahnke and Radke\(^{46}\) as well as previous work at Loughborough\(^{14}\),\(^{15}\).

Experiments carried out at very low flow rates are reported, which allow the measurement of the diffusion coefficient for aqueous HCl in a saturated bed of beads. These results can be compared with the predictions and results of Section 2.3, particularly the results of Leaist\(^{24}\). However, unlike Leaist, the experimental arrangement provides a system with a substantially constant concentration boundary condition: the concentration driving the mass transfer only slightly changes during the experiment. In Leaist’s experiment the concentration at the boundary was a variable.

The experiments are then extended to higher surface shear rates and the effect of surface shear on the rate of transport of HCl investigated. Ideas from Section 2.4 are used as the starting point for the development of the induced velocity model introduced in Chapter 5. The model is extended from one to two dimensions and compares well with the experimental results as shown in Chapter 6.

Experiments are also carried out using the conductivity probes, introduced in Chapter 1, enabling the effect of surface shear rate and probe dimensions on the probe’s effectiveness to be evaluated. The probe construction and experimental method are covered next in Chapter 3.
3. Solids Concentration Probe

3.1 Theory

The probe monitors the conductivity of a dispersion or slurry using a pair of external electrodes and internal electrodes are used to determine the conductivity of the liquid phase free from dispersed solids. The underlying theory allowing the probe measurements to be converted into a value for volume concentration of solids is well established and has been discussed in Chapter 2. The concentration $c_v$ is given by-

$$c_v = 1 - \left( \frac{\kappa_m}{\kappa_c} \right)^\frac{1}{n}$$

(3.1)

where $\kappa_m$ is the conductivity of the mixture of solids and fluid and $\kappa_c$ the conductivity of the fluid continuous phase. The exponent $n$ is approximately 1.5 but must be determined experimentally for each solid used if accurate results are required particularly if conducting solids are used.

A schematic of the probe is shown in Fig. 3.1, the external electrodes give a value for $\kappa_m$ and the internal electrodes give $\kappa_c$. The probe must first be calibrated using a conducting liquid with no dispersed solids so that measurements from the internal electrodes can be converted into values equivalent to readings at the external electrode for the same liquid. Thus from the probe measurements for a non-conducting suspended solid, $c$, is given to a good approximation by-

$$c_v = 1 - \left( \frac{\kappa_m}{\kappa_c} \right)^\frac{1}{1.5}$$

(3.2)

To calibrate for exponent $n$, a minimum of a single set of measurements of concentration and conductivity is required, since the log-log plot of conductivity ratio against one minus solids concentration must pass through the origin-

$$n = \frac{\ln(\kappa_m)}{\ln(1-c_v)}$$

(3.3)
3.2 Design of Probe
The probe has a pointed tip to prevent major disturbance to the flow in the tube in which it is inserted. The external electrodes are sharpened to a point to concentrate the electric field at the tip and are made from thoriated tungsten to make them highly resistant to wear. The internal electrodes are annular stainless steel discs, they are surrounded by PVC which the rest of the probe is constructed from and sandwiched between the electrodes is a porous material made of sintered polyethylene known as Vyon and supplied by Porvair. The wires to the electrodes are contained in a central cavity which is filled with resin.

![Schematic of conductivity probe showing key dimensions but not to scale.](image)

The original prototype had a whole series of internal electrodes in order to discover how much Vyon was needed between the electrodes to give a calibration constant close to unity. The latest probes have two internal electrodes of thickness 1 mm with one similar stainless steel disc between them which acts as a guide for the electric field, either side of this 'field guide' is a Vyon disc of thickness 1.7 mm.
Fig. 3.2 Diagram showing electric circuit and arrangement of probe electrodes.

The power to the probe is an AC supply of approximately 5 V, frequency 16 kHz. The electrode pairs can be switched between and are in series with a bias resistor. The voltage across the electrodes is measured using a true RMS voltmeter and the conductance between the external electrodes, $S_m$ is obtained from the voltage measurement thus:

$$S_m = \frac{R_b V_m}{V_s - V_m}$$

(3.4)

where $R_b$ is the bias resistance, $V_m$ is the measured voltage across the electrodes and $V_s$ is the supplied voltage; $S_c$, the conductance between the internal electrodes is obtained similarly. Before the probe is used it must be calibrated by taking measurements with the probe immersed in a conducting liquid containing no solids to give the calibration constant $k$ where:

$$S_m = k S_c$$

(3.5)

Equation (3.4) gives a conductance, not a conductivity value but since it is a conductivity ratio, $\kappa_m/\kappa_e$, that is ultimately being measured there is no need to convert the conductance to a conductivity as they are proportional. That is:

$$\frac{S_m}{k S_c} = \frac{\kappa_m}{\kappa_e}$$

(3.6)
hence, substituting into equation 3.1 gives-

\[ c_v = 1 - \left( \frac{S_m}{k} \right)^{1/2} \]  \hspace{1cm} (3.7)

as the equation for the measured solids concentration.

3.3 Response Time

The probes which had been constructed previously had a minimum diameter of 11 mm and showed an appreciable time lag in adjusting to a step change in the conductivity of the liquid phase as shown by Fig. 3.3.

The most obvious approach for reducing the time delay was to make the probe diameter smaller thus reducing the time for the solution within the pores of the Vyon coming to equilibrium with the bulk solution when there is a change in bulk electrolyte concentration. There are two constraints, firstly the physical constraint as to how small a probe of this design can be made and secondly there must be sufficient separation between the internal electrodes and the bulk solution to prevent electric field tracking along the probe surface.

![Probe Time Delay](image)

**Fig. 3.3** Graph showing extent of time delay for prototype probe. In this experiment the liquid conductivity was abruptly decreased by adding water after 20 minutes. The solid used was Talc and the calibration constant, \( n = 2.1 \).
Taking these constraints into account the smallest probe that could be constructed using the available resources was of 8 mm diameter. A probe with a tip of diameter 8 mm and two otherwise identical probes of tip diameters, 12 mm and 16 mm were constructed in order to investigate the precise effect of varying the probe diameter. These 3 probes are shown in Fig. 3.4 below, refer back to Fig. 3.1 for a diagram of the 16 mm probe.

![The three probes of different diameters.](image)

**Fig. 3.4 The three probes of different diameters.**

### 3.4 Probe calibration

The relation between conductivity and concentration for HCl is very close to being linear over a wide concentration\[^94\], so for the purposes of these experiments, which are over a relatively narrow concentration range, it was considered completely linear. This is the basis for using electrical measurements to give the HCl concentration. The internal cells of the probes were calibrated using varying concentrations of HCl, the results are shown below. The large difference between the largest probe and the two smaller ones suggests that either there was still some trapped air in the large probe or there is a significant degree of tracking to the probe surface for the smaller probes.
3.5 Flow Past Probes and Surface Shear
The Vyon discs are close to the leading edge of the probe so the flow is not fully developed, for this reason the surface shear was calculated from a consideration of the developing laminar sublayer. The following equation for the surface shear stress, given by Coulson and Richardson\(^{[95]}\), was used-

\[
\frac{R}{\rho u_s^2} = 0.03Re_x^{0.2} \tag{3.8}
\]

where \(R\) is shear stress, \(\rho\) is density and \(Re_x\) is a Reynolds number-

\[
Re_x = \frac{u_s \rho x}{\mu} \tag{3.9}
\]

where, \(u_s\) is superficial velocity, \(\mu\) is viscosity and \(x\) is the distance from the leading edge.
3.6 Characterising Vyon
The Vyon used for the three probes was characterised by measuring the porosity, density and permeability of representative samples. The Vyon was also examined under a microscope (Fig. 3.6).

![Figure 3.6: Photograph of Vyon used in probe construction and 1 mm graticule.](image)

3.6.1 Porosity
The density of the Vyon was first measured using a helium pycnometer, then the porosity was measured by weighing the amount of distilled water retained in the pore space when a sample of Vyon was immersed in water and placed under vacuum.

The dry Vyon, which consisted of a number of small pieces each less than one centimetre square, was first weighed and then, after being saturated, the Vyon was carefully removed from the water using tweezers and weighed immediately to give the following results.
Table 3.1 Results of experiment to determine Vyon porosity.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of dry Vyon, g cm$^3$</td>
<td>0.988</td>
</tr>
<tr>
<td>Mass of dry Vyon, g</td>
<td>0.528</td>
</tr>
<tr>
<td>Volume of Vyon, cm$^3$</td>
<td>0.535</td>
</tr>
<tr>
<td>Mass of saturated Vyon, g</td>
<td>1.367</td>
</tr>
<tr>
<td>Volume of water, cm$^3$</td>
<td>0.839</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.611</td>
</tr>
</tbody>
</table>

3.6.2 Permeability

The permeability of the Vyon was investigated by measuring the variation in flow rate with pressure drop across a sample. This experiment was carried out using a simple arrangement consisting of a compressed air supply, a rotameter, a manometer and a sample holder all connected with flexible tubing.

![Diagram](image)

**Fig. 3.7 Set up for permeability experiment.**

The results were fitted to Carman's equation\(^{[96]}\)

\[
\frac{R_l}{\rho u^2_{l}} = 5Re^{-1}_l + 0.4Re^{-0.1}_l
\]

(3.10)

where, \(u_l\) is the gas velocity through the pore space, \(\rho\) is density, \(R_l\) is the component of the drag force per unit area of particle surface in the direction of motion and \(Re_l\) is a Reynolds number.
\[ Re_1 = \frac{u_c \sigma}{\sigma (1-\epsilon) \mu} \]  

(3.11)

where, \( u_c \) is superficial gas velocity, \( \sigma \) is specific surface, \( \epsilon \) is porosity and \( \mu \) is viscosity. The fitting parameter used to give the required value for the Reynolds number in Carman’s equation was the specific surface, \( \sigma \). The permeability, \( B \), could then be calculated from-

\[ B = \frac{1}{K''} \frac{\sigma^2}{\sigma^2 (1-\epsilon)^2} \]  

(3.12)

where \( K'' \) is Kozeny’s constant which has a commonly accepted value of 5. The results of this experiment are shown below.

**Fig. 3.8** Graph of data from permeability experiment showing least squares fit for Carman equation using a porosity of 0.61.
Table 3.2 Results of permeability experiment.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Air density, kg m⁻³</td>
<td>1.20</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.61</td>
</tr>
<tr>
<td>Viscosity</td>
<td>1.80 x 10⁻⁵</td>
</tr>
<tr>
<td>Sample thickness, m</td>
<td>1.72 x 10⁻³</td>
</tr>
<tr>
<td>Cross sectional area, m²</td>
<td>1.19 x 10⁻⁵</td>
</tr>
<tr>
<td>Kozeny Constant</td>
<td>5</td>
</tr>
<tr>
<td>Specific surface, m⁻¹</td>
<td>3.82 x 10⁴</td>
</tr>
<tr>
<td>Permeability, m²</td>
<td>2.04 x 10⁻¹⁰</td>
</tr>
<tr>
<td>Equivalent spherical diameter, m</td>
<td>1.57 x 10⁻⁴</td>
</tr>
</tbody>
</table>

The equivalent spherical diameter, \( d \), is the diameter of a sphere with the same specific surface, \( \sigma \), as the Vyon sample and is given by

\[ d = \frac{\sigma}{\delta} \]  

(3.13)

3.7 Experimental Procedure
The probe was inserted in a simple flow circuit consisting of a feed tank, a mono-pump and a bypass to allow the flow past the probe to be varied. Diffusion through the Vyon was monitored by recording the variation in the readings from the internal cell when HCl was added to the feed tank.

Before doing any experiments the Vyon in the probes was saturated by immersing in water and placing under vacuum until repeating the process gave no further reduction in the measured voltage between the internal electrodes. Subsequently the probe tips were kept saturated at all times.
Experiments were performed using the flow circuit shown above, there was an additional valve for draining the system which is not shown. The feed tank had a capacity of approximately 50 litres and PVC tubing of internal diameter 29 mm was used apart from the return from the probe position to the feed tank and the last section of the bypass return to the tank which were made from flexible tubing of similar diameter. The probe was inserted with the protruding electrodes oriented horizontally and the body of the probe was positioned centrally within the tube. The section of tube containing the probe was horizontal, downstream from the part of the probe containing the electrodes was an outlet from the tube pointing vertically upwards and a flexible tube was connected to this returning to the feed tank.

When running an experiment the feed tank was partially filled with dilute hydrochloric acid, the concentration was checked using a conductivity probe which had been calibrated against HCl concentration. The required probe was placed in position and the pump was turned on. The reading from the internal electrode pair was monitored periodically until a steady reading was reached. A measured amount of HCl was then added to the feed tank and the voltmeter was set to take readings at regular intervals. The HCl concentration in the feed tank was again checked using the conductivity meter just after the addition of acid and periodically during the experiment. Temperature variations during the experiments were also monitored.
Initial experiments were carried out using tap water but a few of the later experiments used distilled water in an attempt to achieve more consistent results. The volume flow rate past the probe was measured by collecting the fluid returning to the feed tank from the probe in a measuring cylinder and timing with a stopwatch. Equation (3.8) was then used to calculate the surface shear at the probe.

The concentration of HCl within the probes was inferred from the voltage measurements, the concentration being proportional to the reciprocal of electrical resistance, with the initial conditions being taken as the necessary fixed point thus the concentration $C(t)$ at time $t$ was given by-

$$c(t) = \frac{S_c(t)}{S_c(0)} c(0)$$  \hspace{1cm} (3.14)

where, $S_c$ is the measured conductance between the internal electrodes.
4. Experimental Cells

4.1 Introduction

The response time of the probe relies on mass transfer through porous media, thus a study of the effects of porous structure and surface flow rate on the rate of dispersion of ions in porous media is appropriate. In order to achieve this, an experimental cell was constructed which would allow the determination of concentration profiles within porous beds. The first porous medium to be used was ballotini because of its high degree of uniformity and easy availability in different sizes.

4.2 Experimental Design

4.2.1 Initial Cell and flow circuit

The first cell was based to some degree on the cell of Jahnke and Radke\cite{46} described in Chapter 2 and shown in Fig. 2.3, in particular a similar flow configuration was used with flow entering at the edge of the cell and being distributed around the circumference by a weir to aid uniform radial flow towards the centre. When a cell of this type was first used a dye test was carried out and the dye was seen to rapidly and uniformly cover the whole surface of the bed.

The cell was constructed from perspex with a PVC piston, allowing extrusion, sectioning and analysis of the bed contents at the conclusion of an experiment, and a separate lid which was bolted on to the top. It had a series of flush mounted, diametrically opposed, stainless steel electrodes to measure the conductivity at varying bed depths. At the third level from the top, there were two additional pairs of electrodes as a means of checking the uniformity of the electrolyte concentration within the plane. Initial experiments were carried out with potassium nitrate so that, after extrusion, concentration measurements could be taken using Atomic Absorption Spectroscopy. Flow was produced using a variable speed peristaltic pump.

Experiments were carried out in a constant temperature box which was constructed from wood with a removable perspex front, the temperature was controlled by means of a 30 Watt heater mat (RS catalogue No. 731-360) which was connected to a
temperature switch set at 25 ± 0.5°C. The box also contained a fan to circulate the air
preventing establishment of a temperature gradient.

![Cell diagram](image)

**Fig. 4.1** Cell diagram for first cell showing indication of flow pattern.

### 4.2.2 Electrical circuitry

The basic electric circuit was very similar to that for the probes in the previous chapter except that there were eight electrode pairs instead of just two. The signal generator used was a Rapid Electronics 85-1205 audio generator set at a frequency of 10 kHz in the form of a sine wave. The AC voltage oscillated symmetrically about zero to ensure that there was no net movement of ions within the cell and when measurements were not being taken none of the electrodes were on, preventing unwanted effects such as localised heating.

Switching between electrode pairs was computer controlled, the DC output from an internal Blue Chip digital input/output board was increased to a level high enough to switch the relays by a line driver, the components used were four Quad 2-Input OR Gates from National Semiconductor. The Digital Voltmeter (a BlackStar 4503 Intelligent Multimeter) was also connected to the computer using an RS-232C Interface enabling immediate data transfer. For each electrode pair both electrodes were switched so that when an electrode was activated the only electrode connected to
earth was the opposite electrode thus preventing leakage to earth at any of the other earth electrodes. The bias resistor was adjustable in the range 680 to 6120Ω.

![Simplified circuit diagram showing just one electrode pair.](image)

**Fig. 4.2 Simplified circuit diagram showing just one electrode pair.**

### 4.2.3 Computer program

A program was written in Microsoft Q-Basic to control switching the electrodes and storing the data from the DVM on a PC. The program cycles through the 8 electrode pairs recording the voltage drop across them at specified time intervals. When not taking readings a graph of conductivity against time for the 8 electrode pairs is displayed. At the conclusion of each experiment the program was stopped and the data files imported into a spreadsheet for analysis. A flowchart for the program is shown in Fig. 4.3 on the following page.

Firstly the program switches the multimeter to measure AC volts and the necessary variables are initialised. The user is then prompted to enter a filename, the value of the bias resistance used, the time interval required between measurements and, optionally, calibration constants for the electrodes. If no calibration constants are entered then each electrode pair has a default value of 1. The program then opens a file for the supply voltage and each electrode using the file name given with extensions .1, .2, .3 etc., before starting the timer and moving on to the data acquisition part of the program.
Chapter 4 - Experimental Cells

Fig. 4.3 Flowchart for computer program (NB when n = 0 the measured voltage is the total voltage drop across the circuit).
For the first voltage reading, all the electrodes are disconnected from the voltage supply, the program takes ten readings from the Voltmeter and calculates the relative standard deviation. If this is less than 0.015 then the mean of the ten readings is taken as the correct value and written to the appropriate file together with the current timer value, if not a further ten readings are taken until a set of readings with a relative standard deviation of less than 0.015 is obtained.

The program subsequently activates each electrode pair in turn and, after a brief pause to allow the meter to stabilise, acquires a reading for each pair as just described.

As well as being written to files on the PC's hard drive, all the data is stored in an array allowing a graph to be plotted on the screen of conductance against time for all the electrode pairs. Writing the data to file as it is acquired, means that data is not lost if there is power failure or the computer crashes during an experiment. After plotting the graph on the screen the computer waits until it is time for another set of readings. During this time the program may be halted by pressing the 'e' key on the keyboard.

A listing of the latest version of the program described above is given in Appendix A. A separate program was used for calibrations which allowed the data acquisition procedure to be triggered manually by pressing a key and another program for testing the operation of the electrode pairs was written which allowed manual activation of individual electrode pairs.

