

Quantifying the pore structure of cement-based materials using backscattered electron microscopy

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Declaration

I hereby declare that this thesis, submitted for the degree of Doctor of Philosophy of the University of London and the Diploma of Imperial College London, is the result of my own investigations. Information derived from ideas, published or unpublished work of other researchers has been specifically acknowledged in the text and a list of references is given. I hereby certify that the work presented in this thesis has not been submitted in any form to this or any other institution, for any degree, diploma or other qualification.

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Abstract

This thesis aims to develop backscattered electron microscopy and image analysis methods for accurate quantitative characterisation of the pore structure in cement-based materials, so that a better understanding of its nature and influence on molecular transport properties can be achieved.

Phase segmentation is a crucial stage for image analysis. In order to accurately segment pores from a backscattered electron image, a new method called ‘Overflow’, is developed. ‘Overflow’ is found to be more objective and reliable than existing methods, requiring significantly fewer images to achieve statistical confidence.

Quantitative electron microscopy at high-resolution requires consideration of the electron beam-sample interactions and the signal formation process in the electron microscope. For this, a Monte Carlo technique is used to simulate the electron-solid interactions in cement-based materials. This allows for the determination of the signal sampling volume, optimal imaging strategy and theoretical resolution limit for pore imaging.

This thesis gives evidence that ‘patch microstructure’, a recently reported phenomena, is an artefact of sample preparation. An improved sample preparation method for backscattered electron microscopy is proposed.

A new image analysis tool that measures microstructural gradients at interfaces, at the highest possible resolution, has been developed. This method is based on Euclidean Distance Mapping, is more efficient than conventional methods and is unrestricted by feature geometry or boundary conditions. New information regarding the pore structure gradient at the interfacial transition zone is obtained, which may resolve the inconsistencies between experimental observation and computational modelling on the role of the interfacial transition zone in molecular transport.

Mortar samples with a range of pore structure characteristics are prepared and tested for oxygen diffusion, oxygen permeation and water absorption. Pores relevant to transport are segmented, quantified using image analysis and correlated to the measured transport coefficients to formulate predictive relationships. Two transport prediction models are developed for diffusivity and permeability. The accuracy and limitations of these prediction models based on extracted two-dimensional pore information are discussed.

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Notation

Roman letters

A	Cross-sectional area (m ²)
A°	Pore area (m ²)
A_{AH}	Anhydrous cement area (m ²)
A_o	Atomic weight (g/mole)
A_A	Area fraction
A_p	Cement paste area (m ²)
A_R	Richardson's constant (A/cm ² K ²)
Afm	Monosulphate
Aft	Ettringite
AH	Anhydrous cement
AH_o	Initial volume fraction of anhydrous cement
AH_p	Area fraction of anhydrous cement
BSE	Backscattered electron
C	Signal contrast
C_2	Oxygen concentration at inlet (m ³ /m ³)
C_1	Oxygen concentration at outlet (m ³ /m ³)
C_A	Concentration of Gas A (mol/m ³)
C_c	Chromatic aberration coefficient (~1cm)
C_s	Spherical aberration coefficient (~2cm)
C_3S	3CaO.SiO ₂
C_2S	2CaO.SiO ₂
C_3A	3CaO.Al ₂ O ₃
C_4AF	4CaO.Al ₂ O ₃ .Fe ₂ O ₃
CH	Calcium hydroxide
C-S-H	Calcium silicate hydrates
C.V.	Coefficient of variation
D	Diffusion coefficient (m ² /s)
D_o	Oxygen diffusivity in air (m ² /s)
D_{AB}	Ordinary diffusivity of Gas A (m ² /s)
D_{KA}	Knudsen diffusivity of Gas A (m ² /s)
d	Pore diameter (nm)
d_o	Diameter of gas molecule (nm)
d_c	Chromatic aberration (nm)
d_f	Aperture diffraction (nm)
d_G	Gaussian probe diameter (nm)
d_p	Effective probe diameter (nm)
d_s	Spherical aberration (nm)
E	Accelerating voltage (keV)

e	Electron charge ($= 1.59 \times 10^{-19}$ C)
F	Formation factor
G_0	Percentage of O ₂ in the inflow stream
G_1	Percentage of O ₂ in the outflow stream
HP	Hydration products
ITZ	Interfacial transition zone
i	Absorbed water per unit area (g/m ²)
i_p	Probe current (A)
J_A	Flux of Gas A (mol/m ² .s)
J_B	Flux of Gas B (mol/m ² .s)
J_c	Emission current density (A/cm ²)
k	Permeability coefficient (m ²)
k_B	Boltzmann constant ($= 1.38 \times 10^{-23}$ J/K)
k_g	Apparent gas permeability (m ²)
k_{int}	Intrinsic gas permeability (m ²)
L	Thickness of sample (m)
L_A	Boundary length per unit area (m ⁻¹)
L_L	Intercept line fraction
L_W	Molar heat of water vaporisation ($= 40.7$ kJ/mol)
LSCM	Laser scanning confocal microscopy
MIP	Mercury intrusion porosimetry
N	Number of counts
n	Number of images
N_A	Avogadro number ($= 6.022 \times 10^{23}$)
P	Pressure (N/m ²)
P_1	Inlet pressure (N/m ²)
P_2	Outlet pressure (N/m ²)
P_m	Mean pressure (N/m ²)
P_L	Number of intersection points per unit length (m ⁻¹).
P_P	Point count fraction
P_v	Vapour pressure (Pa)
P_{vs}	Vapour saturation pressure (Pa)
Q	Flow rate (m ³ /s)
R	Ideal gas law constant ($= 8.3145$ J/mol.K)
r	Pore radius (m)
R_1	Flow rate of nitrogen stream (mL/min)
R_2	Flow rate of oxygen stream (mL/min)
P_1	Pressure of oxygen stream (bar)
P_2	Pressure difference between the oxygen and nitrogen stream (bar)
R_{BSE}	Backscattered electron escape surface radius
RH	Relative humidity (%)
S	Sorptivity coefficient (g/m ² .min ^{0.5})
SE	Secondary electron
$S.E.$	Standard error
SEM	Scanning electron microscope