4.2.4 Concentration Measurements and Calibration
The circuit was initially checked by connecting a carbon resistor between the connections to the electrode pairs to ensure that the correct value of resistance between the electrodes was being obtained. The variation of impedance with frequency was also studied before the frequency of 12 kHz was finally chosen. The concentration of HCl between each electrode pair was measured in the same way as the internal probe concentration was measured in Chapter 3. The initial concentrations $c_0$ within the porous media and in the feed tank were evaluated at the start of each experiment by measuring their conductivities using a conductivity meter. The concentration at time $t$ can be determined from measurement of the voltage across any
given pair of electrodes. The voltage measurement can be converted to a conductance $S$ using Equation (3.4) rewritten here-

$$S = \frac{R_b V_m}{V_s - V_m}$$  \hspace{1cm} (4.1)

where, $R_b$ is the bias resistance, $V_m$ is the measured voltage between the electrodes and $V_s$ is the supply voltage. Since $S$ is proportional to $c$, the concentration at time $t$ can then be given by-

$$c = \frac{S}{S_0} c_0$$  \hspace{1cm} (4.2)

which is a repetition of Equation (3.14).

Using this method it is important to ensure the accuracy of the conductivity meter. This can be done by keeping a standard solution to check the meter every time it is used.

It should be noted that it was not possible to add acid of known concentration to clean, dry ballotini to give the required initial concentration of acid within the bed because surface impurities dissolving and possibly reactions at the ballotini surface changed the concentration of acid in solution. This was observed as a change in the liquid conductivity when dilute acid was added to dry ballotini. Another reason for using conductivity to measure initial concentrations was that it allowed rapid turn round between experiments.

Initially a calibration of the cell electrodes was carried out between each experiment in order to check the extent of drift and ensure the response remained linear. The experimental cell was filled with six solutions of HCl at different concentrations, covering the range used in the experiments, conductance readings were taken for each pair of electrodes for each solution. At the same time a reading from the conductivity meter was taken as a check on the meter calibration. The HCl solutions were made up by diluting 1.18 SG HCl with distilled water, then later standardised by titration against a 0.1 M sodium hydroxide standard.
A set of calibrations was also carried out with ballotini in the cell to show that the response was still linear, the results are shown in Fig. 4.4 and Fig. 4.5 below.

**Fig. 4.4** Calibration graph for all 8 electrode pairs for the cell shown in Fig. 4.7 with 910 micron ballotini in the cell.

**Fig. 4.5** Calibration for electrode pair 4 for the 4 different sizes of ballotini used.

Calibrations with no ballotini showed similar or normally even higher linearity for all the experimental cells. Further calibration data is presented in Appendix B.
4.2.5 Sources of error

4.2.5.1 Natural Convection
One possible source of error that needed to be considered was natural convection due to the density difference between the electrolyte solution from the feed tank and the solution initially in the bed. Using Equation (2.33) -

\[ v_d = \frac{R_g}{\mu} (\rho_0 - \rho_\infty) \]  

(4.3)

for the convective velocity gives negligible values at the concentrations which were eventually used for most of the experiments, for example for HCl with a concentration difference of 0.003 mol l\(^{-1}\), \(v_d\) has a value of approximately \(3 \times 10^{-13}\) m s\(^{-1}\). If the diffusing species being studied is particularly dense or the concentration gradients are large this effect can still be significant however. Some early experiments were carried out with the cell inverted and a porous support inserted to support the ballotini, difficulties were encountered with air bubbles occurring within the bed however and, in view of the above calculation, this idea was not pursued.

4.2.5.2 Pulsed flow
Another possible complicating factor was the pulsed nature of the flow from the peristaltic pump. The flow was first smoothed by introducing a bypass tube back to the feed tank and later by introducing a constant head tank to provide the flow with the pump being used to return the liquid from a small lower reservoir back up to the tank (see Fig. 4.10). This latter arrangement eradicated all pulsing over the surface of the beads in the cell. The flow did sometimes decrease over time however and was adjusted during experiments when necessary.

4.2.5.3 Trapped air bubbles
For the smallest ballotini (under 75 μm) there was found to be a problem with trapped air bubbles in the cell after filling. In order to remove these bubbles a flange was made which fitted on top of the cell this allowed a layer of liquid to be left above the surface after filling the cell. The cell was then placed under vacuum to remove the bubbles before removing the flange and proceeding with the experiment in the normal way.
Carrying out this procedure with larger ballotini in the cell it was observed that no bubbles emerged from the bed.

**4.2.5.4 Positioning of electrodes and electrode material**

Although good results for similar cells with flush mounted electrodes have been published elsewhere\(^{24}\) it proved impossible to produce sufficiently reliable, reproducible results from the cell described above. To attempt to overcome these difficulties new cells were constructed with electrodes which protruded by 5 mm from the cell wall and were insulated around their bases. These electrodes were much less sensitive to any wall effects with the point of the electrode being at least 5 particle diameters from the cell wall for the largest ballotini used. This design precluded the use of a piston for extruding beds so the new cells were constructed with fixed bases. HCl, even at the concentrations used, was found to have an effect on the measurements from stainless steel electrodes (see Fig. 4.6) so for the final cell (Fig. 4.7) gold plated electrodes with pointed tips were used (male crimp pins RS Catalogue No. 85-1205).

![Figure 4.6](image-url)  
*Fig. 4.6 Stability test for stainless steel electrodes with HCl and KNO₃.*
During cell development, the ring of electrodes at the same level, present in all the cells, were useful in checking the consistency of the results. The lack of any systematic discrepancy between these measurements was evidence to support a uniform radial flow distribution at the top of the cell.

*Fig. 4.7 Final version of cylindrical cell.*

*Fig. 4.8 Cell diagram, approximately to scale with measurements shown in mm. The numbering of the electrode pairs used in reporting all results is also shown.*
Fig. 4.9 Diagram showing position of inlet relative to electrodes.

4.3 Finalised experimental procedure

HCl was added to a slurry of the ballotini in distilled water with stirring until the desired concentration, as measured with a conductivity meter, was reached. Most of the excess liquid was transferred to a measuring cylinder and enough ballotini poured into the cell to just fill it. After tapping the cell, further ballotini was added until the cell was full with a smooth surface to the bed. The lid was then bolted on to the cell with the inlet always at the same position (Fig. 4.9) and the space above the bed filled with liquid from the measuring cylinder by pouring slowly through the inlet tube. The cell was transferred to the constant temperature box and the outlet and inlet were sealed by connecting the tubes to the feed tank and the rotameter with the valves closed to prevent any flow. The measuring cylinder was covered and also placed in the constant temperature box.

The experiment was started some hours later (normally the following morning), to allow time for thermal equilibration. The conductivities of the liquid in the feed tank and the measuring cylinder were measured before starting the computer program, fully opening the valve between the feed tank and the cell, opening the valve between the cell and the rotameter sufficient to give the required flow rate and turning the pump on. The experiment was then run for 24 hours, occasionally the valve was adjusted slightly to maintain a steady flow rate. The concentration at different heights in the bed was recorded every ten minutes for the first 6 hours and subsequently every hour using the circuitry and computer program described earlier in this chapter.
Fig. 4.10 Experimental set up.

At the conclusion of an experiment the rig was turned off and the cell emptied with the ballotini being kept immersed in dilute HCl between experiments. The data was transferred to a spreadsheet for conversion to concentration values and further analysis.

4.4 Flow across bed surface

All flow through the cell was laminar even at the highest flow rate used of 2.25 ml s$^{-1}$. The region of the highest Reynolds number was the inlet tube where it had a maximum value of approximately 800. The flow was assumed to distribute around the circumference of the cell and then flow uniformly across the surface of the bed towards the outlet at the centre.

The flow across the surface of the bed constantly accelerated as a result the flow will not have been fully developed and it is not straightforward to calculate the shear rate at the surface. The shear force is not expected to be effected by the roughness of the bed surface however, since the following relation$^{[99]}$ holds throughout the range of velocities assuming the bed surface is flat other than gaps between particles -
where \( e \) is the height of obstructions, \( u_e \) is the flow velocity at height \( e \), \( \rho \) is density and \( \mu \) is viscosity.

### 4.5 Rectangular Cell

In view of the accelerating flow across the surface of the cylindrical cells a new cell was designed with uniform flow across the surface. The results from this cell would be easier to analyse in terms of surface shear since it would be uniform. A diagram of the cell is shown in Fig. 4.12 in addition to the photograph below (Fig. 4.11). In this cell there is straight line flow across the bed surface, the flow being straightened by a porous medium (pan scourer material) placed near the inlet tube.

Dye tests with this cell showed uniform flow across the bed surface with only a slight decrease in flow at the edge of the reservoir in the area away from the bed surface. After the first series of experiments were completed the lid of this cell was modified to narrow the gap above the surface of the bed thus increasing the maximum surface shear rate using the same range of volume flow rates.

![Cell for studying one dimensional concentration profiles.](Fig. 4.11)
Fig. 4.12 Diagram showing internal dimensions (mm) of rectangular cell, the later modification is shown dotted.

4.6 Characterising Beds of Ballotini

4.6.1 Porosity measurements

The density of the different ballotini used were measured using a Helium Pycnometer and taking the mean of 5 readings. Porosity measurements were made for the three different sizes of ballotini in two different measuring cylinders one of larger diameter than the most used cell, which was 44 mm in diameter and the other smaller. The ballotini were poured into the measuring cylinder as a slurry, the cylinder was then tapped several times on a bench top giving a similar packed bed to those used in the cell. The total bed volume was recorded then the ballotini was dried and weighed to allow calculation of the porosities. Similar experiments were also carried out using the rectangular cell, the volume was found by measuring the amount of liquid required to fill the cell by means of a graduated pipette. The results are shown below-
Table 4.1 Density and porosity data for beds of ballotini.

<table>
<thead>
<tr>
<th>Nominal bead size, μm</th>
<th>Density, g cm⁻³</th>
<th>Porosity, 51 mm diameter cylinder</th>
<th>Porosity, 37 mm diameter cylinder</th>
<th>Porosity, 10x20 mm rectangular cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>2.85</td>
<td>0.38</td>
<td>0.39</td>
<td>0.38</td>
</tr>
<tr>
<td>300</td>
<td>2.51</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
</tr>
<tr>
<td>500</td>
<td>2.93</td>
<td>0.36</td>
<td>0.36</td>
<td>0.38</td>
</tr>
<tr>
<td>900</td>
<td>2.98</td>
<td>0.38</td>
<td>0.38</td>
<td>0.41</td>
</tr>
</tbody>
</table>

4.6.2 Size and shape of ballotini

All the ballotini used was examined under a microscope and none of the samples contained significant numbers of highly non-spherical particles. A photograph of the largest size of beads used is shown in Fig. 4.13.

The particle sizes were measured by three different methods, all four sizes were measured in the CorelDraw graphics package from digital photographs taken using an optical microscope, the larger two sizes were checked by measuring a number of particles using vernier callipers and all but the largest size were measured using a Mastersizer from Malvern Instruments.

The Mastersizer measurements do not give a direct measurement of the diameter in the same way as the other two methods but they provide confirmation that the previously measured values are reasonable and show that the width of the size distributions had not been underestimated. The sizing data are tabulated below, the ‘Measured size’ is given to the nearest 10 microns and is the mean particle size from image analysis except for the largest particles where the calliper measurement did not agree with the size measured from the images.
Table 4.2 Ballotini size distribution data, all sizes are given in microns.

<table>
<thead>
<tr>
<th>Nominal size</th>
<th>Measured size</th>
<th>Image Analysis</th>
<th>Callipers</th>
<th>Master Sizer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>Min.</td>
<td>Max.</td>
</tr>
<tr>
<td>&lt;75</td>
<td>30</td>
<td>33</td>
<td>12</td>
<td>84</td>
</tr>
<tr>
<td>130</td>
<td>130</td>
<td>127</td>
<td>103</td>
<td>155</td>
</tr>
<tr>
<td>300</td>
<td>240</td>
<td>238</td>
<td>96</td>
<td>320</td>
</tr>
<tr>
<td>500</td>
<td>510</td>
<td>506</td>
<td>388</td>
<td>602</td>
</tr>
<tr>
<td>900</td>
<td>910</td>
<td>862</td>
<td>759</td>
<td>1,037</td>
</tr>
</tbody>
</table>

Below is a photograph of the 910 micron ballotini and there are further photographs and size distribution data in Appendix C.

Fig. 4.13 910 micron ballotini.
5. Modelling

5.1 Modelling the pore space for packed spheres

For the initial modelling it was sufficient just to consider the porosity of the packed beds together with a tortuosity factor but for further model development a more detailed understanding of the pore structure was necessary. Sphere packings have been introduced in Section 2.6 and this section builds on that introduction. It was decided not to use regular orthorhombic packing because, although the beds had approximately the correct porosity, this packing is highly anisotropic. Instead the model of Mayer and Stowe was used and is described in detail below.

5.1.1 Model to give variable porosity

The packing of a bed of monosized spheres can be modelled using a unit cell with equal side lengths and 6 identical faces.

![Diagram of unit cell](image)

**Fig. 5.1** Single face of unit cell.

This will give a packing which is closer to being isotropic than the orthorhombic structure with a porosity of any value between 0.259 and 0.476 defined by a single acute angle, \( \theta \). The porosity, \( \varepsilon \), is given by-

\[
\varepsilon = 1 - \frac{\pi}{6} (1 - 3 \cos^2 \theta + 2 \cos^3 \theta)^{-\frac{1}{2}}
\]  

(5.1)
Chapter 5 - Modelling

The two limiting cases ($\theta = 60^\circ$ and $\theta = 90^\circ$) give the unit cells for simple cubic and hexagonal close packing as shown in Fig. 2.5.

\[ \text{Variation of porosity with angle} \]

\begin{align*}
\text{Porosity} & \quad \text{Angle} \\
0.5 & \quad 60 \\
0.45 & \quad 65 \\
0.4 & \quad 70 \\
0.35 & \quad 75 \\
0.3 & \quad 80 \\
0.25 & \quad 85 \\
0.2 & \quad 90 \\
\end{align*}

Fig. 5.2 Porosity against $\theta$ as given by equation (5.1).

The hydraulic mean diameter of the narrowest point of each opening (represented by the black area in Fig. 5.1) is-

\[ H = \frac{4d}{\pi} (\sin \theta - \frac{\pi}{4}) \quad (5.2) \]

where $d$ is the diameter of a sphere which is also the side length of the unit cell.

The volume of each pore space, $V$, is-

\[ V = \frac{d^2}{4} \sqrt{1 - 3 \cos^2 \theta + 2 \cos^3 \theta - \frac{\pi}{6}} \quad (5.3) \]

A simplified model is to use cube shaped pores joined by cylindrical tubes of diameter, $H$ and of the appropriate length to give the required porosity as shown below.
Fig. 5.3  Cube and cylinder model, to scale for $\theta = 70^\circ$.

Alternatively the exact structure may be described mathematically. One possible set of equations for the co-ordinates of the centres of the spheres in an infinite lattice is-

\[ x\text{-coordinate- } Ad \cos \frac{\theta}{2} \]

\[ y\text{-coordinate- } (2B + 1)d \sin \frac{\theta}{2} + Cd \sqrt{1 - \frac{1 - 3 \cos^2 \theta + 2 \cos^2 \theta}{1 - \cos^2 \theta}} \quad \text{(For odd } A) \]

\[ 2Bd \sin \frac{\theta}{2} + Cd \sqrt{1 - \frac{1 - 3 \cos^2 \theta + 2 \cos^2 \theta}{1 - \cos^2 \theta}} \quad \text{(For even } A) \]

\[ z\text{-coordinate- } Cd \sqrt{\frac{1 - 3 \cos^2 \theta + 2 \cos^2 \theta}{1 - \cos^2 \theta}} \]

Where A, B, and C are any integer.
Fig. 5.4 Ray-traced images of the packing showing the planes, $X=0$, $Y=0$ and $Z=0$ as defined by equations (5.4), (5.5) and (5.6) with $\theta = 70^\circ$ (obtained using POV-RAY).
5.2 Finite difference modelling

5.2.1 Initial Model

The initial modelling was for one-dimensional diffusion. The starting points were Fick’s laws in one dimension which were introduced in Chapter 2 and can be found in any standard text on diffusion

\[ J = -D \frac{\partial c}{\partial x} \quad (5.7) \]

and

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (5.8) \]

where, \( J \) is the flow rate of matter, \( D \) is the diffusion coefficient, \( t \) time, \( c \) concentration and \( x \) the length co-ordinate.

The assumptions made for initial modelling were-

1) The concentration across the top surface of the bed remained constant throughout the experiment (which is a reasonable approximation as the volume of the feed tank was an order of magnitude greater than the total volume of the cell).

2) The initial concentration throughout the bed was constant.

3) Diffusion was the only mechanism for mass transfer of HCl from the stock solution into the bed.

4) Diffusion was uniform across the width of the bed, allowing the model to be one dimensional.

5) Over the range of concentrations involved, diffusion of HCl through the bed could be accurately described by a single value for the diffusion coefficient (i.e. \( D \) was not a function of \( c \)).

Following the procedure described by Smith, in order to make the solution general, the parameters involved were non-dimensionalised as follows-
Chapter 5 - Modelling

- Non-dimensional distance, \( X = x/l \)
- Non-dimensional time, \( T = D/t^2 \)
- Non-dimensional concentration, \( C = c/c(0) \)

Where \( x \) is distance in cm, \( l \) is length of cell in cm, \( D \) is diffusion coefficient in cm\(^2\) s\(^{-1}\), \( t \) is time in seconds, \( c \) is concentration in mol dm\(^{-3}\) and \( c(0) \) is the concentration of the stock solution.

\[
\begin{array}{c|c|c}
\hline
X & C=1 & C=0 \\
\hline
X=0 & \text{C=0} & \text{X=0} \\
\hline
X=1 & \text{C=1} & \text{X=1} \\
\hline
\end{array}
\]

**Fig. 5.5** Initial condition for model, diffusion takes place through the top surface (dashed line), there is no mass transport through the solid lines.

On non-dimensionalising, Fick's Second Law (equation (5.8)) becomes simply-

\[
\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial X^2} \tag{5.9}
\]

By the forward difference approximation-

\[
\frac{\partial C}{\partial T} \approx \frac{C_{X+\delta X, T}-C_{X,T}}{\delta T} \tag{5.10}
\]

and using Taylor's theorem-

\[
\frac{\partial^2 C}{\partial X^2} \approx \frac{C_{X+\delta X, T-2C_{X,T}+C_{X-\delta X, T}}}{(\delta X)^2} \tag{5.11}
\]

where, \( C_{XT} \) is the concentration at time \( T \), at height \( X \) and \( \delta X \) and \( \delta T \) are small intervals in height and time respectively.
Substituting equations (5.10) and (5.11) into equation (5.9) leads to the following equation for a general point on the finite difference grid-

$$C_{x,T+6T} = C_{x,T} + \frac{\delta T}{\delta X^2}(C_{x-\delta X,T} - 2C_{x,T} + C_{x+\delta X,T})$$  \hspace{1cm} (5.12)

For this to give an accurate solution the following condition must be met-

$$\frac{\delta T}{\delta X^2} \leq 0.5$$  \hspace{1cm} (5.13)

The remaining problem to be considered was the boundary condition at the closed end of the cell. This was dealt with by assuming a flat concentration profile in the final segment of the cell. The flux across the boundary between this segment and the one above is calculated from Fick’s first law using the backwards difference formula for the concentration gradient at that point. The increase in concentration in the bottom segment is then given by dividing the amount of flux across the boundary in time $\delta T$ by the depth of the segment, $\delta X$ to give the following equation-

$$C_{X_{\text{max}},T+\delta T} = C_{X_{\text{max}},T} + \frac{\delta T}{\delta X^2}(C_{X_{\text{max}}-\delta X,T} - C_{X_{\text{max}},T})$$  \hspace{1cm} (5.14)
The results obtained by performing these calculations on a spreadsheet with $\delta T = 2 \times 10^{-4}$ and $\delta X = 1/36$ are shown in Fig. 5.7

**Finite Difference Diffusion Model**

![Graph showing concentration over time for different X co-ordinates](image)

**Fig. 5.7** Results from non-dimensionalised diffusion model at 3 different X co-ordinates with $\delta T = 2 \times 10^{-4}$ and $\delta X = 1/36$.

These non-dimensional results can be converted to ‘real’ figures and compared with experimental results. The diffusion coefficient may be used as a fitting parameter giving a value for the tortuosity factor of the porous medium in which the experiment was performed.

### 5.2.2 Cylindrical geometry for probes

The probes have a different geometry which is best described using radial co-ordinates. In radial co-ordinates, Fick's second law becomes:

$$\frac{\partial c}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r D \frac{\partial c}{\partial r} \right)$$

(5.15)
Fig. 5.8 Initial conditions for radial model.

Non-dimensionalising as in the previous section ($R$ the non-dimensional radial position is $r/A$ where $r$ is radial distance from centre of probe and $A$ is radius of probe) the following finite difference equation was obtained.

$$C_{R,T+\delta T} = C_{R,T} + \delta T \left( \frac{C_{R+\delta R,T} - 2C_{R,T} + C_{R-\delta R,T}}{\delta R^2} + \frac{1}{R} \frac{C_{R+\delta R,T} - C_{R-\delta R,T}}{2\delta R} \right)$$ (5.16)

At the inner radius of the porous disc the equation needs to be modified similarly to the simple one-dimensional equation.

$$C_{R_{\text{min}},T+\delta T} = C_{R_{\text{min}},T} + \delta T \left( \frac{C_{R_{\text{min}}+\delta R,T} - C_{R_{\text{min}},T}}{\delta R^2} + \frac{1}{R_{\text{min}}} \frac{C_{R_{\text{min}}+\delta R,T} - C_{R_{\text{min}},T}}{2\delta R} \right)$$ (5.17)

5.2.3 Incorporating natural convection into diffusion model

The effect of natural convection had not been included in the modelling initially because the density differences involved are very small. However the Darcy velocity ($v_d$) may be calculated if the densities of the static lower fluid ($\rho_\omega$) and the more dense fluid above ($\rho_0$) and the dynamic viscosity of the static fluid ($\mu$) are known using the following equation.

$$v_d = \frac{B_g}{\mu} (\rho_0 - \rho_\omega)$$ (5.18)
Where $B$ is the constant from the Kozeny-Carman equation and is given by:

$$B = \frac{1}{K''(1-\varepsilon)^2 \sigma^3}$$  \hspace{1cm} (5.19)

where $\varepsilon$ is porosity, $\sigma$ is specific surface and $K''$ is Kozeny's constant which has a value of approximately 5. Since the model is for beds of spherical particles $\sigma$ can be replaced by $6/d$ where $d$ is the sphere diameter. For spheres of diameter $5 \times 10^{-4}$ m and a porosity for the packing of 0.4, $k$ is approximately $2 \times 10^{-10}$ thus giving a value for $\nu_d$ of $3 \times 10^{-13}$ m s$^{-1}$ at the start of a typical experiment. The initial velocity is also the maximum velocity, since as the experiment proceeds the sharp boundary between more dense and less dense solutions gradually becomes ‘smeared’ lessening any density differences between neighbouring regions of fluid. Hence, the velocity due to natural convection is clearly too small to have a measurable effect on these experiments.

Equation (5.18) may be used to give a finite difference solution to the equation-

$$\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2} + V \frac{\partial C}{\partial x}$$  \hspace{1cm} (5.20)

where $V$ is non-dimensional Darcy velocity

Thus, Equation (5.9) becomes-

$$C_{x,X=0} = C_{x,T} + \frac{\delta T}{\partial x} (C_{x-\delta x,T} - 2C_{x,T} + C_{x+\delta x,T}) + \frac{(V_{in}C_{S,AX,T} - V_{out}C_{X,T})\delta T}{\delta x}$$  \hspace{1cm} (5.21)

where $V_{in}$ and $V_{out}$ are the Darcy velocities from equation (5.18) at the upper and lower surfaces of the $X$th segment. The problem with using this approach in our system would be that there is no flow out of the bottom of the cell so the model would give a continual increase of matter in the bottom-most element of the finite difference grid. However a similar equation to this has been used to model our system as explained in the following sections.
5.3 Modelling Effect of Surface Shear Rate

From the experimental data it quickly became evident that the rate of transport of HCl into the beds of ballotini was dependent on the flow rate across the surface. It was decided to correlate this effect with the surface shear to allow a general correlation for all experimental configurations.

Two approaches were considered-

1) Using equation (5.9) but now calling \( D \) a dispersion coefficient \( (D') \) to allow for enhanced mass transport. \( D' \) can be correlated with surface shear.

2) Modifying equation (5.21) replacing \( V_m \) and \( V_{ou} \) with an 'induced velocity' term, \( u \) to allow for the enhanced mass transport. This velocity term may also be correlated with surface shear.

The increase in mass transport due to the surface shear decreases with increasing x co-ordinate so \( u \) (in approach 2) or \( D' \) (in approach 1) are functions of \( x \). The shear-induced mass transport does not have the concentration gradient as its driving force in the same way as diffusion so approach 2 which allows the diffusive and shear-induced effects to be treated separately was favoured. Allowing \( D \) to vary with \( x \) causes complications for the model because the time interval \( \delta t \) is dependent on the value of \( D \), this is not a problem with the induced velocity approach giving a second reason for preferring it.

Using this approach, Equation(5.20) becomes-

\[
\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2} + U \frac{\partial C}{\partial x}
\] (5.22)

where \( U \) is non-dimensional induced velocity as a function of non-dimensional distance \( X \) and the finite difference equation is-

\[
C_{X,T+\delta T} = C_{X,T} + \frac{\delta T}{\delta X}(C_{X-\delta X,T} - 2C_{X,T} + C_{X+\delta X,T}) + \frac{(U_{X-\delta X}C_{X-\delta X,T} - U_{X,T}C_{X,T})\delta T}{\delta X}
\] (5.23)
The use of the same equation as for situations where there is density driven fluid convection does not mean that in this case there is any net fluid convection. The term 'induced velocity' does not correspond to any bulk fluid velocity but was chosen to describe the apparent velocity of ions required to account for the change in HCl concentration within the bed which occurs due to the enhancement in mass transfer caused by surface shear.

There is one additional constraint on the model in that the maximum value of the induced velocity must correspond to travelling a distance no more than the width of one x increment in a single time step that is-

\[ U_{\text{max}} \delta T \leq \delta X \]  

(5.24)

### 5.3.1 Calculating Surface Shear

#### 5.3.1.1 One-dimensional experiments

For the cell designed to have uniform flow across the surface and for the probes \( V \) is a function of surface shear and \( X \) and the model is still one dimensional. For these experiments, the flow across the bed surface was laminar and the surface shear rate could be calculated simply using the equation-

\[ \gamma = \frac{6\bar{v}}{h} \]  

(5.25)

where, \( \gamma \) is wall shear, \( \bar{v} \) is the mean velocity and \( h \) is the height of liquid above the bed surface.

#### 5.3.1.2 Cylindrical Cell

In the cylindrical cell, there is accelerating flow from the circumference towards the centre of the cylinder. The fluid velocity and also the surface shear rate are both proportional to the reciprocal of the radial position measured from the centre. Equation (5.25) is again used but with \( \bar{v} \) as a function of radial position-
where, $Q$ is volume flow rate and $r$ is radial position. For values of $r$ smaller than the radius of the exit tube $v$ was assumed to remain constant.

\[ \bar{v} = \frac{Q}{2\pi rh} \]  \hspace{1cm} (5.26)

5.3.1.3 Probes
For the probe experiments the situation is more complicated because there is turbulence at the higher flow rates used and there is developing flow across the surface of the porous discs as they are situated close to the tip of the probe. The equation for the surface shear in developing flow used is based on the Reynolds number for flow near a leading edge and was introduced previously in Chapter 3, equations (3.8) and (3.9).

5.3.2 Two dimensional model for cylindrical cell
Because the surface shear is not uniform across the radius of the cylinder, $u$ also varies. This causes a radial concentration profile within the bed which is not flat, so radial as well as axial diffusion must be taken into account and a two-dimensional grid of concentration values must be used. There is still radial symmetry so the grid

Fig. 5.9 Graph of radial velocity profile using actual cell dimensions with a volume flow rate of 1 ml/s.
consists of the plane formed by a single radius extended along the length of the cylinder (i.e. rotational symmetry can be assumed).

![Diagram of two-dimensional modelling of cylindrical cell]

**Fig. 5.10** Layout for two-dimensional modelling of cylindrical cell.

### 5.3.2.1 Detail of Finite Difference Grid

The exact positioning of the grid points relative to the cell boundaries are shown below. The cell is divided up into squares with each square having the values for concentration and induced velocity calculated for the point at the centre of the square. At the bed surface, the whole of the top increment is taken to be above the surface and down the centre of the bed the centre of the \( y = 0 \) increment is taken to coincide exactly with the centre of the bed.
Combining equations (5.21) and (5.16) the following equation can be arrived at for $C_{XR,T=\delta T}$, the non-dimensional concentration at time $T + \delta T$ at co-ordinate $(X, R)$-

$$C_{XR,T=\delta T} = C_{XR,T} + \frac{\delta T}{\delta X^2}(C_{XR,T} - 2C_{XR,T} + C_{XR,T}) + \left(\frac{U_{X,R} \cdot C_{XR,T} - U_{X,R} \cdot C_{XR,T}}{\delta X}\right)\delta T$$

$$+ \delta T \left(\frac{C_{XR,T} - 2C_{XR,T} + C_{XR,T}}{\delta R^2} + \frac{1}{R} \frac{C_{XR,T} - C_{XR,T}}{2\delta R}\right)$$

(5.27)

where $U$ is a function of $R$, $X$ and surface shear to be determined empirically from experimental data. When $R$ is zero the radial diffusion is set at zero since, by symmetry, the radial concentration gradient at the centre of the cylinder is zero, so-

$$C_{X0,T=\delta T} = C_{X0,T} + \frac{\delta T}{\delta X^2}(C_{X0,T} - 2C_{X0,T} + C_{X0,T}) + \left(\frac{U_{X,0,R} \cdot C_{X0,T} - U_{X,0,R} \cdot C_{X0,T}}{\delta X}\right)\delta T$$

(5.28)

The other boundaries are dealt with in a similar way to the one dimensional models giving-
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\[ C_{X,R_1+T+\delta T} = \frac{\delta T}{\delta X^2} (C_{X,R_1+T+\delta T} - 2C_{X,R_1+T} + C_{X,R_1+3\delta T}) + \frac{(U_{X,R_1+T} - U_{X,R_1+2\delta T})}{\delta X} + \delta T \left( \frac{C_{X,R_1+T} - C_{X,R_1-\delta T}}{\delta R^2} + \frac{1}{R} \frac{C_{X,R_1+T} - C_{X,R_1+3\delta T}}{2\delta R} \right) + C_{X,R_1+T} \] (5.29)

for the concentration at the circumference and

\[ C_{X,R_2+T+\delta T} = C_{X,R_2+T} + \frac{\delta T}{\delta X^2} (C_{X,R_2+T} - 2C_{X,R_2+T} + C_{X,R_2+3\delta T}) + \frac{(U_{X,R_2+T} - U_{X,R_2+2\delta T})}{\delta X} + \delta T \left( \frac{C_{X,R_2+T} - C_{X,R_2-\delta T}}{\delta R^2} + \frac{1}{R} \frac{C_{X,R_2+T} - C_{X,R_2+3\delta T}}{2\delta R} \right) \] (5.30)

for the concentration at the bottom of the cell.

5.3.3 Predicting experimental results for cylindrical cell

A number of steps are necessary to predict the experimental results for the cylindrical cell.

1) Use data from one dimensional experiments to find relation of induced velocity to surface shear and bed depth for the appropriate bead size (Steps 1 and 2 are dealt with in detail in Chapter 6).

2) The diffusion coefficient and cell depth are the same for each set of experiments so the non-dimensionalisation is identical and the relation from step 1 for non-dimensional induced velocity can be substituted directly into Equation (5.27).

3) Use Equations (5.28 - 5.30) to calculate concentration values at each grid point for the required length of time.

4) Convert concentrations to values proportional to electrical resistance by taking the reciprocal.

5) Average reciprocal values along the line between each electrode pair for which results are being predicted.

6) Convert back to a concentration value which should be proportional to the experimentally measured conductance.
The experimental and predicted vertical concentration profiles can then be compared. This procedure is carried out using a LotusScript Macro in a Lotus 1-2-3 spreadsheet, the complete macro is reproduced in Appendix A. The Script is effectively a program written in BASIC which outputs the required data directly into a spreadsheet and runs much more quickly than an equivalent program initially written in Q-BASIC.

A discrete unit cell approach was used so each grid point in the finite difference scheme corresponded to a single pore space. The physical parallel is considering each pore space to be perfectly mixed with restricted transport through the pore throats.

5.3.3.1 Using data from one dimensional experiments

A reasonable fit was obtained by assuming an exponential relation between induced velocity \( u \) and bed depth \( x \):

\[
u = Ae^{-Bx}
\]

(5.31)

this equation can then be fitted to the data from the one dimensional experiments by varying \( A \) and \( B \). The data and fits using the model are shown together in Chapter 6. The values obtained can then be inserted in equation (5.27) to give the required equation for modelling experiments in the cylindrical cell, these predictions together with the data are also shown in Chapter 6. A graph showing the type of radial concentration profiles predicted is given below for conditions corresponding to the experiment in Fig. 6.40.

It was also planned to correlate \( A \) and \( B \) with the hydraulic mean diameter of the pore throats for the different packings.
Fig. 5.12 Predicted radial concentration profiles, at the depths shown in the legend, after 3 hours for 510 micron ballotini with a volume flow rate of 2.16ml s⁻¹.

5.3.3.2 Sensitivity
The sensitivity of the model results to the length of the time increment used was studied. A value of approximately 0.1 for $\delta T/\delta X^2$ was found to be suitable as decreasing $\delta T$ by a factor of 10 was found to have little effect on the results as shown below in Fig. 5.13. All the test runs for the model were run with initial concentration values of 1 in the bed and 2 at the surface.

For the smaller particles the array size restrictions in LotusScript meant that it was not possible to hold all the necessary data in an array so an investigation was carried out to discover whether an adequate approximation could be obtained by using less than one grid point for every pore space. For this investigation the same value of $\delta T/\delta X^2$ was used for each value of $\delta x$. One comparison is shown in Fig. 5.14 below. There is a bigger difference than for a similar change in $\delta T$ so it is better to use the discrete model with one grid point for each pore space if possible, but for small pores an approximation can be obtained by using less than one grid point per pore space which will save on computing time.
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Fig. 5.13 Effect of varying time increment, a grid for the largest size of ballotini was used and the values for $\frac{\delta T}{\delta X^2}$ were 0.11 and 0.011.

Fig. 5.14 Effect of using different values for $\delta X$ in the model, the same equation for the induced velocity was used in each case.
6. Results and Discussion

6.1 Introduction
In this chapter the results of experiments with the two cells introduced in Chapter 4 and the conductivity probes introduced in Chapter 3 are presented, compared with the model from Chapter 5 and the findings discussed. The conductivity probes were introduced before the description of the cell experiments to aid the understanding of the reasons for carrying out the experimental program using the cells. However in this chapter the order is reversed for two reasons; firstly most of the experiments using the probes were performed at the end of the project and secondly the analysis of the data for these experiments is based on the method used to analyse the data from the cell experiments.

6.2 Cell Experiments
The results presented here were all obtained using the two cells described in some detail in Chapter 4 and are compared with the model described in Chapter 5. Earlier experiments did not produce results of sufficient reproducibility to be presented but were useful in developing the method as discussed in Chapter 4.

6.2.1 Calibration with beads in position
The calibration experiments performed with ballotini in the cylindrical cell have further implications other than simply demonstrating a linear response of measured conductivity with HCl concentration. By comparing the measured conductivities with glass beads present to the values for bulk solution, the validity of some of the equations considered in Chapter 2, relating conductivity ratios to porous medium properties and diffusivities, may be assessed.

The results of these experiments showed a clear trend of decreasing conductivity with decreasing particle size as shown in Figures 6.1 and 6.2 below. The relative conductance for each size of beads was determined using a graph similar to Figure 6.1 for each of the electrode pairs, the relative conductance being the gradient of the data points for the bead size in question divided by the gradient with no beads present.
These relative values were then averaged across the six electrode pairs used (results from pairs 3 and 7 were not used because of problems with connections at these electrodes during part of the experiment) and plotted in Figure 6.2.

![Figure 6.1 Results for electrode 4.](image)

![Figure 6.2 Variation of conductivity with bead size, as measured in the cylindrical cell.](image)

This shows that the common assumption that conductivity ratio depends only on porosity and tortuosity is incorrect, since the values for porosity and tortuosity must be very similar for all four particle sizes. According to Taffinder and Batchelor and
Chapter 6 - Results and Discussion

others, the conductivity ratio should be, at least approximately, equal to the diffusivity ratio, so these results should give a direct measure of the effective diffusion coefficient, \( D \), given the value of \( D \) for bulk solution. The values for the tortuosity, \( \tau \), in the equation

\[
S = \frac{S_\infty}{\tau}
\]  

(6.1)
of each bed are tabulated below.

**Table 6.1 Tortuosity values from conductivity experiments (using porosity values from Table 4.1).**

<table>
<thead>
<tr>
<th>Bead size, ( \mu m )</th>
<th>Tortuosity, ( \tau )</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>1.46</td>
</tr>
<tr>
<td>240</td>
<td>1.36</td>
</tr>
<tr>
<td>510</td>
<td>1.18</td>
</tr>
<tr>
<td>910</td>
<td>1.12</td>
</tr>
</tbody>
</table>

The implication of these calibration results is that \( D \) increases with particle size such that the relation between the two can be approximated as a straight line. The gradient in Fig. 6.2 appears to decrease with increasing particle size and the conductivity ratio certainly would not be expected to rise above the value of the porosity as that would correspond to a tortuosity value of less than one or, in other words, a conductivity in the pore solution higher than in bulk solution of the same concentration.