S/N	Signal-to-noise ratio
S_p	Pore specific surface (m^{-1})
S_V	Surface density (m^{-1})
s	Sample standard deviation
s^2	Sample variance
T	Temperature (K)
t	Time (s)
V_a	Aggregate volume fraction
V_V	Volume fraction
W	Work function (= 4.5eV for tungsten)
w/c	water-to-cement ratio
Y_A	Mole fraction of Gas A
$\bar{y}$	Sample mean
Z	Atomic number
$\bar{Z}$	Mean atomic number
Z_{BSE}	Backscattered electron penetration depth
Z_{max}	Maximum penetration depth of electrons

Greek letters

α	Degree of hydration
α_p	Probe convergence angle
β	Brightness ($A/cm^2.sr$)
δ	Constrictivity factor
ε	Signal collection efficiency
η	Backscatter coefficient
$\bar{\eta}$	Mean backscatter coefficient
η_p	Dynamic viscosity (Ns/m^2)
λ	Mean free path of electrons (cm)
λ_e	Electron wavelength (nm)
λ_o	Mean free path of gas molecules (nm)
μ	Population mean
ϱ	Density (g/cm^3)
ρ_p	Vapour density (g/m^3)
ρ_{vs}	Vapour saturation density (g/m^3)
σ	Population standard deviation
σ^2	Population variance
σ_{rel}	Relative standard deviation
Γ	Pore perimeter (m)
τ	Tortuosity factor
Φ_p	Cement paste porosity
Φ_{cap}	Capillary porosity

Contents

Declaration	2
Abstract	3
Acknowledgements	4
Notation	5
Contents	8
List of Tables	12
List of Figures	13
 Chapter 1 Introduction	 20
1.1 Research motivation.....	20
1.2 Objectives and scope	23
1.3 Thesis outline	23
 Chapter 2 Literature review	 25
2.1 Pore structure and properties	25
2.1.1 Gel pores, capillary pores, cracks and air voids	26
2.1.2 Interfacial transition zone	28
2.1.3 Hollow-shell hydration grains	32
2.2 Methods for characterising the pore structure	35
2.3 Backscattered electron imaging of cement-based materials	38
2.4 Stereology	40
2.5 Image analysis	43
 Chapter 3 Methodology	 45
3.1 Sample preparation	45
3.1.1 Materials	45
3.1.2 Mix proportions	47
3.1.3 Mixing and curing	48
3.1.4 Sample conditioning	49
3.2 Backscattered electron microscopy	54
3.2.1 Sample preparation for microscopy	54

3.2.2 Sample preparation damage and artefacts	61
3.2.3 Scanning electron microscope	63
3.2.4 Brightness and contrast	66
Calibration for brightness and contrast	69
3.2.5 Choice of magnification and pixel spacing	71
3.2.6 Sampling issues	73
3.2.7 Number of fields and estimates of error	75
3.3 Image analysis	76
3.4 Molecular transport testing	78
3.4.1 Oxygen diffusion	78
Test method	80
3.4.2 Oxygen permeation	82
Test method	82
Klinkenberg correction for gas slippage	84
3.4.3 Water absorption	86
Test method	87
3.5 Chapter summary	90
 Chapter 4 Pore segmentation	91
4.1 Introduction	91
4.2 Resolution, brightness and contrast	93
4.3 Development of a pore segmentation method	94
4.4 Experimental	98
4.4.1 Aggregate segmentation	100
4.4.2 Pore segmentation	104
4.4.3 Averaging pore volume fraction	105
4.5 Results and discussion	108
4.6 Conclusions.....	111
 Chapter 5 Monte Carlo simulation of electron-solid interactions	112
5.1 Introduction	112
5.2 Physics of the electron-solid interactions	114
5.3 Monte Carlo simulation of the electron-solid interactions	115
5.4 Experimental	118
5.5 Results	121
5.5.1 Verification of the Monte Carlo code	121

5.5.2 Effect of accelerating voltage and probe diameter	124
5.5.3 Depth of the interaction volume	125
5.5.4 Sampling volume of backscattered electrons	127
5.5.5 Sampling volume of characteristic X-rays	129
5.6 Discussion	131
5.7 Conclusions.....	132
Chapter 6 Monte Carlo simulation of BSE signal variation at pore boundaries	133
6.1 Introduction	133
6.2 Sampling of subsurface material	134
6.3 BSE signal variation across pore-solid boundaries	139
6.4 Verification of the Overflow pore segmentation technique	144
6.5 Resolution of backscattered electron microscopy for pores	147
6.6 Discussion	155
6.7 Conclusions.....	156
Chapter 7 Patch microstructure: Fact or artefact?	157
7.1 Introduction	157
7.2 Epoxy impregnation	162
7.3 Experimental	166
7.4 Observations	167
7.5 Discussion	175
7.6 Conclusions.....	177
Chapter 8 ITZ: Characterising its microstructural gradients using Euclidean Distance Mapping and its role in molecular transport	179
8.1 Introduction	179
8.2 Euclidean Distance Mapping for phase analysis	182
8.3 The Interfacial Transition Zone	188
8.4 Heterogeneity of the ITZ	197
8.5 Role of ITZ in molecular transport	200
8.5.1 Experimental	201
8.5.2 Results and discussion	204
8.6 Conclusions.....	208

Chapter 9 Predicting molecular transport from image analysis	210
9.1 Introduction	210
9.2 General considerations	212
9.3 Experimental	216
9.3.1 Specimen preparation, curing and conditioning	216
9.3.2 Molecular transport testing	218
9.3.3 Backscattered electron imaging	218
9.3.4 Image analysis	219
9.4 Results	221
9.4.1 Porosity, specific surface and degree of hydration	221
9.4.2 Correlations between transport properties and pore structure	225
9.4.3 Predicting diffusivity from pore structure	230
9.4.4 Predicting permeability using a Kozeny-Carman model	233
9.5 Discussion	237
9.6 Conclusions.....	240
 Chapter 10 Thesis summary including main conclusions	241
 Chapter 11 Recommendations for further research	244
 References	247
 Appendices	
Appendix I Calculation for brightness, probe current and probe diameter	262
Appendix II Standard error, relative standard error, confidence interval and number of fields required for statistical significance	266
Appendix III Entropy maximisation.....	270
Appendix IV Publications arising from this research	271