Expected values for \( D \) \( \text{cm}^2 \text{s}^{-1} \) in the bulk solution can be calculated using the Nernst-Hartley relation as given by Robinson and Stokes.

\[
D^0 = \frac{RT(z_f + z_p)}{F^2 \lambda_0^2 \sqrt{\frac{z_f + z_p}{z_f^2 + z_p^2}}} 
\]  

(6.2)

Where, \( F \) is the Faraday constant in C mol\(^{-1}\), \( R \) is the gas constant in J K\(^{-1}\) mol\(^{-1}\), \( T \) is the absolute temperature in K, \( z \) is valency, \( \lambda_0 \) is limiting equivalent conductivity in
\( \Omega^{1} \text{ cm}^{2} \text{ mol}^{-1} \), \( \nu \) is the number of ions formed from 1 mole of electrolyte and subscripts 1 and 2 refer to the two different diffusing ions of opposite charge.

For a 1:1 electrolyte this can be simplified since, in order to conserve electroneutrality, \( \nu_1 = \nu_2 \).

\[
D^0 = \frac{2RT}{F^2} \frac{\nu_1 \nu_2}{(\nu_1^2 + \nu_2^2)}
\]

(6.3)

Using literature values\(^{100}\), this gives a value for \( D \) of approximately \( 3.3 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \) for HCl. These values will be slightly lower at the concentrations used in accordance with the equation-

\[
D = D^0 \left( 1 + \frac{d \ln \gamma_c}{d \ln c} \right)
\]

(6.4)

where \( \gamma_c \) is the activity coefficient and \( c \), concentration. The activity coefficient remains close to unity for the concentrations used, the actual value being around 0.97 as seen from the graph below.

**Fig. 6.3** Plot of literature data\(^{101}\) for the activity coefficient of aqueous HCl at low concentrations.
6.2.2 Diffusion at low flows in cylindrical cell

The graphs on the following pages show results from experiments with low surface flow rates for each of the different sizes of ballotini. In each case a diffusion coefficient of \(2.26 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}\) is used for the theoretical curves. This is a theoretical diffusion coefficient obtained by dividing the value from the Nernst-Hartley equation by \(\sqrt{2}\) which is predicted to be the correct factor to allow for the tortuosity of unconsolidated porous media\(^{102}\) and is also close to the value obtained by Leaist\(^{24}\) in his experiments with ballotini. The actual best fit diffusion coefficients from a combined least squares best fit for results from electrode pairs 3, 4 and 7 which are at bed depths 20, 30 and 40 mm respectively are shown in the table below. Data from the electrodes at bed depths of 5 and 50 mm were not used for the fits because the 50 mm electrodes showed no significant increase in concentration over the period of the experiments and the results from the 5 mm electrodes were erratic due to their proximity to the surface. Data points for all the electrode pairs have been included in the graphs however.

Table 6.2 Showing the value of the best fit diffusion coefficient for each size of ballotini.

<table>
<thead>
<tr>
<th>Bead Size, (\mu\text{m})</th>
<th>Best fit diffusion coefficient, (\text{m}^2 \text{ s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>1.7</td>
</tr>
<tr>
<td>130</td>
<td>2.7</td>
</tr>
<tr>
<td>240</td>
<td>2.2</td>
</tr>
<tr>
<td>510</td>
<td>2.1</td>
</tr>
<tr>
<td>910</td>
<td>2.9</td>
</tr>
</tbody>
</table>

In all these experiments the maximum surface shear rate was less than 1 \(\text{s}^{-1}\). The first graph shows a typical spread for the results from the three pairs of electrodes at the same bed depth (refer to Figures 4.8 and 4.9 for diagrams of the electrode positions). It can be seen that there is a high degree of agreement between the three measurements with two of them being indistinguishable on the scale of the graph. In
all subsequent graphs the data shown for a bed depth of 30 mm is the data from electrode pair 4 which was in line with the other 5 electrode pairs.

Fig. 6.4 Graph showing the measured results from the three coplanar electrode pairs (4, 5 and 6) for the experiment with 130 micron beads.
Fig. 6.5 75 micron beads, showing datapoints and predicted curves for $D = 2.26 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (top pair of electrodes were not functioning).

Fig. 6.6 130 micron beads, showing datapoints and predicted curves for $D = 2.26 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.
Fig. 6.7 240 micron beads, showing datapoints and predicted curves for $D = 2.26 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ (top pair of electrodes not functioning).

Fig. 6.8 510 micron beads, showing datapoints and predicted curves for $D = 2.26 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$.
The same clear trend seen in the calibration experiments is not seen in this case. The under 75 micron results appear to show lower mass transfer but examination of Fig. 6.5 shows that there was a sloping baseline for this experiment which would have caused an underestimation of the diffusion coefficient, also there is a wider relative deviation in particle size for these beads so probably lower porosity and higher tortuosity. The results for the 910 micron particles appear to show highest mass transfer but that is not enough to establish the trend since the next quickest appears to be the 130 micron experiment with the two intermediate sizes giving very similar and lower values for $D$. In this instance, the conclusion is that $D$ is probably independent of particle size with the differences observed being attributable to small differences in porosity and possibly, in the case of the largest particles, to wall effects.

The tortuosity value from the diffusion coefficient is close to the value from the conductance measurements for the smallest particles but the larger particles give a lower value for tortuosity of approximately 1.1 it would be interesting to carry out further experiments to find whether the tortuosity determined from conductivity...
might level off at approximately the same value obtained from diffusion measurements.

6.2.3 Why are conductivity ratio and diffusivity ratio apparently different?
It is not altogether surprising that electrical conductivity and diffusivity should respond differently to changes in porous structure. Considering an individual ion, in the case of diffusion it undergoes a random walk with no net external force whereas the ability of an ion to act as a conductor of charge between two point electrodes depends on its mobility in one dimension along the line of the electric field between the electrodes which passes through the ion.

Another factor to consider is that in these experiments the two phenomena have been studied for the same beds but in mutually perpendicular directions so the question of the degree of anisotropy could be important.

Also, for diffusion the positive and negative ions must move at the same velocity in order to prevent charge separation and conserve electroneutrality whereas for electrical conduction charge separation is created. This means that for electrical measurements the effect due to the more mobile ion may dominate whereas for diffusion the less mobile ion tends to dominate by ‘holding back’ the more mobile ion.

If surface conductance is important there will be higher resistance for smaller particles because contacts between particles are points of high resistance but this effect is expected to be negligible[83] as mentioned in Chapter 2.

6.3 Rectangular cell experiments
The experiments using the rectangular cell gave generally smoother, more reliable results although there were still some anomalies. The results were fitted using the ‘induced velocity’ model introduced in Chapter 5. The equation used for the induced velocity, \( u \) decreased exponentially moving away from the bed surface according to the equation.
where $x$ is the distance below the bed surface and $A$, the pre-exponential factor, and $B$, the velocity index, were varied to find the best overall fit for the six electrode pairs in each experiment.

In the non-dimensionalised finite difference grid $\delta x$ was $1/36$ and $\delta t 1.13 \times 10^{-4}$ which meant that, using a value for $D$ of $2.26 \times 10^{-9}$ m$^2$ s$^{-1}$, the experimental data points exactly coincided in time with theoretical points allowing the expression for induced velocity giving the least squares error to be determined by trial and error using a spreadsheet macro.

The important figures for the experiments carried out are tabulated below. In the Cell column, ‘o’ refers to the original cell and lid and ‘n’ refers to experiments using the newer lid giving a narrower chamber above the bed. For the experiment shown in Fig. 6.17 electrode 5 was not functioning so the values for $A$, $B$ and the total error for that experiment refer to a fit using the data from the remaining five electrodes.
Table 6.3 Summary of experiments using rectangular cell, including the A and B values from Equation (6.5).

<table>
<thead>
<tr>
<th>Size, μm</th>
<th>A</th>
<th>B</th>
<th>Total least squares Error</th>
<th>Surface Shear, s⁻¹</th>
<th>Cell</th>
<th>Fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>910</td>
<td>7</td>
<td>2</td>
<td>3.72E-005</td>
<td>0.1</td>
<td>o</td>
<td>6.10</td>
</tr>
<tr>
<td>910</td>
<td>15</td>
<td>2</td>
<td>2.24E-005</td>
<td>0.2</td>
<td>o</td>
<td>6.11</td>
</tr>
<tr>
<td>910</td>
<td>73</td>
<td>2.7</td>
<td>5.87E-005</td>
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Fig. 6.10 910 micron beads, shear 0.10 s⁻¹.

Fig. 6.11 910 micron beads, shear 0.17 s⁻¹.
Chapter 6 - Results and Discussion

Fig. 6.12 910 micron beads, shear 1.15 s⁻¹.

Fig. 6.13 910 micron beads, shear 3.02 s⁻¹.
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Fig. 6.14 910 micron beads, shear 12.5 s\(^{-1}\).

Fig. 6.15 910 micron beads, shear 24.0 s\(^{-1}\).
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Fig. 6.16 910 micron beads, shear 37.0 s\(^{-1}\) (model on the edge of stability as can be seen from the 0.5 cm line)

Fig. 6.17 510 micron beads, shear 0.14 s\(^{-1}\).
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Fig. 6.18 510 micron beads, shear 3.1 s\(^{-1}\) (modified cell).

Fig. 6.19 510 micron beads, shear 3.1 s\(^{-1}\) (original cell).
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Fig. 6.20 510 micron beads, shear 10.7 s⁻¹.

Fig. 6.21 510 micron beads, shear 19.9 s⁻¹.
**Fig. 6.22** 510 micron beads, shear 35.5 s⁻¹.

**Fig. 6.23** 240 micron beads, shear 2.1 s⁻¹.
**Fig. 6.24** 240 micron beads, shear 11.7 s⁻¹.

**Fig. 6.25** 240 micron beads, shear 23.2 s⁻¹.
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**Fig. 6.26** 240 micron beads, shear 35.7 s⁻¹.

**Fig. 6.27** 130 micron beads, shear 0.12 s⁻¹.
Fig. 6.28 130 micron beads, shear 3.1 s⁻¹.

Fig. 6.29 130 micron beads, shear 35.9 s⁻¹.
General observations from these results are that a very good fit can be obtained but on some occasions there is more deviation. It should be noticed that it is not just experiments with very low induced velocities which give good fits (e.g. Fig. 6.21 is for an experiment with relatively high surface shear). Comparison of Fig. 6.18 and Fig. 6.19 shows the consistency of results for the modified and unmodified cell since these two experiments were performed at the same surface shear. Other than some apparently random deviations from smooth curves two other effects are sometimes observed, both for the cylindrical and the rectangular cells:

1) The final concentration according to the electrical measurements does not always coincide satisfactorily with the original measured concentration in the feed tank (e.g. Fig. 6.12).

2) A downward drift, although normally quite gradual, in the concentration values determined from the electrical measurements was often observed (e.g. Fig. 6.26), occasionally an upward drift was observed which did not appear to be due to diffusion of HCl as can be seen in some of the results for the 130 micron particles (e.g. Fig. 6.27).

Both of these could have been partly due to temperature drift, although steps were taken to minimise this. Since the constant temperature box was not equipped to cool the cell when the ambient temperature was above 25°C neither was it able to maintain a temperature more than approximately ten degrees above the ambient temperature. Experiments occasionally had to be delayed until the ambient temperature was more suitable. Electrical heating due to the measurements would have been negligible since each electrode pair was only activated for a few seconds in each hour. From literature data\textsuperscript{103} it is apparent that the percentage change per degree in conductivity of aqueous 0.005M HCl at 25°C is approximately 1.5%. The theoretical temperature range during experiments was 24.5 - 25.5°C so, even allowing for an extra 0.5°C either side the conductivity would be expected to fluctuate by less than 3%. Any change that was observed would be expected to slowly oscillate as the heater switched on and off during the experiment but this has not been observed. The conclusion is that
temperature effects make a small contribution to any deviation from expected behaviour but are not significant in explaining these two effects.

Another explanation for the occasions when the apparent concentration at the top two electrode pairs rose above the initially determined feed tank concentration could be due to some physical rearrangement of the bed leading to a higher porosity and hence higher than expected electrical conductivity in the top portion of the bed. No visual evidence for this was observed however.

Below are graphs for the pre-exponential factor, $A$, and velocity index, $B$, in Equation (6.5) for the three largest sizes of ballotini.

**Fig. 6.30 910 micron.**

**Fig. 6.31 510 micron (points for shear of 3.1 with original cell excluded).**
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\[ \gamma \]

\[ \begin{array}{c|c|c}
\text{Particle size, \( \mu m \)} & \text{A} & \text{B} \\
\hline
910 & 8.67\gamma & -1.91-0.108\gamma \\
510 & 13.02\gamma & -33.7+0.495\gamma \\
240 & 1.17\gamma & -38.2+0.744\gamma \\
\end{array} \]

The \( A \) value for the three different sizes passes close to the origin suggesting that using the same diffusion coefficient in each case is a valid approximation at this level of accuracy. It is interesting that for the largest particles the drop off in induced velocity appears to be more rapid at higher flow rates whilst for the smaller particles the opposite trend is observed. A point to notice is that for the two smaller particle sizes the equation for \( B \) cannot be valid at higher shears because \( B \) would become positive giving an induced velocity which increased exponentially moving away from the exposed surface.

The induced velocity profiles for each of the three sizes of beads at a surface shear rate of 10 \( s^{-1} \) are shown in Fig. 6.33 below using Equation (6.5) with values for \( A \) and \( B \) given by Table 6.4. The graph shows the magnitude of the induced velocity in SI

**Fig. 6.32** 240 micron.

**Table 6.4** Pre-exponential factor and velocity index in terms of surface shear, \( \gamma \), as given by the trend lines in the graphs above.
units which is of the order of $10^{-5}$ m s$^{-1}$ near the surface. The rate of decay increases significantly more rapidly for smaller particles.

![Graph](image)

**Fig. 6.33** Induced velocity against distance below surface for a surface shear of 10 s$^{-1}$.

These results were used to model the results obtained previously using the cylindrical cell, following the procedure outlined in Chapter 5. Results for experiments with 910 and 510 micron particles are shown below, together with the model predictions. The equations used for the $A$ and $B$ values were the equations for the regression lines in Fig. 6.30 and Fig. 6.31 above with the regressions for the $A$ values being forced through the origin.

An attempt at an overall correlation with a Peclet number, using the surface fluid velocity for the $v$ term and the bead diameter as the characteristic length, was not successful.
6.4 Cylindrical cell at higher shear rates - comparison with model
In this section the results of simulations of cylindrical cell experiments are compared with experimental data for the same flow rate and particle size. The lines on these graphs are not fits of the data as in the previous section but they are predictions based on the induced velocity model where the relation between induced velocity, surface shear and position in bed has been determined from entirely independent experiments carried out in a different cell with a different flow configuration. The method is described in Section 5.3.2 with the key Equation being (5.27). As a brief recap, the model uses a two dimensional finite difference grid with horizontal and vertical diffusion and an induced velocity which is a function of surface shear and bed depth as determined empirically in Section 6.3 above. The macro used to produce these graphs is listed in Appendix A. The graphs are given in order of ascending surface shear firstly for the 510 then the 910 micron beads.

Fig. 6.34 510 micron beads, flow 0.08 ml s⁻¹.
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Fig. 6.35 510 micron beads, flow 0.43 ml s⁻¹.

Fig. 6.36 510 micron beads, flow 0.66 ml s⁻¹.
Fig. 6.37 510 micron beads, flow 0.86 ml s⁻¹.

Fig. 6.38 510 micron beads, flow 1.16 ml s⁻¹.
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Fig. 6.39 510 micron beads, flow 1.3 ml s$^{-1}$.

Fig. 6.40 510 micron beads, flow 2.16 ml s$^{-1}$.
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Fig. 6.41 910 micron beads, flow 0.04 ml s⁻¹.

Fig. 6.42 910 micron beads, flow 0.17 ml s⁻¹.
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Fig. 6.43 910 micron beads, flow 0.33 ml s⁻¹.

Fig. 6.44 910 micron beads, flow 0.43 ml s⁻¹.
Fig. 6.45 910 micron beads, flow 0.5 ml s⁻¹.

Fig. 6.46 910 micron beads, flow 1.2 ml s⁻¹.
**Fig. 6.47** 910 micron beads, flow 1.4 ml s⁻¹.

**Fig. 6.48** 910 micron beads, flow 1.8 ml s⁻¹.
Some of the predictions here for the 510 micron beads are quite successful and looking at the variability in the data it would be unlikely to find a model giving a considerably better fit averaged over all the experiments. It should be remembered that for these experiments the curves shown depend entirely on the data obtained using the other cell with no adjustments made to try and get a better fit for the specific experiment. For the 910 micron beads the model seems to considerably exaggerate the rate of increase in concentration towards the bottom of the cell at higher shear rates. The immediate reason for this can be explained to a large extent simply by referring back to the experiments with the rectangular cell and the 910 μm ballotini which were used to give the equation for $U$ at this bead size and show a relatively rapid increase in concentration at the lower electrode positions.

6.5 Probe experiments
When testing the probes it became clear that with the external and internal earth electrodes wired together, the external earth electrode interfered with the readings from the internal electrodes. This was shown by a significant change in the measured voltage from the internal electrodes depending on whether the external earth electrode was also immersed in the electrolyte solution or raised above the surface. For these experiments the measurements of interest were those from the internal electrodes so the external electrodes were covered with insulator.

6.5.1 Flow rate test
A test was carried out using the smallest probe to check the effect of shear on the voltage measurement obtained from the internal electrodes. The supply voltage remained at $4.838 \pm 0.001$ V during the experiment. For the result at zero flow the pump was switched off, for the rest of the measurements the flow was adjusted using the valves on the apparatus, the results are shown in the table below in the order in which the measurements were taken.
Table 6.5 Flow rate test data.

<table>
<thead>
<tr>
<th>Flow rate, ml s⁻¹</th>
<th>Surface shear (from Equation 3.5) s⁻¹</th>
<th>V_m ± 0.0005V</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>1300</td>
<td>2.8755</td>
</tr>
<tr>
<td>140</td>
<td>280</td>
<td>2.874</td>
</tr>
<tr>
<td>19</td>
<td>8</td>
<td>2.873</td>
</tr>
<tr>
<td>1.1</td>
<td>0.05</td>
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<td>0</td>
<td>0</td>
<td>2.902</td>
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<td>140</td>
<td>280</td>
<td>2.87</td>
</tr>
</tbody>
</table>

These results show that as long as there is some flow the flow rate does not significantly affect the measurement. The difference for the measurement at zero flow corresponds to a 2 - 3% difference in resistance at this concentration and the discrepancy may have been due to interference between the pump and the measuring circuit. This could be tested by taking measurements with the probe removed from the rig, but in proximity to the pump, and investigating any effects due to operation of the pump.