List of Tables

Table 3.1 Composition of cement.....	45
Table 3.2 Specific gravity at saturated and surface dry condition (SSD), moisture content and absorption values for aggregates.....	46
Table 3.3 List of pixel spacing and field of view of images digitised to 1024 x 768 pixels and 1940 x 1455 pixels, captured at various magnifications up to 2000x	73
Table 4.1 Mixture proportions	100
Table 4.2 Statistical analyses	109
Table 5.1 Major phases in cement-based materials arranged according to increasing backscatter coefficient. Atomic contrast is calculated from the backscatter coefficients of successive phases	120
Table 5.2 Calculated values of brightness (β), Gaussian probe diameter (d_G), chromatic aberration (d_c), spherical aberration (d_s), aperture diffraction (d_d) and effective probe diameter (d_p) at several accelerating voltages (E) [See Appendix I]	121
Table 8.1 Mixture composition for ITZ study	188
Table 8.2 Mixture proportions for mortar (1, 2, 3) and paste (4) samples, for molecular transport testing. Notation: SF = silica fume, SP = superplasticiser	203
Table 9.1 Mixture proportions for transport prediction study	217
Table 9.2 Curing and conditioning regimes.....	217
Table 9.3 Average values for paste porosity, specific surface and degree of hydration.....	222
Table 9.4 Average transport coefficients	226

List of Figures

Figure 3.1 Grading curves for Thames valley sand and gravel	46
Figure 3.2 Sample designation	48
Figure 3.3 Paste, mortar and concrete samples sectioned using the automatic abrasive cutter	50
Figure 3.4 Characteristic mass loss curves for A) pastes; B) mortars; and C) concretes during conditioning, after curing in cling film for 3 days. The period is measured from the end of curing	53
Figure 3.5 Apparatus for A) vacuum impregnation, and B) for subsequent pressuring	56
Figure 3.6 A) Grinding and polishing media used, and B) Struers LaboPol-5 with sample holder LaboForce-3	58
Figure 3.7 Olympus BX-51 petrographic microscope	58
Figure 3.8 Surface quality of the cement paste as the sample is ground and polished at successively finer grit sizes. Note that the images are not from the same area. Images are captured in ordinary reflected light mode, field of view is 300x300µm. The sample is P 0.35 - 3d.	59
Figure 3.9 Images of the final polished surfaces of paste, mortar and concrete samples, captured using an ordinary desktop scanner (A-C) and a petrographic microscope in fluorescent imaging mode (D-F). Field of view is approximately 15 x 17mm for the scanned images and 1832 x 1374µm for the fluorescent micrographs	60
Figure 3.10 JEOL 5410LV Scanning Electron Microscope	65
Figure 3.11 Effect of brightness and contrast settings on the appearance of the BSE image (sample is P 0.3 – 3d, images captured at 500x, field of view: 240 x 180µm)	67
Figure 3.12 Calibration of the brightness and contrast settings using a pure aluminium standard cast in epoxy	70
Figure 3.13 Effect of fluctuation of the beam condition on the position of the epoxy and aluminium peaks over a two-hour monitoring period. The curves marked * are not corrected for beam fluctuation and show a gradual decrease in peak grey values for epoxy and Al over time	70
Figure 3.14 Effect of magnification on the resolution and field of view of the image. Images are digitised to 1940 x 1455 pixels, sample is M 0.5 (50S) 3d	72
Figure 3.15 Screenshot of analySIS®	77

Figure 3.16 Oxygen diffusion test apparatus	81
Figure 3.17 Oxygen permeability test apparatus	83
Figure 3.18 Typical plots for Klinkenberg corrections for paste (28-days), mortar (3-days) and concretes (7-days)	85
Figure 3.19 Water absorption test set-up	88
Figure 3.20 Water absorbed per unit area vs. square root of time plots for paste (28-days), mortar (3-days) and concrete (7-days) samples	89
Figure 4.1 BSE images of paste regions from two different mortars at 28 days. The brightness histogram for the low w/c ratio mortar did not show a distinct peak for pores. Field of view is 267 μ m x 200 μ m	95
Figure 4.2 A) BSE image of a single capillary pore and B) variation of grey value along the horizontal white line shows ambiguity of the pore boundary. Field of view is approximately 20 μ m x 18 μ m	96
Figure 4.3 Schematic illustrating the influence of beam interaction volume on the BSE signal near the inter-phase boundary of a high and a low atomic number (Z) material when the hypothetical boundary is a) perpendicular and b) inclined to the specimen surface. Adapted from Goldstein et al. [1981]	96
Figure 4.4 Change in area segmented (white pixels) at different threshold levels. Between thresholds 80 and 110, a sudden increase in segmented area is observed when the surrounding paste is also selected	97
Figure 4.5 Change in area segmented with grey value for the pore in Fig. 4.3. The threshold value for porosity can be estimated from the inflection point	98
Figure 4.6 Application of the overflow criteria to determine a global threshold level for porosity	99
Figure 4.7 Using Sobel and morphological filters for aggregate segmentation. Sample is M 0.7 (63S) 3d, image captured at 150x, field of view is 800 x 600 μ m	102
Figure 4.8 Errors generated from the aggregate segmentation method in Fig. 4.7. Sample is M 0.7 (63S) 3d, image captured at 500x, field of view is 240 x 180 μ m	103
Figure 4.9 Using manual boundary tracing method to segment aggregate particles. Sample is M 0.7 (63S) 3d, image captured at 500x, field of view is 240 x 180 μ m	104
Figure 4.10 Four segmented BSE images showing the aggregate (white), pores (grey) and hydrated cement paste (black) phases. The cement paste area varies depending on the amount of aggregate present. Sample is M 0.7 (63S) 28d, images captured at 500x, field of view is 267 x 200 μ m	107
Figure 4.11 Cumulative average porosity for Mortar A and Mortar B. The proposed segmentation method requires fewer frames to achieve a stable porosity value	110

Figure 5.1 Schematic showing signal generation in the electron microscope for typical cementitious materials (from Scrivener [2004])	113
Figure 5.2 Monte Carlo simulations of electron-solid interactions in calcium hydroxide at 20keV. Figs. (A-D) are independent simulations of 25 electron trajectories to illustrate the stochastic process of the technique. Fig. (E) is a simulation of 2×10^3 electron trajectories. Elastic scattering occurs where the electron changes direction. The electron trajectory is followed until it loses all of its energy (grey lines) or is backscattered (black lines). For each trajectory, the spatial location, energy distribution and generated X-rays are tracked	117
Figure 5.3 Screenshots of CASINO (Version 2.42)	119
Figure 5.4 Testing the accuracy of the Monte Carlo simulation by comparing the simulated and experimentally measured [Joy, 1995b] or calculated [Reuter, 1972] BSE coefficients for A) all elements between Li and Ca in the periodic table; and B) main phases in cement-based materials (see Table 5.1)	123
Figure 5.5 Effect of accelerating voltage on the maximum penetration depth of electron trajectories in calcium hydroxide	124
Figure 5.6 Effect of probe diameter on the 90th percentile maximum penetration depth ($Z_{\max}$) of all electrons and surface radius (R_{BSE}) of backscattered electrons for calcium hydroxide at accelerating voltages of 5, 10 and 20keV	125
Figure 5.7 Cumulative distribution of penetration depth of electrons at 20keV and 10keV accelerating voltage for selected phases: 1) C_4AF ; 2) C_3S ; 3) CaCO_3 ; 4) CH; 5) C-S-H; 6) Aft; and 7) Aft	126
Figure 5.8 Distribution of penetration depth, Z_{BSE} and escape surface radius, R_{BSE} of backscattered electrons at 20keV and 10keV accelerating voltage for selected phases: 1) C_4AF ; 2) CH; and 3) Aft. The symbol ($\diamond$) marks the 90th cumulative percentile	128
Figure 5.9 Cumulative distribution of backscattered electron energy at 20keV and 10keV accelerating voltage for selected phases: 1) C_4AF ; 2) CH; and 3) Aft	129
Figure 5.10 Depth and lateral distribution of non-absorbed X-rays in Aft at 20keV and 10keV. Symbols: 1) $\text{CaK}\alpha$; 2) $\text{SK}\alpha$; 3) $\text{AlK}\alpha$; 4) $\text{OK}\alpha$ and 5) $\text{CaL}\alpha$	130
Figure 6.1 Cumulative distribution of BSE penetration depth (Z_{BSE}), BSE escape surface radius (R_{BSE}) and maximum electron penetration depth ($Z_{\max}$), for araldite epoxy at 10keV and 20keV accelerating voltages.....	135
Figure 6.2 Effect of sampling subsurface material on the generated BSE signal: A) Monte Carlo simulation on a two-layer composite comprising of araldite epoxy (i.e. pore) as top layer and C-S-H as substrate; B) Cross-section of the two-layer composite model where the thickness of the top epoxy layer is varied.....	137

Figure 6.3 Change in the observed BSE signal at 10keV and 20keV as the epoxy thickness (i.e. pore depth) is varied. The vertical dotted line marks the maximum BSE penetration depth for pure epoxy.....	138
Figure 6.4 Effect of sampling subsurface pores on the generated BSE signal for C-S-H at 10keV and 20keV. The vertical dotted line marks the maximum BSE penetration depth for pure C-S-H.....	138
Figure 6.5 Change in the shape and size of the electron interaction volume as a 10keV electron beam is scanned across a CH-pore boundary. The simulations were done at: A) -2 μ m; B) -0.5 μ m; C) +0.5 μ m; and D) +2 μ m from the boundary.....	140
Figure 6.6 Change in BSE signal across pore-solid boundaries where the solid phase can be Aft, C-S-H, CH or C ₄ AF. The simulations are performed at 10keV (A, B) and 20keV (C, D).....	141
Figure 6.7 A) Image of a pore cropped from a larger 500x BSE image of C 0.4 – 28d, captured at 10keV; B) variation in grey value along the white horizontal dotted line; C) the threshold value for the pore is estimated from the inflection point of the cumulative brightness histogram; D) segmented pores.....	143
Figure 6.8 A) A hypothetical 10 μ m diameter epoxy-filled circular pore placed at the centre of a 20 x 20 μ m C-S-H matrix; and B) a generated BSE line scan along the white horizontal dotted line through the pore centre.....	144
Figure 6.9 Cumulative brightness histogram for the pore model in Fig. 6.8 (A) obtained from Monte Carlo simulation. The symbol ($\diamond$) marks the threshold grey value (= 70) that gives the correct pore volume fraction of 19.6%	146
Figure 6.10 Model of a multi-layer composite comprising of alternating C-S-H and epoxy layers representing capillary pores of various dimensions from 10nm to 1 μ m	148
Figure 6.11 Change in BSE coefficient across epoxy layers of various thicknesses at 10keV and 0.1 μ m pixel spacing. Note that the figure only plots data from $\pm$ 1.5 μ m from the centre of each epoxy layer.....	149
Figure 6.12 Change in BSE coefficient across epoxy layers of various thicknesses at 20keV and 0.1 μ m pixel spacing. Note that the figure only plots data from $\pm$ 1.5 μ m from the centre of each epoxy layer.....	150
Figure 6.13 Change in BSE coefficient across epoxy layers of various thicknesses at 10keV and 0.01 μ m pixel spacing. Note that the figure only plots data from $\pm$ 0.3 μ m from the centre of each epoxy layer.....	151
Figure 6.14 BSE contrast for epoxy layers of various thicknesses with respect to neighbouring C-S-H layers at 10keV and 20keV.....	152
Figure 6.15 A) Comparison between the Overflow segmented thickness and the actual thickness of the epoxy layers for values ranging from 10nm to 10 μ m; and B) segmentation error plotted against epoxy thickness.....	154