6.5.2 Response time Experiments

Most of the probe experiments were performed using the smallest probe of diameter 8 mm but experiments were also performed with the two larger probes. Below is a comparison for the 8 mm and 12 mm probe at the same surface shear rate of approximately 0.4 s⁻¹ followed by two graphs summarising the experiments with the 8 mm probe.
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**Fig. 6.49** Comparison of 8 mm and 16 mm diameter probes with surface shear of 0.4 s\(^{-1}\).

**Fig. 6.50** Results for small probe at different surface shear rates (as given in the legend in s\(^{-1}\)) with a similar step up in HCl concentration for each experiment using tap water containing added HCl.
In these experiments the HCl concentration, as measured using the conductivity meter was found to decrease significantly with time when tap water was used, no adequate explanation for this was found but switching to deionised water reduced this effect. The model can still be used for a continuously varying HCl concentration by making the value of surface concentration a function of time. Also it was difficult to run experiments over a long time scale due to leakage and heating at the pump so the experiments were run over short time periods making it unnecessary to make the surface HCl concentration in the model a function of time. One other difference from the cell experiments is that the probe is a relatively large distance from the feed tank so an immediate step change in the external acid concentration at the probe when acid is added to the feed tank can not be assumed at very low flow rates.

The diffusion coefficient appears to be less than the value for the beds of ballotini at approximately 1 - 1.1 x 10⁻³ cm² s⁻¹. This corresponds to a tortuosity factor of 3 compared to 1.4 for ballotini despite the apparently higher porosity of the Vyon. A different value for the tortuosity factor is not surprising since the two structures are quite different, as can be seen from Fig. 3.6. Although Vyon is made by sintering small particles it is evident that the resulting structure is not particularly similar to an
assembly of spheres with point contacts. Values of 3 - 3.5 for the tortuosity factor of activated carbon measured using potassium chloride have been reported\textsuperscript{[104]} so a tortuosity of around 3 for a consolidated medium is quite reasonable.

The lack of similarity between the structures of the Vyon and the beds of ballotini means that the results from the previous experiments using the rectangular cell cannot be used to predict the magnitude of the induced velocity within the probe in the same way they were used for the cylindrical cell experiments in Section 6.4.

The data from the experiments for the small probe was used to find the value for the diffusion coefficient of HCl in the Vyon and a relation between induced velocity and surface shear. The following equation was found to give a reasonable fit to the data-

\[
U = 500 \exp\left(\frac{-\left(1-R\right)}{0.000217}\right)
\]  

(6.6)

where \(U\) and \(R\) are the non-dimensional induced velocity and radial position respectively and \(\gamma\) is the surface shear (s\(^{-1}\)). Results for the larger two probes were then simulated and compared with the available data. The results are shown below.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.52}
\caption{Simulations for surface shear of 0.1 s\(^{-1}\) and step concentration change from 1 to 2.}
\end{figure}
Fig. 6.53 Simulations for surface shear of 1000 $s^{-1}$ and step concentration change from 1 to 2.

Below are comparisons of the model with the data for individual experiments, the concentration has been normalised against the initial value in each case. For some of the experiments two steps up in concentration were made whilst maintaining the same flow rate.
Table 6.6 Probe experiments, * denotes an experiment where deionised water was used.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Flow, ml s(^{-1})</th>
<th>Surface Shear from equations 3.8 &amp; 3.9, s(^{-1})</th>
<th>Initial Conductivity, mS</th>
<th>Final Conductivity, mS</th>
<th>Fig.</th>
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Fig. 6.54 Small probe, shear $1010 \text{ s}^{-1}$

Fig. 6.55 Small probe, shear $651 \text{ s}^{-1}$

Fig. 6.56 Small probe, shear $651 \text{ s}^{-1}$
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Fig. 6.57  Small probe, shear 293 s\(^{-1}\)

Fig. 6.58  Small probe, shear 293 s\(^{-1}\)

Fig. 6.59  Small probe, shear 257 s\(^{-1}\)
Figure 6.60  Small probe, shear 257 s\(^{-1}\)

Figure 6.61  Small probe, shear 39 s\(^{-1}\)

Figure 6.62  Small probe, shear 21 s\(^{-1}\)
**Fig. 6.63** Small probe, shear 19 s⁻¹

**Fig. 6.64** Small probe, shear 19 s⁻¹

**Fig. 6.65** Small probe, shear 2.4 s⁻¹
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Fig. 6.66 Small probe, shear 2.4 s⁻¹

Fig. 6.67 Small probe, shear 0.3 s⁻¹

Fig. 6.68 Small probe, shear 0.1 s⁻¹
**Fig. 6.69**  *Medium probe, shear 1224 s⁻¹*

**Fig. 6.70**  *Medium probe, shear 1224 s⁻¹*

**Fig. 6.71**  *Medium probe, shear 312 s⁻¹*
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Fig. 6.72 Medium probe, shear 312 s⁻¹

Fig. 6.73 Medium probe, shear 21 s⁻¹

Fig. 6.74 Medium probe, shear 0.4 s⁻¹
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*Fig. 6.75*  Large probe, shear 1680 s⁻¹

*Fig. 6.76*  Large probe, shear 1680 s⁻¹

*Fig. 6.77*  Large probe, shear 425 s⁻¹
The experiments with the small probe show the expected trend of shorter response time at higher surface shear and are generally of the expected shape although the fits are not particularly close when the same values of the fitting parameters are used for all the experiments. The experiments with two steps in concentration all show high similarity in the response to the steps even when the shape of the curve is somewhat unexpected as is the case for several of the experiments with the larger probe. The response time of the larger probes does not appear to be increased relative to the small probe as much as expected by the model and particularly for the largest probe the response appears to occur in two separate stages with a rapid initial increase in
measured conductance, which cannot be due to diffusional transport of ions to the centre of the probe, followed by a plateau before a further more gradual increase.

Clearly the response time of the probe can be significantly improved by operating at higher shear rates so ideally the probe when used would be in a position where there is rapid flow. In a slow flowing system some form of stirrer or constriction in the pipe work could be used. However it would be important that any arrangement to increase the surface shear on the probe did not distort the local dispersed solids concentration around the probe.

6.6 Summary

Most of the results reported can be explained satisfactorily but there are a few points which can not be fully explained-

1) The responses of the two larger probes sometimes take on a shape where there appear to be two separate stages in the increase of concentration within the probe.

2) The conductivity of the HCl solution used in the probe experiments drifted down appreciably particularly when tap water rather than deionised water was used to dilute the acid.

3) The conductivity of the beds of ballotini was found to increase with increasing particle size as discussed in Section 6.2.1.

4) Two effects were observed on occasion during the cell experiments and have been discussed previously in Section 6.3 on page 106. These were a baseline drift (normally a decrease in conductivity with time) and discrepancy between the final bed conductivity and the value expected from the measured conductivity of the stock solution.

The only further comments to make about points one and two are that further experiments need to be done before conclusions can be drawn. One of the first of these would be to run the rig with no probe present to check whether the conductivity drift observed is related to the presence of the probe.
Point 3 is of particular interest because it contradicts the common prediction that the size of spheres in a packing should not influence the effective conductivity if the porosity is maintained the same. This result cannot be fully explained, the surface properties of ballotini could have a part to play as could wall effects at the edge of the cell but the conditions of the experiments minimise both these effects. As discussed in Section 2.5, the pore sizes are relatively large and the electrolyte concentration high enough such that the size of the electric double layer is negligible compared to the total pore volume. In order to minimise any effects due to the region of high porosity adjacent to the cell walls, the cell is designed with electrodes which protrude 5 mm from the cell wall and are electrically insulated apart from the pointed tips (for details see Chapter 4). For the largest particles, the cell diameter is equivalent to approximately 50 particle diameters so wall effects would not normally be expected to make a significant to the overall properties of the packing. The influence of wall effects on this correlation between particle size and bed conductivity could be checked by carrying out further experiments using cells of different diameters.

The same factors are relevant to point 4, as well as additional considerations due to the fact that in this case the experiments took place over a longer time period of approximately 24 hours. The beads were given time to equilibrate with the pore solution before each experiment. The type of glass used (Lead glass) is chemically durable compared with other types of glass such as Pyrex glass which was used by Leaist[24] for experiments run under virtually identical conditions but over longer times. In view of these factors, surface properties are again not believed to be a major cause of the effects observed. One possible explanation, mentioned in Section 6.3 is slight bed rearrangement during the experiments, resulting in an increase in the packing density at the bottom of the cell and a corresponding decrease at the top. This would give higher than expected conductivity values at the top of the bed and low values at the bottom.

To conclude, there are a few minor discrepancies in the results for the cell experiments but overall the technique has been successfully applied to give reliable results. Future workers using the technique will need to consider the effects
mentioned above if they wish to make further improvements. The general conclusions for the practical and modelling work follow in Chapter 7.
7. Conclusions

7.1 Cell Experiments

An AC resistance technique can be used to measure effective diffusion or dispersion coefficients in porous media. The use of the type of cell described in Chapter 4 is best suited to studying unconsolidated media such as sphere packings. To study consolidated media the same basic technique could be used by inserting electrodes into the sample under investigation. The technique need not be limited to cells open at one end but could be used for a column open at both ends to solutions of different concentrations.

It was found best to use electrodes which were sharpened to a point and protruded several particle diameters from the cell wall thus eliminating wall effects. For systems containing dilute hydrochloric acid, gold-plated electrodes gave more reliable results than stainless steel electrodes.

A cylindrical cell with a single inlet tube at the circumference, outlet at the centre and a weir to distribute the flow (see Fig. 4.1) was found to give radially symmetric concentration profiles as measured by 3 separate pairs of electrodes at the same height in the cell.

Measured diffusion coefficients for HCl agreed well with previously reported results and theoretical predictions. However, for measuring diffusion coefficients to high accuracy a sealed cell similar to that used by Harned\textsuperscript{[22],[23]} or Leaist\textsuperscript{[24]} (but with protruding electrodes as described in Chapter 4) maintained under very precise constant temperature conditions is likely to give the best results.

For approximately mono-sized sphere packings the effective diffusion coefficient was found to be independent of particle size for the same porosity to within experimental error. The electrical conductivity of a bed of ballotini saturated with a very dilute hydrochloric acid solution, however, increases approximately linearly with particle size in the range 0.1 - 1 mm. This finding is contrary to the common assumption that the ratios of bulk to effective conductivity and bulk to effective diffusivity for a porous medium are equal. Electrical measurements are often used to predict the
approximate rate of diffusion through a medium (for example, for chloride through concrete). This is a useful technique but can not be expected to give an exact prediction.

When the shear rate at the cell surface is negligible the diffusion coefficient can be determined but at higher flow rates the rate of mass transport is increased above that of pure diffusion by an amount dependent on particle size as well as surface shear for beds of spheres.

7.1.2 Modelling
Diffusion in cells of finite length can be modelled using a finite difference solution to Fick's law allowing for the closed end of the cell as described in Chapter 5.

The increase in mass transport due to surface shear can be modelled by adding, to the Fick's law description of the transport, a velocity term which decays exponentially moving away from the surface exposed to flow and is termed here the 'induced velocity'.

The relation between induced velocity and surface shear for a given porous medium, determined under conditions of uniform flow across the surface, can be applied to situations where the surface shear varies in a defined manner. The model has been applied to cylindrical beds of spheres with radial flow across the surface accelerating from the circumference towards the centre. For this work the model was extended to two dimensions with radial as well as axial diffusion. The model was successful in predicting the results for the 510 micron beads but less satisfactory for the 910 micron particles.

7.2 Probe Experiments
The probe should be designed in future with a switch between the internal and external earth electrodes to prevent the effect mentioned in Chapter 3, where both earth electrodes interact with whichever live electrode is activated.
Chapter 7 - Conclusions

The probe experiments show a considerably shorter response time for the smallest probe but a quicker response is still desirable. Some of the factors to be taken into consideration are-

1) The probe could not be made smaller using the current design and the facilities available to us and if the probe could be made considerably smaller there would be a potential problem with flux tracking due to the inevitable proximity of the internal electrodes to the probe surface.

2) A replacement for the Vyon could be used, the results have shown that diffusion through Vyon is approximately half as quick as diffusion in beds of glass beads so perhaps a porous material with a pore structure more closely resembling that of a packing of spheres could be used.

3) Many systems will contain solid particles smaller than the pore size for the Vyon used in our experiments so a material with a smaller pore size would need to be used which would tend to increase the response time.

For a given probe design the following can be specified -

- The minimum diameter for suspended solid particles
- A measure of the response time. For example, the minimum surface shear rate at which the measured value of conductivity between the internal electrodes has corrected by 90% of the total change within 30 seconds of a step change in electrolyte concentration.

The current probe could not be used for control applications where there is only very slow flow. However, if the surface shear at the probe would always be above 1000 s\(^{-1}\) then a response time of approximately one minute could be achieved which is approaching an acceptable time so given an improved probe or higher surface shear use of the probe in control is feasible.

The probe could also be used to give approximate solids concentrations for any system, where response time is not critical, containing a partially conducting liquid and non-conducting solid. No calibration would be needed other than the initial
determination of the constant required to make the readings from the two electrode pairs equivalent.

7.2.1 Modelling
The one dimensional model for the cell experiments was converted to radial co-ordinates to describe the results for experiments with the probes. The results for the small probe, which was used for most of the experiments, gave satisfactory agreement with the model to within experimental error (as shown in Figs 6.54-6.68).

7.3 Suggestions for future work
There are a number of opportunities for further work building on what has been presented here-

1) More experiments with the rectangular type cell to investigate variation of the pre-exponential factor, $A$ and velocity index, $B$ for the induced velocity over a wider range of surface flow rates would allow modelling of the type done for the cylindrical cell in situations where higher shears are involved.

2) The effect of using differently structured porous media should also be investigated using this type of cell. The model could then be used for these additional materials in other situations, including the two described here i.e. where there is radial flow and in the solids concentration probes. Ideally a correlation between the values for $A$ and $B$ and common measurable parameters describing porous media such as porosity, permeability and pore size distribution could be arrived at allowing the model to be used for any porous medium of known properties without having to carry out any initial experiments. This would allow selection of suitable porous materials for the probe to give rapid response times whilst excluding all solid particles above the required limit.

3) Tomographic experiments, using electrical resistance tomography for example, for a cylindrical cell with accelerating radial flow at the surface could be carried out to get data for comparison with the predictions of the two dimensional model described in Chapter 5. So far these predictions
have only been compared with experimental data which varies in one dimension by averaging them radially.

4) Extending the range of particle sizes for which measurements of the conductivity of the porous medium were made, particularly down to smaller particles, would also be useful to establish whether the tortuosity as measured electrically continues to increase with decreasing particle size.

5) Experiments with the current probe could be carried out with solids in the system to check the operation of the probe under more realistic conditions and investigate the degree of fouling of the porous discs. These types of tests would also need to be carried out on any future probes.
References


References


References


References


[52] DUMANSKI 1908 *Kolloid-Z.* **3** 210


References


Appendix A
Program Listings

A.1 Data Acquisition
Below is the Microsoft Q-BASIC program which was used to control data acquisition
during experiments as described in Chapter 4.

10 CLS
20 OUT &H20B, &H80
30 OPEN "COM2:9600,N,8,1" FOR RANDOM AS #1
40 PRINT #1, CHR$(70) + CHR$(50): REM Sets DVM to ac Volts
50 PRINT #1, CHR$(82) + CHR$(48): REM Sets DVM to auto-scale
60 K(1) = K(2) = K(3) = K(4) = K(5) = K(6) = K(7) = K(8) = 1
65 t = 600
70 days = 0
75 cycles = 0
80 seconds = 0
95 DIM B(9, 400)
100 INPUT "Filename": file$
110 INPUT "Bias Resistance": R
120 INPUT "Number of electrode pairs in use": e
130 INPUT "Would you like to enter calibration constants for the electrodes (Y/N)": QS
140 IF QS = "Y" THEN GOSUB 1000
150 FOR i = 1 TO (e + 1)
160 i$ = STRS(i)
170 num$ = RIGHTS(i$, 1)
180 name$ = "c:\data\" + file$ + "." + num$
190 OPEN name$ FOR OUTPUT AS #(i + 1)
200 PRINT #(i + 1), i - 1
210 NEXT i
230 TIMES = "00:00:00"
240 TIMER ON
260 GOSUB 400
280 DO
282 IF seconds > INT(TIMER) THEN LET days = days + 1 AND seconds = INT(TIMER)
285 IF INT(TIMER) + (days * 86400) - TIME >= t THEN GOSUB 400
290 LOOP UNTIL INKEY$ = "e"
300 TIMER OFF
310 CLS
320 END

400 CLS
410 n = 0
412 IF seconds > INT(TIMER) THEN LET days = days + 1
414 seconds = INT(TIMER)
416 TIME = INT(TIMER) + days * 86400
418 seconds$ = STR$(TIME)
420 GOSUB 600
430 PRINT #2, seconds$, mean$
435 B(0, cycles) = VAL(seconds$): B(1, cycles) = VAL(mean$)
440 FOR n = 1 TO e
450 PRINT n
460 OUT &H208, 2 ^ (n - 1): REM Activates electrode pair n
470 SLEEP 1.5
480 GOSUB 600
490 PRINT #(n + 2), mean$
495 B(n + 1, cycles) = (B(1, cycles) - VAL(mean$)) / (R * VAL(mean$))
500 NEXT n
510 OUT &H208, 0
520 GOSUB 1100
525 cycles = cycles + 1
527 IF cycles = 37 THEN LET t = 3600
530 RETURN

600 DO
640 LET sum# = 0
650 LET sumsq# = 0
660 FOR A = 1 TO 10
670 PRINT #1, CHR$(83) + CHR$(13): REM Requests current reading from DVM
680 INPUT #1, M$
690 PRINT M$
700 sum# = sum# + VAL(M$)
710 sumsq# = sumsq# + (VAL(M$))^2
720 NEXT A
730 LET mean# = sum# / 10
740 PRINT "Mean ": mean#
750 var = sumsq# / 10 - mean#^2
760 PRINT var
770 LET variance = ABS(var)
780 LET rsd = variance^.5 / mean#
790 PRINT "RSD ": rsd
800 LOOP UNTIL rsd < .015
810 meanb(n) = (FIX(100000 * mean#)) / 100000
820 mean$ = STRS(meanb(n))
830 RETURN

1000 FOR z = 1 TO 8
1010 PRINT "Calibration constant for pair", z
1020 INPUT K(z)
1030 NEXT z
1040 RETURN

1100 CLS
IF cycles = 0 THEN RETURN
XMAX = seconds + (days * 86400)
YMAX = B(2, cycles) * 1.2
SCREEN 12
LINE (200, 400)-(550, 80), , B
FOR F = 1 TO e
COLOR F + 7
LOCATE F, 1: PRINT F
FOR D = 1 TO cycles
LINE (200 + (B(0, D - 1) / XMAX) * 350, 400 - (B(F + 1, D - 1) / YMAX) * 320) -(200 + (B(0, D) / XMAX) * 350, 400 - (B(F + 1, D) / YMAX) * 320)
NEXT D
NEXT F
COLOR 15
LOCATE 6, 20
PRINT INT(YMAX * 1000000) / 100
LOCATE 26, 24
PRINT "0"
LOCATE 27, 26: PRINT "0"
LOCATE 27, 67: PRINT XMAX
LOCATE 27, 67: PRINT "0"
LOCATE 15, 2: PRINT "Conductance/S(E-04)"
LOCATE 28, 40: PRINT "Time/seconds"
RETURN
Appendix A - Program Listings

A.2 Analysis of Rectangular Cell Experiments

The LotusScript program below was used to determine the $A$ and $B$ values giving the best fit for the experiments in the rectangular cell. The best fit graphs are shown in Figures 6.10 - 6.29.