Figure 7.1 BSE images of patch microstructure obtained from Diamond [2003]	158
Figure 7.2 Patch microstructure is inconsistent with conventional ITZ/bulk paste model, e.g. the hard core/soft shell model [from Diamond, 2003]	159
Figure 7.3 A) Patch microstructure observed on an OPC mortar (w/c 0.6, sand 50% vol., 28-day cured) where dark porous cement paste appears to be intermixed with bright, almost non-porous paste. Particles marked 'O' represent sand particles that are fully surrounded by porous cement paste while particles marked 'X' are in contact with both porous and dense patches. Field of view is 1333 x 1000 μ m; B) Magnified portion of (A) showing the boundary between the porous and dense patch is sharp and distinct. Field of view is 381 x 286 μ m	161
Figure 7.4 The importance of epoxy for providing atomic contrast in pore imaging. Schematic showing the effect of epoxy on the detected BSE signal, when an electron beam is scanned across an epoxy-filled pore (A) and an 'empty' pore (B)	162
Figure 7.5 Epoxy impregnation using conventional procedure: a) the sample is first de-aired; b) then epoxy is introduced under vacuum; c) and finally the vacuum is released	163
Figure 7.6 Schematic of the new epoxy impregnation method: a) The dried sample is first cast in clear epoxy resin; b) when the resin has hardened, the bottom face is dry-ground to expose a fresh and plane surface for observation; c) the sample is placed under vacuum for several hours to evacuate the pores; d) a de-aired fluorescent epoxy resin is added while the sample is still under vacuum; e) and finally the vacuum is released and a 2.5 bars gas pressure is applied for 30 minutes	164
Figure 7.7 Cross sections of mortar samples showing the depth of resin penetration using the conventional vacuum impregnation method (A, B) and the new technique (C, D). The epoxy penetration front is less than 1mm on samples that were impregnated using the conventional method. Full depth penetration is evident for the w/c 0.6 mortar (C) and a penetration of around 3mm for the w/c 0.4 mortar (D). The deeper epoxy penetration provides confidence that the observation plane remains saturated with epoxy after the grinding and polishing stages	165
Figure 7.8 Area matching BSE images of those shown in Fig. 7.3, after re-impregnation and re-polishing. The originally dense patches are now filled with capillary pores and hollow-shell pores that were previously unseen. By monitoring the change in diameter of the spherical air void (indicated with an arrow in (A)), the amount of material that has been removed from the re-grinding and re-polishing is estimated to be around 50 μ m. The microcrack (indicated with arrows in (B)) is also visible in Fig. 7.3B	168
Figure 7.9 Area matching images of before (A) and after (B) epoxy re-impregnation. In (A), the porous patches appear to form a continuous path, suggesting that molecular/ionic transport may occur via these interconnected porous patches. In (B), the dense patches have 'disappeared' upon epoxy impregnation. Some areas (circled) contain a higher local concentration of large, unreacted cement grains, but these are not 'patch microstructure' (w/c ratio 0.6, field of view: 1333 x 1000 μ m)	169
Figure 7.10 Area matching images of before (A) and after (B) epoxy re-impregnation. In (A), the large sand particle at the top right corner was originally in contact with both dense and porous patches. An empty air void can also be seen (arrowed) in the dense patch (w/c ratio 0.4, field of view: 889 x 667 μ m)	171

Figure 7.11 Area matching images of before (A) and after (B) epoxy re-impregnation. Image (A) gives a false impression that the sand particle at the top right corner is surrounded by an ITZ that is much more porous than the adjacent bulk paste (w/c ratio 0.6, field of view: 667 x 500 μ m)	172
Figure 7.12 Higher magnification image of a sharp boundary between a dense and a porous patch (A) which disappears after re-impregnation (B) (w/c ratio 0.6, field of view: 267 x 200 μ m)	173
Figure 7.13 Higher magnification image of a sharp boundary between a dense and a porous patch (A) which disappears after re-impregnation (B). The paste region between the two closely spaced sand particles appears more porous than the bulk paste, suggesting the ITZ effect (w/c ratio 0.4, field of view: 178 x 133 μ m)	174
 Figure 8.1 Conventional dilation-subtraction strip method for phase analysis	181
Figure 8.2 Euclidean distance mapping applied to an image of a white circle in black background. The binary image (A) is converted to a greyscale image (B) where each background pixel has a brightness value equal to its Euclidean distance to the nearest foreground pixel. Image (C) is a pixel map of the boxed area, showing incremental grey value (rounded off to the nearest integer) of the pixels from the feature boundary	183
Figure 8.3 Generating a Euclidean Distance Map (EDM) of the pore phase from the aggregate boundary	185
Figure 8.4 Use of EDM for quantitative phase analysis at the aggregate-paste interface ...	186
Figure 8.5 Applying the EDM method on a random section of an OPC concrete. The porosity distribution from the aggregate-paste interface is obtained by normalising the brightness histogram of the pore EDM to the brightness histogram of the paste EDM	187
Figure 8.6 Detectable anhydrous cement (A) and porosity distribution (B) plots at single pixel strip width, measured from the aggregate-paste interface for sample C 0.4. Arrow in Fig (A) shows the effect of CH deposits on aggregate surface, on the porosity gradient. Values are the average of 30 frames	190
Figure 8.7 Detectable porosity distribution plots showing different ITZ characteristics observed in C 0.4: A) very porous ITZ; B) relatively dense ITZ with large amount of CH deposits on the aggregate surface (arrowed); and C) mixture of porous and dense ITZs. The averaged result will depend on the relative proportion of the porous and dense ITZ. Note that the bond cracks visible in A and C are not tallied. White border represents the 50 μ m strip (field of view: 267 x 200 μ m)	192
Figure 8.8 Detectable anhydrous cement (A) and porosity distribution (B) plots at single pixel strip width, measured from the aggregate-paste interface for sample M 0.6. Values are the average of 30 frames	193
Figure 8.9 Schematic showing the packing effects of two different sized unreacted cement grains (A & B) against a large aggregate particle (C), after a period of hydration that has consumed the smaller grains. Adapted from Crumbie [1994]	194

Figure 8.10 Detectable porosity distribution plots showing different ITZ characteristics in sample M 0.6 as a result of varying amounts of CH deposit on the aggregate surface. White border represents the 50 μ m strip (field of view: 267 x 200 μ m)	196
Figure 8.11 Coefficients of variation for the average detectable porosity and anhydrous cement plotted against distance from aggregate surface for A) C 0.4; and B) M 0.6	199
Figure 8.12 Oxygen diffusivity, oxygen permeability and water sorptivity plotted against sand volume fraction	206
Figure 8.13 Normalised transport coefficients plotted against paste volume fraction.....	207
Figure 8.14 Cement paste porosity measured from water absorption test. Error bars represent plus/minus one standard deviation	208
Figure 9.1 Effect of conditioning humidity on A) oxygen diffusivity; B) oxygen permeability; and C) sorptivity of mature pastes (> 7 years) containing GBBS (Mix S) and PFA (Mix P) at w/c 0.35 and 0.42 respectively. Plotted values are an average of three measurements. Error bars represent plus/minus one standard deviation	215
Figure 9.2 Flow chart for sample preparation and testing. Discs marked 'M' are for microscopy, 'T', 'C' and 'B' (Top, Centre and Bottom) are for transport testing. End discs ('X') are discarded. All dimensions in mm	217
Figure 9.3 Variation of detectable porosity and specific surface with the number of frames analysed. A relatively stable value was obtained after analysing twenty frames.....	222
Figure 9.4 Comparison between detectable paste porosity and theoretical capillary porosity as predicted by Powers' model [Powers & Brownyard, 1948]	225
Figure 9.5 BSE images of samples conditioned at 105°C and 20°C. Samples conditioned at 105°C were found to be affected by microcracking (arrowed). (500x magnification, field of view: 240 x 180 μ m).....	227
Figure 9.6 Percentage increase in transport coefficients as a result of conditioning at 105°C. The transport properties of M 0.35 are more affected by microcracking compared to M 0.7	228
Figure 9.7 Relationships between transport coefficients with Φ_p and S_p . Error bars indicate plus-minus one standard deviation.....	229
Figure 9.8 Variation of constrictivity factor, δ , as a function of the ratio of minimum to maximum pore radius, q , for a sinusoidal pore channel [Bernabé & Olson, 2000].....	232
Figure 9.9 Predicted and measured values of oxygen diffusivity. 90% of the predicted values were accurate to within a factor of two and 100% to within a factor of five in relation to the measured values.....	233
Figure 9.10 Predicted and measured values for permeability, using Eq. 9.12.....	236
Figure 9.11 Predicted and measured values for permeability, using Eq. 9.14.....	236

Chapter 1 Introduction

1.1 Research motivation

Concrete is by far the most widely used construction material in the world, but the fundamental mechanisms underlying its behaviour are poorly understood due to its complexity. Over ten times more concrete is produced than all other construction materials put together, about 1m^3 per year for every person on the planet, some 6 billion m^3 per year. This makes concrete the world's second most heavily consumed material after water. The US Geological Survey predicts that concrete usage will double over the next 40 years.

Although not usually regarded as an advanced material, concrete is chemically and physically complex and has high economic, social and environmental impact. The common perception of concrete is as an inert, everlasting material. However, concrete continuously undergoes microstructural changes and is affected by various deterioration processes, several having emerged as being serious problems only over the past decade. In some environments, good construction practice and concreting materials alone cannot guarantee the required service-life. Premature deterioration of concrete structures is a major and growing worldwide problem. For example, in the UK, around half of construction turnover is devoted to repair and maintenance, a large fraction of which is spent on concrete structures. There is consequently a great deal of commercial interest in the durability of concrete structures.

Structures deteriorating prematurely present a safety hazard. Cement manufacturing is an energy intensive industry and the emission of greenhouse gasses, about one tonne of CO_2 per tonne of cement produced, creates an environmental concern. Demands for enhanced performance, safety, economics and environmental protection create an increasingly pressing need to be able to determine, with an acceptable degree of confidence, the projected service-life of concrete structures. The challenge now facing practicing engineers is to design and build structures that not only satisfy the specified structural requirements, but also achieve the performance levels required from a durability standpoint. However, this is not possible, if the processes undermining durability that occur at the micro- and nano-scale levels, i.e. molecular / ionic transport in pores, are not well understood.

At least ten different concrete deterioration processes have been recognised [Buenfeld, 1997]. With the exception of mechanical wear due to abrasion and spalling effects of fire, all other deterioration processes are directly linked to the transport of aggressive agents into concrete. Therefore, the durability of concrete largely depends on the ease with which fluids, both liquids and gases, can enter into and move through concrete [Neville, 1997]. The major transport mechanisms participating in concrete deterioration include pressure-induced water flow, water absorption, water vapour diffusion, ionic diffusion, gas diffusion, pressure-induced gas flow and electrical conductivity [Buenfeld, 1997]. Corrosion of embedded steel occurs when the passivity of steel resulting from the alkaline pore-solution has been removed, most commonly by carbonation or chloride ingress, and is sustained by the availability of moisture and oxygen. Carbonation rate depends on gas permeability and is also influenced by moisture content. Sulphate attack is controlled by the rate of penetration of sulphate ions into concrete, which requires moisture for mobility, and so does chloride ingress. For frost damage to occur, concrete has to be above a critical degree of water saturation in a freeze/thaw environment and hence is rate-controlled by water movement. In alkali-aggregate reaction, the transport of water, alkali and gel will affect the rate of deterioration. In essence, molecular/ionic transport into concrete via its pore structure can be considered as the rate-controlling step in all chemical degradation processes [Buenfeld, 1997]. Therefore, determining the ionic/molecular transport rates is the key element to service-life prediction models.