Sub sixel

```lotusscript
    <![<<C:\lotus\work\123\Wexp3model>>Window 1].Activate
    CurrentApplication.UpdateSheetDisplay = False
    Dim document1 As Document
    For n = 1 To 13
        CurrentApplication.OpenDocument
        "C:\lotus\work\13thin"+n+".123","1-2-3 Workbook (123;WK*)",False,True,True,,
        Set document1=CurrentApplication.ActiveDocument
        document1.Activate
        [real:J750..real:M803].CopyToClipboard
        <![<<C:\lotus\work\123\Wexp3model.123>>Window 1].Activate
        [real:AE750].Paste,False,PasteData + PasteStyleAndNumberFormats +
        PasteFormulas + PasteBorders + PasteDrawObjectsWithRange,,
        document1.Activate
        [real:N750..real:O803].CopyToClipboard
        <![<<C:\lotus\work\123\Wexp3model.123>>Window 1].Activate
        [real:AK750].Paste,False,PasteData + PasteStyleAndNumberFormats +
        PasteFormulas + PasteBorders + PasteDrawObjectsWithRange,,
        document1.Activate
        [real:D4].CopyToClipboard
        [Window 1].Close
        <![<<C:\lotus\work\123\Wexp3model.123>>Window 1].Activate
        [real:D4].Paste ,,,,,,
        Call script
    Next n
    For m = 2 To 9
```
CurrentApplication.OpenDocument
"C:\lotus\work\123\Id""+m+".123","1-2-3 Workbook (123;WK*)",False,True,True,
Set document1=CurrentApplication.ActiveDocument
document1.Activate
[real].TurnTo
[real:J750].Select
[real:J750..real:M803].Select
Selection.CopyToClipboard
[<<C:\lotus\work\123\Vexp3model.123>>Window 1].Activate
[real].TurnTo
[real:AE750].Select
Selection.Paste,False,PasteData + PasteStyleAndNumberFormats + PasteFormulas + PasteBorders + PastesDrawObjectsWithRange,...
[Window 1].Activate
document1.Activate
[real].SetOrigin [real:F741]
[real:N750..real:O803].Select
Selection.CopyToClipboard
[<<C:\lotus\work\123\Vexp3model.123>>Window 1].Activate
[real:AK750].Select
Selection.Paste,False,PasteData + PasteStyleAndNumberFormats + PasteFormulas + PasteBorders + PastesDrawObjectsWithRange,...
[Window 1].Activate
[real:D4].Select
Selection.CopyToClipboard
[real:D4].Select
Selection.Paste ...,...
document1.Activate
[real:D4].Select
Selection.CopyToClipboard
[Window 1].Close
[<<C:\lotus\work\123\Vexp3model.123>>Window 1].Activate
[real:D4].Select

A.6
Appendix A - Program Listings

Selection.Paste .....,

Call script

Next m

End Sub

Sub script

.WHATIFTable2 [C:B5..C:AQ36], [find:K2], [find:J2]
CurrentApplication.SearchValues = True
[C:D3].CopyToClipboard
[C:A4].Select
CurrentApplication.SearchString=Selection.Contents
found=[C:C6..AQ36].Find(1)
[C].MoveCellPointer $EndUp, 1
 .CopyToClipboard
found=[C:C6..AQ36].Find(1)
[C].MoveCellPointer $EndLeft, 1
 .CopyToClipboard
[C:D1].Paste .False, PasteData + PasteStyleAndNumberFormatters + PasteFormulas + PasteBorders + PasteDrawObjectsWithRange,....
[C:B1].CopyToClipboard
[D:M5].Paste .....,
[C:D1].CopyToClipboard
[D:B16].Paste .....,
.WHATIFTable2 [D:B5..D:W26], [find:K2], [find:J2]
[D:D3].CopyToClipboard
[D:A4].Select
CurrentApplication.SearchString=Selection.Contents

A.7
Appendix A - Program Listings

found=[D:C6..W26].Find(1)

[D].MoveCellPointer $EndUp, 1
.CopyToClipboard

[D:B1].Paste ,False,PasteData + PasteStyleAndNumberFormats + PasteFormulas + PasteBorders + PastesDrawObjectsWithRange,...

found=[D:C6..W26].Find(1)

[D].MoveCellPointer $EndLeft, 1
.CopyToClipboard

[D:D1].Paste ,False,PasteData + PasteStyleAndNumberFormats + PasteFormulas + PasteBorders + PastesDrawObjectsWithRange,...

[D:B1].CopyToClipboard

[D:B27].Select

[D].MoveCellPointer $EndDown, 1

[D].MoveCellPointer $Down, 1
Selection.Paste,,,,

[D:D1].CopyToClipboard

[D:C27].Select

[D].MoveCellPointer $EndDown, 1

[D].MoveCellPointer $Down, 1
Selection.Paste,,,,

[D:A4].CopyToClipboard

[D:D27].Select

[D].MoveCellPointer $EndDown, 1

[D].MoveCellPointer $Down, 1
Selection.Paste ,False,PasteData + PasteStyleAndNumberFormats + PasteFormulas + PasteBorders + PastesDrawObjectsWithRange,...

Call savegraph

End Sub

Sub savegraph

[D:B1].CopyToClipboard

[findif.J2].Paste,,,,

[D:D1].CopyToClipboard
Appendix A - Program Listings

[findif:K2].Paste ......
[Chart 2].CopyToClipboard
[E].TurnTo
.Paste $PictureFormat,False,.....
[E].MoveCellPointer $Down, 25

End Sub
A.3 Analysis of Cylindrical Cell Experiments

Below is the LotusScript program used to generate the graphs for the 910 micron bead experiments (Figs 6.41 - 6.48) in the cylindrical cell in Lotus 1-2-3 97. First experimental data is imported from a Quattro Pro spreadsheet before running the simulation for the correct concentration and flow rate, the comparison between the predicted and actual results are displayed on a graph which had already been set up on the spreadsheet, the file is then saved. A new set of data is then imported and the whole procedure repeated. A similar program was used for modelling the experiments with 510 micron beads (Figs 6.34 - 6.40). The equations used are described in Chapter 5.

'cylfit910e_1

Sub main
    CurrentApplication.UpdateSheetDisplay = False
    Dim thisdoc As Document
    Dim document1 As Document
    For f = 1 To 8
        Set thisdoc = CurrentApplication.ActiveDocument
        CurrentApplication.OpenDocument "C:\Work\910_" + f + ".wb", "Quattro Pro (WQ1;WB1;WB2)", False, True, True,
        Set document1 = CurrentApplication.ActiveDocument
        [real].TurnTo
        [real:B750..real:Q803].Select
        Selection.CopyToClipboard
        thisdoc.Activate
        [A:B103].Select
        Selection.Paste,True,PasteData + PasteStyleAndNumberFormats + PasteFormulas + PasteBorders + PasteDrawObjectsWithRange,..
        document1.Activate
        [real:D4].Select
        Selection.CopyToClipboard
        thisdoc.Activate

A.10
Appendix A - Program Listings

document1.Activate
[real:N4].CopyToClipboard
thisdoc.Activate

document1.Activate
[real:D2].CopyToClipboard
thisdoc.Activate

[A:T1].Paste ,,,
document1.Close
thisdoc.Activate

[A:p1].Select
bedconc=Val(Selection.Contents)
[A].MoveCellPointer SRight,2
surfconc=bedconc+Val(Selection.Contents)
[A].MoveCellPointer SRight,2
volflow=Val(Selection.Contents)
diametermm=0.91  
'Particle diameter in mm
length=6
diffco=2.26E-05
deltahours=0.25
deltat=.00001  
'Time increment
xcells=CInt(60/diametermm)  
'Number of elements in vertical direction
ycells=CInt((22-(0.5*diametermm))/diametermm)  
'Number of elements in horizontal direction
conv=(8.7*(12*volflow)/(Pi*0.31))  
'Maximum value of dimensionless convective velocity
skip = CInt((deltahours*diffco*3600/length^2)/deltat)  
'Data is inserted into spreadsheet every 'skip' cycles

count=0

Dim A() As Single
Redim A(ycells, xcells, 1)

For n = 0 To ycells
    A(n, 0, 0) = 1
    A(n, 0, 1) = 1
    'Sets concentration at surface
Next n

hours% = 24

cycles% = CInt((hours% * diffco * 3600 / length^2) / deltat)

Current.Application.UpdateSheetDisplay = True

[A:B5].Select
Selection.Contents = "0"

[A].MoveCellPointer $Right, 1
Selection.Contents = bedconc

[A].MoveCellPointer $Right, 1
Selection.Contents = bedconc

[A].MoveCellPointer $Right, 1
Selection.Contents = bedconc

[A].MoveCellPointer $Right, 1
Selection.Contents = bedconc

[A].MoveCellPointer $Down, 1

[A].MoveCellPointer $Left, 6

For t = 1 To cycles%
    vold = (8.7 * (12 * volflow) / (Pi * 0.31))

    For z = 1 To xcells - 1
        v = (8.7 * (12 * volflow) / (Pi * 0.31)) * Exp((-1.91 - 0.108 * (12 * volflow) / (Pi * 0.31)) * (z) / xcells)

        A(0, z, 1) = A(0, z, 0) + (deltat / (1 / xcells)) * 2 * (A(0, z - 1, 0) - 2 * A(0, z, 0) + A(0, z + 1, 0)) + (deltat / (1 / xcells)) * (vold * A(0, z - 1, 0) - v * A(0, z, 0))

        If A(0, z, 1) > A(0, z - 1, 0) Then A(0, z, 1) = A(0, z - 1, 0)

    vold = v
Next $y$

$vold = 8.7*(12*volflow*(ycells+0.5))/(Pi*2.2*ycells)$

For $z = 1$ To xcells-1

If $A(ycells,z,1)>A(ycells,z-1,0)$ Then $A(ycells,z,1)=A(ycells,z-1,0)$

$vold = v$

Next $z$

$A(ycells,xcells,1)=A(ycells,xcells,0)+(deltat/(1/xcells)^2)*(A(ycells,xcells-1,0) -2*A(ycells,xcells,0)+A(ycells,xcells+1,0))/(xcells^2)+(deltat/(1/xcells)) *(vold*A(ycells,xcells,z-1,0)-v*A(ycells,xcells,z,0))$
Appendix A - Program Listings

\[
\begin{align*}
&\left(1/\text{xcells}\right)^2 \times \left(1/\text{ycells}\right) \times \left(\text{A(ycells, xcells, 0) - A(ycells-1, xcells, 0)}\right)/(2/\text{xcells}) + \left(\text{deltat}/(1/\text{xcells})\right) \times \left(\text{vold} \times \text{A(ycells, xcells - 1, 0)}\right) \\
&\text{If } \text{A(ycells, xcells, 1)} > \text{A(ycells, xcells-1, 0)} \text{ Then } \text{A(ycells, xcells, 1)} = \text{A(ycells, xcells-1, 0)}
\end{align*}
\]

\[
\text{vold} = 8.7 \times (12 \times \text{volflow})/(\Pi \times 0.31)
\]

For \(b = 0\) To \text{ycells}

For \(c = 1\) To \text{xcells}

\(\text{A(b, c, 0)} = \text{A(b, c, 1)}\)

Next \(c\)

Next \(b\)

\(\text{elapsed} = \text{t} \times \text{deltat}\)

I'm total time elapsed in model

\(\text{count} = \text{count} + 1\)

If \(\text{count} < \text{skip}\) And \(\text{t} < \text{cycles}%\) Then Go To Shortcut

Selection.Contents = elapsed*length^2/(diffco *3600)

[A].MoveCellPointer $Right, 1

For \(x = 0\) To \text{Int(17*ycells/22)}

\(\text{Sum} = \text{Sum} + 1/(\text{bedconc} + (\text{surfconr} - \text{bedconc}) \times \text{A(x, Int(xcells/12), 1)})\)

Next \(x\)

\(\text{avg} = (\text{Int(17*ycells/22)} + 1)/\text{Sum}\)

Selection.Contents = \(\text{avg}\)

\(\text{Sum} = 0\)

For \(x = 0\) To \text{Int(17*ycells/22)}

\(\text{Sum} = \text{Sum} + 1/(\text{bedconc} + (\text{surfconr} - \text{bedconc}) \times \text{A(x, Int(xcells/6), 1)})\)

Next \(x\)

\(\text{avg} = (\text{Int(17*ycells/22)} + 1)/\text{Sum}\)

[A].MoveCellPointer $Right, 1

Selection.Contents = \(\text{avg}\)

\(\text{Sum} = 0\)

For \(x = 0\) To \text{Int(17*ycells/22)}

\(\text{Sum} = \text{Sum} + 1/(\text{bedconc} + (\text{surfconr} - \text{bedconc}) \times \text{A(x, Int(xcells/3), 1)})\)

Next \(x\)

\(\text{avg} = (\text{Int(17*ycells/22)} + 1)/\text{Sum}\)

[A].MoveCellPointer $Right, 1
Selection.Contents=avg

Sum = 0

For x = 0 To Int(17*ycells/22)
    Sum = Sum + 1/(bedconc+(surfconc-bedconc)*A(x,Int(xcells/2),1))
Next x

avg=(Int(17*ycells/22)+1)/Sum

[A].MoveCellPointer $Right,1

Selection.Contents=avg

Sum = 0

For x = 0 To Int(17*ycells/22)
    Sum = Sum + 1/(bedconc+(surfconc-bedconc)*A(x,Int(2*xcells/3),1))
Next x

avg=(Int(17*ycells/22)+1)/Sum

[A].MoveCellPointer $Right,1

Selection.Contents=avg

Sum = 0

For x = 0 To Int(17*ycells/22)
    Sum = Sum + 1/(bedconc+(surfconc-bedconc)*A(x,Int(5*xcells/6),1))
Next x

avg=(Int(17*ycells/22)+1)/Sum

[A].MoveCellPointer $Right,1

Selection.Contents=avg

Sum = 0

Avg = 0

[A].MoveCellPointer $Down,1

[A].MoveCellPointer $Left,6

count = 0

Shortcut:

Next t

[A:b1].Select

c=cycles%

Selection.Contents = c
[A:d1].Select
Selection.Contents = (1/xcells)
[A].MoveCellPointer $Right,2
Selection.Contents = (1/ycells)
[A].MoveCellPointer $Right,2
Selection.Contents = ycells
[A].MoveCellPointer $Right,2
Selection.Contents = xcells
[A].MoveCellPointer $Right,2
Selection.Contents = conv/ycells
[A].MoveCellPointer $Right,2
Selection.Contents = v

thisdoc.SaveAs "C:\lotus\work\123\cylft910d_"+f+".123","1-2-3 (123)",False,"",True
Next f

End Sub
A.4 Program for Ray-Tracing sphere packings

This program writes a Ray-Tracing file using Equations 5.4 - 5.6 to position an array of spheres. The angle defining the unit cell may be varied by altering the value for theta in the first line of the program. The array of spheres can be sliced along any plane in this case the X=0 plane has been used. Pov-Ray 1.0 was then used to render the image from the '.pov' file.

\[ \text{Theta} = 70 \times 3.14159 / 180 \]

CLS
\[ A = 1 \]
\[ B = 1 \]
\[ C = 1 \]

INPUT "FILENAME"; file$
OPEN "c:\povray\" + file$ + "pov" FOR OUTPUT AS #1
PRINT #1, "camera {"
PRINT #1, " location <0 0 -9>"
PRINT #1, " look_at <0 0 0>"
PRINT #1, "}"
PRINT #1, "object {"
PRINT #1, "intersection {"
PRINT #1, "plane {<1 0 0>}: REM Slice along x=0 plane"
PRINT #1, " union{"
FOR \[ A = -3 \text{ TO 4 STEP 2} \]
FOR \[ B = -4 \text{ TO 4} \]
FOR \[ C = -4 \text{ TO 4} \]
PRINT A, B, C
PRINT #1, "sphere{<", A * COS(\text{Theta}/2), "", (2 * B + 1) * SIN(\text{Theta}/2) + (C * (1 - (1 - 3 * (COS(\text{Theta}))^2 + 2 * (COS(\text{Theta}))^3) / (1 - (COS(\text{Theta}))^2))^1.5))", C * ((1 - 3 * (COS(\text{Theta}))^2 + 2 * (COS(\text{Theta}))^3) / (1 - (COS(\text{Theta}))^2))^1.5, "> .5}"
NEXT C
NEXT B
NEXT A
FOR A = -4 TO 4 STEP 2
FOR B = -4 TO 4
FOR C = -4 TO 4
PRINT A, B, C
PRINT #1, "sphere {<", A * COS(Theta / 2), "", ((2 * B) * SIN(Theta / 2) + (C * (1 - (1 - 3 * (COS(Theta)) ^ 2 + 2 * (COS(Theta)) ^ 3) / (1 - (COS(Theta)) ^ 2)) ^ .5))", "", C * ((1 - 3 * (COS(Theta)) ^ 2 + 2 * (COS(Theta)) ^ 3) / (1 - (COS(Theta)) ^ 2)) ^ .5, ">", "}"
NEXT C
NEXT B
NEXT A
PRINT #1, "rotate <0 0 0>"
PRINT #1, "}"
PRINT #1, "}"
PRINT #1, "texture { color red 1 phong 1 }"
PRINT #1, "}"
PRINT #1, "object{"
PRINT #1, " light_source { <3 3 -10> color red 1 green 1 blue 1 }"
PRINT #1, "}"
A.5 Ray-Tracing file for Figure 1.1

#include "colors.inc"
#include "textures.inc"
#include "shapes.inc"
camera {
  location <0 95 360>
  sky <1 0 0>
  look_at <0 95 0>
}
object {
  intersection{
    quadric { Cylinder_Y scale <8 8 8>}
    plane {<0 1 0> 155}
    plane {<0 1 0> 0 inverse}
  }
  texture { color red 0.5 green 0.5 blue 0.5 phong 0.2 ambient 0.25}
  translate<0 0 0>
}
object {
  intersection{
    quadric { Cylinder_Y scale <6 6 6>}
    plane {<0 1 0> 35}
    plane {<0 1 0> 0 inverse}
  }
  texture { color red 0.5 green 0.5 blue 0.5 phong 0.2 ambient 0.25}
  translate<0 155 0>
}
object {
  intersection{
    quadric { Cylinder_Y scale <25 25 25>}
    plane {<0 1 0> 5}
    plane {<0 1 0> 0 inverse}
  }
  texture { color red 0.5 green 0.5 blue 0.5 phong 0.2 ambient 0.25}
  translate<0 10 0>
}
object {
  intersection{
    quadric { Cylinder_Y scale <6 6 6>}
    plane {<0 1 0> 1.7}
    plane {<0 1 0> 0 inverse}
  }
  texture { color red 1 green 1 blue 1 phong 0 ambient 0.25}
  translate<0 173 0>
}
intersection{
    quadric { Cylinder_Y scale <6 6 6>}
    plane {<0 1 0> 1.7}
    plane {<0 1 0> 0 inverse}
}
texture { color red 1 green 1 blue 1 phong 0 ambient 0.25}
translate<0 170.3 0>
}
object {
    intersection{
        quadric { Cylinder_Y scale <1.5 1.5 1.5>}
        plane {<0 1 0> 3}
        plane {<0 1 0> 0 inverse}
    }
texture { color red 0 green 0 blue 0}
    rotate <0 0 90>
    translate<11 145 0>
}
object {
    intersection{
        quadric { Cylinder_Y scale <1.5 1.5 1.5>}
        plane {<0 1 0> 3}
        plane {<0 1 0> 0 inverse}
    }
texture { color red 0 green 0 blue 0}
    rotate <0 0 90>
    translate<-8 145 0>
}
object{
    intersection{
        quadric { Cone_Y scale <0.8 1 1>}
        plane {<0 1 0> 0}
        plane {<0 1 0> -7.5 inverse}
    }
texture {color red 0.5 green 0.5 blue 0.5}
    translate <0 197.5 0>
}
object{
    intersection{
        quadric { Cone_Y scale <1 1.5 1>}
        plane {<0 1 0> 0}
        plane {<0 1 0> -2 inverse}
    }
    rotate <0 0 90>
    translate<-13 145 0>
    texture {Silver_Metal}
}
object{
intersection{
  quadric {Cone_Y scale <1 1.5 1>}
  plane [<0 1 0> 0]
  plane [<0 1 0> -2 inverse]
}
rotate <0 0 -90>
translate<13 145 0>
texture {Silver_Metal }
}
object {
  intersection{
    quadric {Cylinder_Y scale <8 8 8>}
    plane [<0 1 0> 190]
    plane [<0 1 0> 0 inverse]
  }
texture {color red 0.5 green 0.5 blue 0.5 phong 0.2 ambient 0.25}
  translate<-60 0 0>
}
object {
  intersection{
    quadric {Cylinder_Y scale <25 25 25>}
    plane [<0 1 0> 5]
    plane [<0 1 0> 0 inverse]
  }
texture {color red 0.5 green 0.5 blue 0.5 phong 0.2 ambient 0.25}
  translate<-60 10 0>
}
object {
  intersection{
    quadric {Cylinder_Y scale <8 8 8>}
    plane [<0 1 0> 1.7]
    plane [<0 1 0> 0 inverse]
  }
texture {color red 1 green 1 blue 1 phong 0 ambient 0.25}
  translate<-60 173 0>
}
object {
  intersection{
    quadric {Cylinder_Y scale <8 8 8>}
    plane [<0 1 0> 1.7]
    plane [<0 1 0> 0 inverse]
  }
texture {color red 1 green 1 blue 1 phong 0 ambient 0.25}
  translate<-60 170.3 0>
}
object {
  intersection{
    quadric {Cylinder_Y scale <1.5 1.5 1.5>}

A.21
plane {<0 1 0> 3}
plane {<0 1 0> 0 inverse}
}
texture { color red 0 green 0 blue 0 }
rotate <0 0 90>
translate<-49 145 0>
}
object {
  intersection{
    quadric { Cylinder_Y scale <1.5 1.5 1.5>}
    plane {<0 1 0> 3}
    plane {<0 1 0> 0 inverse}
  }
texture { color red 0 green 0 blue 0 }
rotate <0 0 90>
translate<-68 145 0>
}
object{
  intersection{
    quadric {Cone_Y scale <0.8 1 1>}
    plane {<0 1 0> 0}
    plane {<0 1 0> -10 inverse}
  }
texture {color red 0.5 green 0.5 blue 0.5}
translate <60 200 0>
}
object{
  intersection{
    quadric {Cone_Y scale <1 1 1>}
    plane {<0 1 0> 0}
    plane {<0 1 0> -2 inverse}
  }
  rotate <0 0 90>
  translate<-73 145 0>
  texture {Silver_Metal }
}
object{
  intersection{
    quadric {Cone_Y scale <1 1 1>}
    plane {<0 1 0> 0}
    plane {<0 1 0> -2 inverse}
  }
  rotate <0 0 -90>
  translate<-47 145 0>
  texture {Silver_Metal }
}
object {
  intersection{
  }


quadric \{ \text{Cylinder}\_Y \text{scale} \langle 8 \ 8 \ 8 \rangle \} 
\text{plane} \{\langle 0 \ 1 \ 0 \rangle \ 155\} 
\text{plane} \{\langle 0 \ 1 \ 0 \rangle \ \text{inverse}\} 
\}
\text{texture} \{\text{color red} \ 0.5 \ \text{green} \ 0.5 \ \text{blue} \ 0.5 \ \text{phong} \ 0.2 \ \text{ambient} \ 0.25\}
\text{translate}\langle 60 \ 0 \ 0 \rangle
\}
\text{object} \{
\}
\text{intersection}\
\quad \text{quadric} \{\text{Cylinder}\_Y \text{scale} \langle 4 \ 4 \ 4 \rangle \} 
\quad \text{plane} \{\langle 0 \ 1 \ 0 \rangle \ 35\} 
\quad \text{plane} \{\langle 0 \ 1 \ 0 \rangle \ \text{inverse}\} 
\}
\quad \text{texture} \{\text{color red} \ 0.5 \ \text{green} \ 0.5 \ \text{blue} \ 0.5 \ \text{phong} \ 0.2 \ \text{ambient} \ 0.25\}
\quad \text{translate}\langle 60 \ 155 \ 0 \rangle
\}
\text{object} \{
\}
\text{intersection}\
\quad \text{quadric} \{\text{Cylinder}\_Y \text{scale} \langle 25 \ 25 \ 25 \rangle \} 
\quad \text{plane} \{\langle 0 \ 1 \ 0 \rangle \ 5\} 
\quad \text{plane} \{\langle 0 \ 1 \ 0 \rangle \ \text{inverse}\} 
\}
\quad \text{texture} \{\text{color red} \ 0.5 \ \text{green} \ 0.5 \ \text{blue} \ 0.5 \ \text{phong} \ 0.2 \ \text{ambient} \ 0.25\}
\quad \text{translate}\langle 60 \ 10 \ 0 \rangle
\}
\text{object} \{
\}
\text{intersection}\
\quad \text{quadric} \{\text{Cylinder}\_Y \text{scale} \langle 4 \ 4 \ 4 \rangle \} 
\quad \text{plane} \{\langle 0 \ 1 \ 0 \rangle \ 1.7\} 
\quad \text{plane} \{\langle 0 \ 1 \ 0 \rangle \ \text{inverse}\} 
\}
\quad \text{texture} \{\text{color red} \ 1 \ \text{green} \ 1 \ \text{blue} \ 1 \ \text{phong} \ 0 \ \text{ambient} \ 0.25\}
\quad \text{translate}\langle 60 \ 173 \ 0 \rangle
\}
\text{object} \{
\}
\text{intersection}\
\quad \text{quadric} \{\text{Cylinder}\_Y \text{scale} \langle 4 \ 4 \ 4 \rangle \} 
\quad \text{plane} \{\langle 0 \ 1 \ 0 \rangle \ 1.7\} 
\quad \text{plane} \{\langle 0 \ 1 \ 0 \rangle \ \text{inverse}\} 
\}
\quad \text{texture} \{\text{color red} \ 1 \ \text{green} \ 1 \ \text{blue} \ 1 \ \text{phong} \ 0 \ \text{ambient} \ 0.25\}
\quad \text{translate}\langle 60 \ 170.3 \ 0 \rangle
\}
\text{object} \{
\}
\text{intersection}\
\quad \text{quadric} \{\text{Cylinder}\_Y \text{scale} \langle 1.5 \ 1.5 \ 1.5 \rangle \} 
\quad \text{plane} \{\langle 0 \ 1 \ 0 \rangle \ 3\} 
\quad \text{plane} \{\langle 0 \ 1 \ 0 \rangle \ \text{inverse}\}
}  
texture { color red 0 green 0 blue 0 }  
rotate <0 0 90>  
translate<71 145 0>  
}  
object {  
intersection{  
quadric { Cylinder_Y scale <1.5 1.5 1.5> }  
plane {<0 1 0> 3}  
plane {<0 1 0> 0 inverse}  
}  
texture { color red 0 green 0 blue 0 }  
rotate <0 0 90>  
translate<52 145 0>  
}  
object{  
intersection{  
quadric {Cone_Y scale <0.8 1 1>}  
plane {<0 1 0> 0}  
plane {<0 1 0> -5 inverse}  
}  
texture { color red 0.5 green 0.5 blue 0.5}  
translate <60 195 0>  
}  
object{  
intersection{  
quadric {Cone_Y scale <1 1.5 1>}  
plane {<0 1 0> 0}  
plane {<0 1 0> -2 inverse}  
}  
rotate <0 0 90>  
translate<47 145 0>  
texture {Silver_Metal}  
}  
object{  
intersection{  
quadric {Cone_Y scale <1 1.5 1>}  
plane {<0 1 0> 0}  
plane {<0 1 0> -2 inverse}  
}  
rotate <0 0 -90>  
translate<73 145 0>  
texture {Silver_Metal}  
}  
object {  
plane{<0 0 1> -100}  
texture {color White}  
}
object {
    light_source { <0 150 360> color red 1 green 1 blue 1
    spotlight
    point_at <0 90 0>
    radius 90
    falloff 45
    tightness 10
    }
}
Appendix B
Calibrations

B.1 Rotameter
The rotameter used to measure the flow rates for the cell experiments was calibrated by measuring the time taken for a fixed volume of water to flow into a measuring cylinder at various rotameter readings, the results are shown below.

*Table B.1 Rotameter calibration*

<table>
<thead>
<tr>
<th>Flow, ml s⁻¹</th>
<th>Rotameter reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>0.5</td>
</tr>
<tr>
<td>0.37</td>
<td>2</td>
</tr>
<tr>
<td>0.68</td>
<td>3.4</td>
</tr>
<tr>
<td>1.03</td>
<td>4.8</td>
</tr>
<tr>
<td>1.53</td>
<td>7</td>
</tr>
<tr>
<td>2.07</td>
<td>9.4</td>
</tr>
</tbody>
</table>

*Fig. B.1 Graph of rotameter reading against flow rate.*
Appendix B - Calibrations

B.2 Cylindrical Cell calibration
The electrode pairs in the cells were calibrated against HCl concentration using six solutions of HCl in the range 0 - 0.02 mol l⁻¹ which had been standardised using a sodium hydroxide standard. Results for the cylindrical cell are shown below. For the analysis of the experimental data the important points are that the response for each electrode is linear and does not change during the running of a single experiment.

**Table B.2 Table of values for measured conductance between electrodes divided by HCl concentration, mol l⁻¹.**

<table>
<thead>
<tr>
<th>Date</th>
<th>Electrode Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/12/96</td>
<td>1</td>
<td>0.1043</td>
<td>0.0994</td>
<td>0.1370</td>
<td>0.1260</td>
<td>0.1459</td>
<td>0.1318</td>
<td>0.1212</td>
<td>0.1359</td>
</tr>
<tr>
<td>20/12/96</td>
<td>2</td>
<td>0.0863</td>
<td>0.0764</td>
<td>0.1026</td>
<td>0.1016</td>
<td>0.1106</td>
<td>0.0988</td>
<td>0.1161</td>
<td></td>
</tr>
<tr>
<td>7/1/97</td>
<td>3</td>
<td>0.0988</td>
<td>0.0951</td>
<td>0.1192</td>
<td>0.1148</td>
<td>0.1336</td>
<td>0.1211</td>
<td>0.1124</td>
<td>0.1254</td>
</tr>
<tr>
<td>10/1/97</td>
<td>4</td>
<td>0.1020</td>
<td>0.1020</td>
<td>0.1286</td>
<td>0.1239</td>
<td>0.1467</td>
<td>0.1298</td>
<td>0.1229</td>
<td>0.1337</td>
</tr>
<tr>
<td>13/1/97</td>
<td>5</td>
<td>0.1057</td>
<td>0.1036</td>
<td>0.1328</td>
<td>0.1267</td>
<td>0.1505</td>
<td>0.1328</td>
<td>0.1257</td>
<td>0.1371</td>
</tr>
<tr>
<td>24/1/97</td>
<td>6</td>
<td>0.1116</td>
<td>0.1057</td>
<td>0.1400</td>
<td>0.1296</td>
<td>0.1521</td>
<td>0.1374</td>
<td>0.1296</td>
<td>0.1393</td>
</tr>
<tr>
<td>31/1/97</td>
<td>7</td>
<td>0.1111</td>
<td>0.1081</td>
<td>0.1390</td>
<td>0.1317</td>
<td>0.1535</td>
<td>0.1381</td>
<td>0.1305</td>
<td>0.1412</td>
</tr>
<tr>
<td>7/2/97</td>
<td>8</td>
<td>0.1128</td>
<td>0.1056</td>
<td>0.1406</td>
<td>0.1326</td>
<td>0.1554</td>
<td>0.1394</td>
<td>0.1328</td>
<td>0.1437</td>
</tr>
<tr>
<td>14/2/97</td>
<td>9</td>
<td>0.1151</td>
<td>0.1084</td>
<td>0.1433</td>
<td>0.1336</td>
<td>0.1551</td>
<td>0.1388</td>
<td>0.1323</td>
<td>0.1430</td>
</tr>
<tr>
<td>17/2/97</td>
<td>10</td>
<td>0.1115</td>
<td>0.1101</td>
<td>0.1441</td>
<td>0.1334</td>
<td>0.1555</td>
<td>0.1389</td>
<td>0.1322</td>
<td>0.1430</td>
</tr>
<tr>
<td>20/2/97</td>
<td>11</td>
<td>0.1133</td>
<td>0.1095</td>
<td>0.1440</td>
<td>0.1336</td>
<td>0.1559</td>
<td>0.1389</td>
<td>0.1313</td>
<td>0.1427</td>
</tr>
<tr>
<td>26/2/97</td>
<td>12</td>
<td>0.1156</td>
<td>0.1094</td>
<td>0.1425</td>
<td>0.1314</td>
<td>0.1506</td>
<td>0.1370</td>
<td>0.1304</td>
<td>0.1420</td>
</tr>
<tr>
<td>20/3/97</td>
<td>13</td>
<td>0.1191</td>
<td>0.1128</td>
<td>0.1461</td>
<td>0.1363</td>
<td>0.1594</td>
<td>0.1403</td>
<td>0.1350</td>
<td>0.1447</td>
</tr>
<tr>
<td>11/4/97</td>
<td>14</td>
<td>0.1148</td>
<td>0.1124</td>
<td>0.1460</td>
<td>0.1363</td>
<td>0.1600</td>
<td>0.1398</td>
<td>0.1344</td>
<td>0.1434</td>
</tr>
<tr>
<td>5/6/97</td>
<td>15</td>
<td>0.1137</td>
<td>0.1161</td>
<td>0.1496</td>
<td>0.1400</td>
<td>0.1648</td>
<td>0.1443</td>
<td>0.1389</td>
<td>0.1495</td>
</tr>
</tbody>
</table>
### Table B.3 $R$ squared values corresponding with table B.2 above.

<table>
<thead>
<tr>
<th>Electrode Number</th>
<th>Date</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3/12/96</td>
<td>0.9993</td>
<td>0.9993</td>
<td>0.9989</td>
<td>0.9997</td>
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<td>0.9996</td>
<td>0.9993</td>
<td>0.9996</td>
</tr>
<tr>
<td></td>
<td>20/12/96</td>
<td>0.9913</td>
<td>0.9906</td>
<td>0.9917</td>
<td>0.9928</td>
<td>0.9953</td>
<td>0.9924</td>
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<td>0.9962</td>
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<tr>
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<td>0.9977</td>
<td>0.9981</td>
<td>0.9978</td>
<td>0.9984</td>
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<tr>
<td></td>
<td>10/1/97</td>
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<td>0.9985</td>
<td>0.9983</td>
<td>0.9988</td>
<td>0.9989</td>
<td>0.9988</td>
<td>0.9987</td>
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</tr>
<tr>
<td></td>
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<td>0.9979</td>
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<td>0.9987</td>
<td>0.9993</td>
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<td>0.9990</td>
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<td>0.9985</td>
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<td>0.9989</td>
<td>0.9990</td>
<td>0.9993</td>
<td>0.9989</td>
<td>0.9992</td>
</tr>
<tr>
<td></td>
<td>31/1/97</td>
<td>0.9983</td>
<td>0.9991</td>
<td>0.9992</td>
<td>0.9992</td>
<td>0.9993</td>
<td>0.9994</td>
<td>0.9991</td>
<td>0.9994</td>
</tr>
<tr>
<td></td>
<td>7/2/97</td>
<td>0.9984</td>
<td>0.9984</td>
<td>0.9992</td>
<td>0.9995</td>
<td>0.9996</td>
<td>0.9997</td>
<td>0.9995</td>
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</tr>
<tr>
<td></td>
<td>14/2/97</td>
<td>0.9989</td>
<td>0.9987</td>
<td>0.9997</td>
<td>0.9994</td>
<td>0.9994</td>
<td>0.9994</td>
<td>0.9992</td>
<td>0.9995</td>
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<tr>
<td></td>
<td>17/2/97</td>
<td>0.9981</td>
<td>0.9995</td>
<td>0.9998</td>
<td>0.9997</td>
<td>0.9997</td>
<td>0.9997</td>
<td>0.9996</td>
<td>0.9998</td>
</tr>
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### Table B.4 Table of values of measured conductance between electrodes divided by conductivity meter reading. (The two extra calibrations not in the tables above used different HCl solutions which had not all been standardised.)

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<th>6</th>
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<td>0.3329</td>
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B.3
## Appendix B - Calibrations

### Table B.5
*R squared values corresponding with table B.4 above.*

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### Table B.6
*Raw data from calibration with ballotini in cell*

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<th>Conductivity meter</th>
<th>Electrode Number</th>
</tr>
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<tbody>
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</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
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<td>0.108</td>
</tr>
<tr>
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B.4
Appendix B - Calibrations

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B.3 Rectangular cell
After an initial calibration the performance of the electrodes in the rectangular cell was monitored by checking the initial values for the resistance between each electrode pair. For the calibration 4 solutions were used.