Tests that measure the rate of molecular/ionic transport are of great interest with respect to determining durability potential. Each transport process can be described by a transport coefficient, and various test methods are available to obtain this. The transport process depends on the driving force, be it a pressure or concentration gradient, capillary suction or a combination of these, while the transported matter can be in the form of ions or molecules. However, due to the slow nature of most transport processes and the long period required to condition the sample prior to testing, it may take months, perhaps years for a dense material, to determine its transport properties reliably. To reduce the test period, the transport process may be accelerated, for example, by applying a high hydrostatic head in a water-permeability test or an electrical field in an ion-diffusion test, but the accelerated process will most likely deviate from the process that occurs naturally. A high-pressure gradient may damage the sample whilst a strong electric field used to drive ions through the sample can result in temperature rise and may induce changes in pore structure and resistivity of the specimen. The validity of accelerated testing is often questionable because the measured coefficients do not reflect actual structures in service.

Since mass transport can only occur via the available connected pore space, an alternative approach to quantifying the transport processes, perhaps in a more efficient and reliable manner than conventional testing, is to first characterise the pore space and then apply that information to mathematical models for predicting the required transport coefficients. This approach is non-trivial, particularly for cement-based materials, where the pore structure is highly random and complex with length scales covering at least six to seven orders of magnitude from the nanometre to the millimetre scale. The initial pore structure depends on the various mix constituents and proportions, and its complexity is compounded by its continuously changing structure due to cement hydration, thermal/moisture exposure history, mechanical treatment and interaction with external species.

To predict mass transport from a quantified pore structure, the challenges involved include understanding how the various transport processes occur in the complex pore structure, identifying and isolating the type of pores controlling transport, measuring the relevant pore properties and developing mathematical models based on sound physical principles for each transport process. This requires, primarily, the development of the right tools to probe (image) the relevant pores at the right length scales and to make direct measurements. Fortunately, techniques for direct examination and quantitative analysis of the microstructure at localised areas are available. Recent advances in various forms of microscopy techniques, such as backscattered electron microscopy, image analysis and computational processing power, have provided the opportunity to tackle this problem. The development of pore structure-property relationships can only be achieved by a precise description of the pore space geometry, which can then be parameterised by means of image analysis and mathematical characterisation.

Another advantage of such microstructural models is their potential to be extended for prediction of any property controlled by the pore structure, notably, strength, elasticity and shrinkage behaviour. Accurate quantitative characterisation of the pore structure, and the overall microstructure in general, allows us to understand the time-dependent behaviour of cement-based materials and to develop better and more durable materials. In a broader sense, porous materials are ubiquitous in everyday life, be they synthetic or naturally occurring. Understanding the transport phenomena through a porous medium has wide-ranging applications, from oil and gas recovery from oil-bearing sandstones to determining the movement of contaminants in soil and the efficiency of industrial packed filter beds.

1.2 Objectives and scope

The aim of this thesis is to develop backscattered electron microscopy and image analysis methods for characterising and quantifying the pore structure in cement-based materials. This thesis hopes to achieve a better understanding of the nature of the pore structure and how it influences molecular transport properties.

Concretes, mortars and pastes with a range of pore structure characteristics will be investigated. Concrete is the material of most practical interest, but is complex, while pastes and mortars are easier to analyse because of their lack of large aggregate particles. The emphasis will be on developing a suitable sample preparation methodology and appropriate image analysis procedures for quantitative characterisation so that accurate and reproducible results are attainable. The study hopes to adopt a more rigorous approach towards quantitative backscattered electron microscopy. This will require consideration of the electron-solid interactions in the electron microscope in order to study the signal sampling volume and signal variation across phase boundaries. At the same time, the theoretical resolution limit of backscattered electron microscopy and measurement errors for pores will be investigated.

Finally, this study hopes to develop simple pore structure-transport models for rapid prediction of transport properties based on the extracted information of the pore structure as input values. It is foreseeable that the accuracy of the models will be limited due to the two-dimensional nature of the imaging technique and size range limitation, but the work presented here would serve as a precursor to development of comprehensive three-dimensional models in the future.

1.3 Thesis outline

This thesis is divided into ten chapters. Chapter 1 outlines the motivation, objective and scope of the study. Chapter 2 provides a literature review on the subjects relevant to the scope of this thesis. Chapter 3 gives the experimental approach, detailed test procedures and instrumentation used.

The main findings of this study are presented in the next six chapters. Conventional image analysis methods for pore segmentation are subjective and error-prone, requiring many images to obtain statistically significant results. This presents an obstacle for practical

applications of quantitative microscopy. In Chapter 4, a new method for pore segmentation that is robust, eliminates operator judgement and requires fewer images to achieve statistical confidence is proposed.

Knowledge of the size of the electron-solid interaction volume and the sampling volume of various signals within it is important for interpretation of images and analytical results obtained from electron microscopy. In Chapter 5, a Monte Carlo method is used to simulate electron trajectories in order to investigate the shape and size of the interaction volume, the spatial and energy distribution of backscattered electrons and characteristic x-rays in cement-based materials. Chapter 6 extends the Monte Carlo simulation from a point analysis to a line scan, in order to investigate the change in detected backscattered electron signals across pore-solid boundaries of known geometry and composition. Results from the simulations are used to verify the pore segmentation method presented in Chapter 4, as well as to determine the theoretical resolution limit and measurement errors for pores.

Chapter 7 deals with the recently reported phenomenon of ‘patch microstructure’, that is, broad dense and porous regions separated by sharp boundaries and occurring randomly in the bulk and interfacial transition zones. No quantitative results are given in this chapter, but the subject matter is important for understanding how mass transport occurs through the microstructure of cement-based materials.

Chapter 8 presents a new image analysis procedure using Euclidean Distance Mapping to compute microstructural gradients at interfaces in composite materials. This method is capable of producing phase distribution plots at the highest resolution very quickly and efficiently compared to conventional dilation-subtraction strip analysis, and is not constrained by feature geometry and boundary conditions. This method is applied to investigate the porosity and unreacted cement distribution, and their spatial variability at the interfacial transition zone. The transport properties of mortars with a range of sand volume fractions are tested to explore the role of the interfacial transition zone in molecular transport.

Chapter 9 forms a preliminary study on the feasibility of using the two-dimensional pore parameters obtained from image analysis as input values to simple analytical pore-transport models for direct computation of transport coefficients. Parameters relating to the three-dimensional pore microgeometry are estimated. The accuracy and limitations of these models are discussed.

Finally, Chapter 10 summarises the key findings from this thesis and Chapter 11 gives various suggestions and recommendations for further work.