Table B.7 Results of initial calibration of rectangular cell, constants are ratio of conductance between electrodes to HCl concentration.

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Table B.8 Showing the initial conductance for each electrode pair divided by the conductivity meter reading for the pore solution for each experiment.

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</tr>
<tr>
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B.5
### Appendix B - Calibrations

<table>
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<th>Expt. No.</th>
<th>Electrode number</th>
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<th>4</th>
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<tr>
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<td>0.117</td>
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</tr>
<tr>
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Appendix C

Particle Sizing

This appendix has a page for each particle size, in order of decreasing size, with a photograph and size distribution data given as the number percentage of particles under each size. At the end of the appendix are the printouts from the Mastersizer. For a photograph of the 910 micron ballotini see Fig. 4.13

Table C.1 910 micron particle size distributions

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Fig. C.1 510 micron particles

Table C.2 510 micron particles size distributions.

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Appendix C - Particle sizing

Fig. C.2 240 micron particles

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**Fig. C.3** 130 micron particles.

**Table C.4 130 Image**

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**Fig. C.4** Less than 75 micron particles.

**Table C.5** Under 75, image

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Analysis Date: 22 Sep 98 14:22  

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UK  
44 (0)1684-892456 Fax: 44 (0)1684-892789
06RF mm Beam: 2.40 mm Sampler: MS1
Ion: 3QAD Analysis: Polydisperse Residual: 0.206 %
ions: None

0.5693 %Vol Density = 2.606 g/cm³ S.S.A. = 0.0091 m²/g
on: Volume D(4, 3) = 274.50 um D(0, 2) = 252.69 um
+ 217.57 um D(0.5) = 271.48 um D(0.5) = 338.92 um
(396E-01 Uniformity = 1.441E-01

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Appendix D

Published Work

1. Diffusion and convection of ions in porous media

D.J. Richardson and R.G. Holdich

This paper was presented as a Poster at the 1998 IChemE Research Event in Newcastle-upon-Tyne and has been imported into this document from the original computer file. The conference proceedings were published on CD-ROM.

2. A Comparison of electrode design for dispersion monitoring using conductivity

R.G. Holdich and D.J. Richardson

This paper was a poster presentation at the 1997 IChemE Jubilee Research Event at Nottingham and is reproduced here from the conference proceedings.
Diffusion and convection of ions in porous media

D.J. Richardson and R.G. Holdich
Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK.

Dispersion experiments have been carried out using an HCl tracer solution flowing across the surface of packed beds of ballotini which have similar porosities but varying particle diameters in the range 0.1 to 1 mm at velocities of up to 0.023 m s\(^{-1}\). The results have been compared with a finite difference model based on Fick’s Laws of diffusion with an added ‘Convective Velocity’ term. At low flow rates the results agree well with a purely diffusive model and for higher flow rates the ‘Convective Velocity’ varies with both flow rate and size of particles and can be correlated with particle Peclet Number.

Key Words: Diffusion, convection, dispersion, porous media, Peclet Number.

INTRODUCTION
A good understanding of the transport of contaminants through saturated, or partially saturated, porous media is important in several areas for example the transport of pollutants in the ground or the migration of chloride through concrete. These pollutants may often be ionic such as salts of heavy metals or other inorganic chemicals. A particularly important case is the confinement of radioactive waste. The aim of this work is to investigate the effect of the structure of a porous medium on the rate of diffusive and convective transport through it.

EXPERIMENTAL
Diffusion experiments were carried out using three different sizes of ballotini and a variety of flow rates in the rig shown in Figure 1. At the outset of each experiment the concentration of HCl in the feed tank was approximately twice that in the cell. Flow was produced by a constant head tank, the flow across the surface of the bed was radial from the circumference towards the centre, this was achieved using a weir around the circumference of the cell to distribute the flow. The concentration of HCl at different heights in the bed could be monitored by voltage measurements since electrolyte concentration is inversely proportional to resistance as described in more detail previously\(^1\).

\[\text{Figure 1: Flow diagram and dimensions of cell}\]

D.2
PROCEDURE

HCl was added to a slurry of ballotini in distilled water with stirring until the desired concentration, as measured with a conductivity probe, was reached. Most of the excess liquid was transferred to a measuring cylinder and the ballotini poured into the cell, after tapping the cell further ballotini was added until the cell was full with a smooth surface. The lid was then bolted on to the cell and the space above the bed filled with liquid from the measuring cylinder by pouring slowly through the inlet tube. The cell was transferred to a constant temperature box at 25°C and the outlet and inlet sealed by connecting the tubes to the feed tank and the rotameter with the valves closed to prevent any flow. After leaving for several hours to ensure that the contents of the cell were at thermal equilibrium with their surroundings, the experiment was started by fully opening the valve between the feed tank and the cell, opening the valve between the cell and the rotameter sufficient to give the required flow rate and turning the pump on.

The experiment was then run for 24 hours, occasionally the valve was adjusted slightly to maintain a steady flow rate. The concentration at different heights in the bed was recorded and data-logged every ten minutes for the first 6 hours and subsequently every hour. Periodically, between experiments the cell was calibrated using HCl of varying concentrations to check the response of the electrodes. The response of the electrodes did not vary significantly with time.

The ballotini used had a high degree of sphericity and three separate narrow size distributions were used (see Figure 2). The porosity of beds of each of the three sizes of ballotini was found to be the same at 0.38 ± 0.01.

![Figure 2: (a) Size distributions for ballotini used, the mean diameters are 0.13, 0.51 and 0.91 mm. The largest sized ballotini was measured by vernier callipers and the other two sizes from microscope images. (b) Image of largest sized ballotini.]

RESULTS

The experiments with very low flow rates gave data which fitted well with a diffusion model which consists of a finite difference equation based on Fick’s laws of diffusion. This model has been described previously1. The diffusion coefficient used to fit the data is the same for each size of ballotini to within experimental error and agrees well with the theoretical diffusion coefficient obtained from the Nernst-Hartley relation4 and adjusted by a tortuosity factor of approximately √2 which has been widely reported for media of this type5,6.

The Nernst-Hartley relation for a 1:1 electrolyte-
\[
D = \frac{2RT}{F^3} \left( \frac{\lambda_1^0 \lambda_2^0}{\lambda_1^0 + \lambda_2^0} \right) \left( 1 + \frac{d \ln y_\pm}{d \ln c} \right)
\]

Using this equation gave a value of \(2.26 \times 10^{-9}\) m\(^2\) s\(^{-1}\) for the diffusion coefficient when adjusted for tortuosity, by dividing by \(\sqrt{2}\).

Figure 3: (a) Results for 0.51 mm ballotini with a flow rate of 0.08 ml s\(^{-1}\) and (b) 0.43 ml s\(^{-1}\). The markers represent the concentrations obtained from electrical resistance measurements at the given depths and the solid lines are predictions using a diffusion coefficient of \(2.26 \times 10^{-9}\) m\(^2\) s\(^{-1}\).

At higher flows there is a more significant departure from the diffusion predictions with dispersion proceeding at a faster rate. The results from the top pair of electrodes (0.5 cm from the flow) were not very reliable and have been omitted from the graphs in this paper. The results from the bottom pair have also been omitted because they showed no significant response during the time allowed for these experiments.

The departure from diffusion is attributed to induced convection in the bed which increases with increasing flow rate. One common approach to modelling this is to simply use an empirically determined dispersion coefficient instead of a diffusion coefficient. Another approach is to add in a constant velocity term in the axial direction which may be called the convective velocity. This approach was inspired by the idea of using an equation for the Darcy velocity to describe free convection in mixtures of fluids of differing densities which has been used by several authors\(^{2,3}\). The density driven velocity for HCl at the concentrations used in our experiments may be calculated but is negligible and does not vary with cross flow rate. However adding in a velocity \((V)\) tends to give a better fit than a dispersion coefficient model, sometimes a very good fit (Figure 4). The main equation used in the model becomes in non-dimensionalised form-

\[
C_{i,j+1}^{*} = C_{x,j}^{*} + \frac{\delta t^{*}}{\delta x^{2}} (C_{i-1,j}^{*} - 2C_{i,j}^{*} + C_{i+1,j}^{*}) + \frac{V^{*} (C_{i-1,j}^{*} - C_{i+1,j}^{*}) \delta t^{*}}{\delta x^{2}}
\]

Where \(C\) is concentration, \(t\) time, \(x\) vertical position and \(i\) and \(j\) are the spatial and time co-ordinates. The non-dimensionalising equations are-

\[
t^{*} = \frac{D t}{L^2}, \quad x^{*} = \frac{x}{L}, \quad C^{*} = \frac{C}{C_0}, \quad V^{*} = \frac{x}{t^{*}}
\]

Where \(D\) is diffusion coefficient and \(L\) total cell length.
DISCUSSION

The results for electrodes 4, 5 and 6, which are all in the same horizontal plane, were always similar which is good evidence for a uniform horizontal concentration profile.

The fact that the effective velocity often varied significantly with position in the bed showed that imposing a constant velocity did not accurately reflect what is actually happening under most conditions. The graph in Figure 4 shows one of the best overall fits but it can still be seen that the rate of dispersion is slightly underestimated for the upper electrode pair and over estimated for the lower ones. Thus it may be necessary to use a velocity which varies with bed depth.

The results for each size of ballotini shown in Figure 5 demonstrate that the rate of penetration of HCl increases with increasing flow rate even at the relatively low flow rates used. There is a fair degree of scatter on the results which could be due to a number of factors including- fluctuations in flow rate during experiments, local variations in porosity, or any disturbance to the rig in addition to any measurement errors and unwanted electrical effects at the boundaries. Alternatively the ‘Convective Velocity’ results may be correlated with the particle Peclet number (Pe) where-

\[ P_e = \frac{v l}{D} \]  

Where \( v \) is cross-flowing fluid velocity, \( l \) is the particle diameter and \( D \) the diffusion coefficient. A graph of this correlation is shown as Figure 6. The fluid velocity used is the maximum velocity reached as the liquid approaches the outlet tube, assuming uniform radial flow. It is planned to carry out experiments with other sizes of ballotini to further investigate this correlation.

Correlating convective velocity with permeability can also be attempted but with the results currently available there are only 3 points and no definite conclusions can be drawn.
Figure 5: Graph of convective velocity against flow rate at a bed depth of 20mm for the three different sizes of ballotini as shown, with regression lines.

Figure 6: Correlation between Peclet number and convective velocity at a bed depth of 20 mm with regression line, the different markers represent data for the different particle sizes as shown.

Although the idea for the model described here came from the real fluid velocities which may be present in free convection the 'Convective Velocity' described here is actually a term which allows for the mixing caused by any induced eddies and micro-turbulence in the bed. It is hoped to develop a model which is related more precisely to the pore structure of the porous media being considered and different approaches are currently under investigation.
A COMPARISON OF ELECTRODE DESIGN FOR DISPERSION MONITORING
USING CONDUCTIVITY

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Experimental evidence of electric flux tracking around interfaces and
boundaries in porous media is presented. In experiments flux tracking
was minimised by using electrodes that protruded 5 mm into a bed of
particles. Using this cell arrangement the diffusion coefficient for
hydrochloric acid in a porous medium of mono-sized particles was
measured as \(2.0 \times 10^{-9} \text{ m}^2 \text{s}^{-1}\), a value slightly lower than that published
previously.

keywords:
Tomography, Porous Media, Diffusion, Flux, Dispersion

INTRODUCTION

Dispersion concentration within a continuous phase of differing electrical conductivity can be
deduced by measurements of the overall electrical conductivity, resistance or impedance. This
principle has been used \textit{in-situ} to determine concentrations of dispersions for many years\(^{(6)}\), and is
still being developed\(^{(2,3)}\). One of the most significant developments in recent years is 2
dimensional imaging of dispersions\(^{(4)}\), and commercial units for such work are now available.
However, regions of localised high porosity close to boundaries and interfaces are well known in
porous media\(^{(6)}\), leading to electric flux tracking around the boundaries; resulting in readings that
may not be representative of the true dispersion concentration.

This paper describes results from an experimental cell, that is being employed for the
measurement of diffusion and convection of material in porous media. The results were used to
develop a reliable experimental cell and are of general relevance to tomographic studies in
particulate systems. In essence, an electrical resistance or conductance technique relies upon the
following equation linking dispersion concentration by volume fraction \((C)\), the resistance due to
the continuous phase \((R_c)\) and the dispersion \((R_d)\)\(^{(4)}\)

\[
\frac{R_c}{R_m} = \frac{\kappa_M}{\kappa_C} = (1-C)^n
\]  

where \(\kappa_M / \kappa_C\) is the conductance ratio between the mixture and continuous phases and \(n\) is an
empirical exponent of value 1.5 for 'ideal' materials\(^{(6)}\). The conductance ratio is the same as the
conductivity ratio if the electrode geometry and flux path length can be assumed to be the same
for all the measurements.

Transport of mass by diffusional means inside porous media can be described by Fick's law
employing an effective diffusivity, incorporating tortuosity. A finite difference solution to the
diffusional mass transfer of material in a single dimension results in the following equation
\[ c_{i,j}^* = c_{i,j-1}^* + \delta t \frac{\partial c_{i,j}^*}{\partial x} \left[ c_{i-1,j-1}^* - 2c_{i,j-1}^* + c_{i+1,j-1}^* \right] \]  

(2)

where \( i \) and \( j \) represent the spatial and time co-ordinates. The non-dimensionalising equations for time, distance and concentration are as follows

\[ t^* = \frac{D \delta t}{L^2} ; \quad x^* = \frac{x}{L} ; \quad c^* = \frac{c}{c_0} \]

where \( t \) is time, \( D \) is diffusivity, \( x \) is distance, \( L \) is total bed depth, \( c \) is diffusing species concentration and \( c_0 \) is the fixed and constant concentration at one end of the porous medium (one boundary condition). The concentration at the other end of the porous medium increases with time, and a second differential equation, based on a material balance can be solved if there is no loss of matter from the system.

**EXPERIMENTAL**

Figure 1 illustrates the equipment used in the studies. The potential difference was measured across an acrylic cell in which ballotini particles of 0.57, 0.93 or 15 mm diameter were placed. Two types of electrodes were employed: one which was flush with the cell wall, the other protruded 5 mm into the cell. The latter electrode was insulated to a distance of 4 mm from the wall and was sharpened to a point to concentrate the electrical flux field. A potential of 5.03 volts was applied to the test cell and a ballast resistor of 1000 Ohms. The cell was filled with a dilute electrolyte solution and the voltage across the cell (between electrode A and B) was measured. As ballotini particles incrementally filled the cell, the potential difference between the electrodes at the base of the column and B was also measured. The heights marked on Figures 1 to 3 are the heights of the top surface of the ballotini particle bed from the electrode pair A-B in the cell.

In the later diffusional studies a flange was added to the top of a similar cell. The flange contained a manifold with an inlet and outlet so that solution containing electrolyte could be pumped gently over the cell. The cell was full of 0.93 mm diameter ballotini particles and solution at a lower salt concentration to the liquid pumped through the manifold. Electrical resistance measurements were taken to assess the concentration of electrolyte with time, and hence the diffusion into the packed bed.

**RESULTS AND DISCUSSION**

The path length between the electrodes A and B was 10 mm closer in the protruding electrodes cell. Hence, for the purposes of comparison, all resistances have been normalised with respect to the initial resistance measured in the presence of solution alone. The same material was used in both cells; in Figure 2 the curves labelled 0.57F and 0.57P represent tests with the 0.57 mm diameter ballotini in the flush and protruding cells respectively. The electric flux field appears to be interfered with as the level of solids approaches the electrodes. When the interface is within 5 mm of the electrodes the measured resistance between A-B increases. After the interface passes the electrodes another 5 mm is required before flux tracking up to the interface and across it ceases to be significant for the protruding electrodes cell. Figure 2 illustrates that this cell is less influenced by the proximity of the interface, for all the materials studied.

In a tomographic study it is common to inject current into a vessel and to provide a ring of sensing electrodes around the vessel. The apparatus illustrated in Figure 1 had the capacity to compare protruding and flush mounted current injecting electrodes: four sensing electrodes were positioned across the base of the vessel, and the potential difference between each of these and electrode B was recorded. The results are presented in Figure 3.
Figure 3(A) illustrates how the potential changed as the cell with protruding electrodes was filled, as well as the potential across the electrodes A-B. The potential rises as the interface passes the source electrodes, and the potential from the sensing electrodes rises in proportion (except for the dip at the point when the interface passes the electrodes). One of the aims of the study was to investigate effects of electrode geometry on electrical measurements taken in porous media. Thus an increase in potential inside the cell due to an increase in overall potential applied to the cell, such as that illustrated in Figure 3(A), does not provide any useful information. Hence the potentials measured by the sensing electrodes were normalised against that applied to the cell, and the results are presented in Figures 3(B) to (D).

The normalised data, Figure 3(B) shows that once the interface has passed the current injecting electrodes the normalised potential returns to within a few percent of the value prior to filling the cell. However, there is a significant difference between the initial and final values for the flush cell on filling. To ensure a fair comparison between the two types of cell the experiment was repeated using the protruding electrode cell and a lower value of the ballast resistor. This resulted in the same potential difference across the electrodes A-B as used in flush cell tests. The results are presented in Figure 3(D). The use of a greater potential did not change the conclusion that the protruding electrode cell is not significantly affected by the height of the bed of particles, unlike the cell employing flush current injecting electrodes.

The results illustrated in Figure 3 show that electrode design, flush or protruding, can have an influence on the measured potential under identical conditions within porous media. In a tomographic study potential is converted into solid concentration via Equation (1), hence a cell design employing flush mounted electrodes under the above circumstances would result in a perceived higher local concentration compared to the protruding type. However, in both cells the solid concentration by volume fraction was 0.60 under all conditions of filling.

The diffusional studies employed a protruding electrode cell, in order to avoid the problem investigated above. The bed comprised 0.93 mm diameter ballotini particles, and the initial studies concerned the investigation of the diffusion of hydrochloric acid into the bed. An example of the results is presented in Figure 4, where the experimental data is compared with the finite difference model, Equation (2), using a diffusivity of 2x10^-9 m^2 s^-1. This value is slightly lower than a recently published study would suggest\(^{20}\), and further tests will be directed towards diffusional and convective studies of electrolytes in porous media.

CONCLUSIONS

Electrical resistance, or conductivity, measurements may be used for monitoring dispersion concentration and solute diffusion within porous media. However, porous media boundaries and interfaces will give rise to non-uniform electric flux fields that may influence the deduced result of local concentration. This was noticeable in the case of the experimental cell that employed electrodes that were flush with the cell wall. The cell employing electrodes protruding by 5 mm into the porous media was not subject to such influence. Further studies into diffusion and convection using this experimental technique are ongoing.

REFERENCES

The 1997 Jubilee Research Event

Figure 1  Schematic diagram of apparatus

Figure 2  Resistance as height of ballotini is raised

Figure 3  Variation in test cell potential during filling

Figure 4  Diffusion in porous media - finite difference model and experimental readings