Chapter 2

Literature review

This chapter presents a literature review on the subjects relevant to the scope of this thesis. Topics covered include the pore structure in cement-based materials, methods for characterising the pore structure, backscattered electron microscopy and quantitative characterisation using stereology and digital image analysis.

2.1 Pore structure and properties

Concrete is a multi-phase material. At the simplest level, it consists of aggregate particles in a continuous cement paste matrix, with the interface between cement paste and aggregate surfaces regarded as a third phase. The hydrated cement paste can be further divided into several phases: the unreacted cement particles, various types of hydration products and pores. In-depth description of the cement chemistry and hydration process, the resulting microstructure and its development with the hydration process is given in major textbooks on cement and concrete science such as Neville [1997], Taylor [1997] and Hewlett [1998].

The hydrated cement paste contains many different types of pores, with sizes that cover several orders of magnitude from the nanometre to the millimetre scale. The pore structure is an important phase as it influences not only mechanical strength, but also elasticity, shrinkage, creep, mass transport and durability. The importance of the pore structure is reflected by the existence of a huge body of work dedicated to its study. The types of pores are conventionally classified as, in the order of decreasing size: entrapped air, entrained air, capillary pores and gel pores. Cracks may also exist, and these are differentiated according to their size and origin. Another distinct type of pore is the hollow-shell hydration grain, also known as Hadley grain, after its discoverer [Hadley, 1972]. The interfacial transition zone (ITZ) is not strictly a pore type, but refers to the cement paste area adjacent to aggregate particles that contains statistically higher amount of porosity. The ITZ has an important influence on the properties of concrete and as such, has been a subject of interest in many studies over the last several decades. Patch microstructure is another form of inhomogeneity in the microstructure that has been recently reported and will be dealt with separately in Chapter 8.

2.1.1 Gel pores, capillary pores, cracks and air voids

The cement hydration process produces nanometre-sized pores known as gel pores, which are interstitial spaces residing in the main hydration products, in particular the calcium silicate hydrates (C-S-H). The C-S-H contain close to 30% volume of gel pores, hence it can hold a large quantity of evaporable water. The total volume of gel pores in cement-based materials increases with the amount of C-S-H, hence with degree of hydration. Gel pores have a size range of 1 to 3nm [Mehta & Monteiro, 1993; Neville, 1997], which is about an order of magnitude bigger than the size of a water molecule ($2.5\text{\AA} \sim 0.25\text{nm}$), but are much smaller than the capillary pores.

Capillary pores are residues of the space originally occupied by the mix water and have dimensions approximately one to two orders or magnitude larger than gel pores [Neville, 1997] or around 0.01 to 10 μm [Powers, 1961; Mindess & Young, 1981]. Capillary pores are progressively filled with hydration products as the paste matures. Hence, the total capillary porosity depends on the amount of water present in the mix, or the free water-to-cement (w/c) ratio and the degree of hydration. As the process of hydration proceeds, the total capillary pore volume decreases, but gel pore volume increases.

Air voids are relatively larger pores that are caused by either incomplete compaction (entrapped air) or intentional air entrainment (entrained air). Entrapped air voids are empty spaces that have not been removed during the compaction process and typically have dimensions up to several millimetres, which are visible by the naked eye. Smaller entrapped air voids tend to be near spherically shaped, while larger entrapped air voids have irregular shapes. Entrained air voids have sizes between 50 and 200 μm [Mehta & Monteiro, 1993], are spherically shaped and evenly distributed in the hydrated cement paste. These are deliberately introduced into the sample for improving freeze-thaw resistance.

The issue pertinent to this study is to identify the type and the size range of pores that are relevant to mass transport in cement-based materials. Gel pores of the order of 2 to 3 nm are too small to have a significant influence on transport in most practical situations. However, gel pores have significant influence on shrinkage and creep while capillary pores are mainly responsible for strength and penetrability [Neville, 1997]. As hydration proceeds, the capillary pores may become blocked by hydration products and this result in a capillary pore system that is interconnected by the finer gel pores.

It is generally assumed that the lower size limit for capillary pores having significant importance to mass transport is about $0.1\mu\text{m}$ [Wesche et al., 1973; Mehta & Manmohan, 1980; Nyame & Illston, 1980; Goto & Roy, 1981]. The International Union of Pure and Applied Chemistry [IUPAC, 1972] classifies pore types depending on how water behaves in them. According to the IUPAC, pores are divided into micropores ($< 2.5\text{nm}$), mesopores (2.5 to 50nm), macropores (50nm to $10\mu\text{m}$) and air voids ($> 10\mu\text{m}$). Micro and mesopores are in a size range where electrostatic interactions between the pores walls and liquid phase extend over a significant fraction of the pore area and so, mass transport through pores of this size is hindered by electrostatic forces. Micropores and the smaller mesopores are considered to form the intrinsic gel pores, while both meso and macro pores make up the capillary pore system. Therefore, it is unlikely that pores much finer than $0.1\mu\text{m}$ will have a significant effect on mass transport.

Hollow-shells are pores left behind within hydrating cement grains. These are ubiquitous, but their role in transport is unknown. Entrapped/entrained air voids are discrete and isolated pores, and are expected to have low contribution to transport. Cracks may also exist in the hardened cement paste; these are differentiated depending on the origin and cause of cracking, for example by mechanical damage, tensile stresses from expansion due to a thermal gradient, reinforcement corrosion, freeze-thaw attack or alkali-silica reaction; and restrained shrinkage due to self-desiccation or moisture movement. In a severely damaged sample, cracks may form an interconnected link and provide a short-circuit path for mass transport to occur rapidly through the cement paste. The amount and nature of the cracks will then have a predominant influence on mass transport over the capillary pore structure.

While aggregates are also porous, their porosity is generally very low compared to the paste. Aggregates are fully enveloped by cement paste and so are expected to have only a secondary influence on transport. The porous cement paste is the only continuous phase in the microstructure where transport predominates so the presence of aggregates only reduces the total porosity, adds to its tortuosity and hence the resistance to mass transport. However, another possible effect of the presence of aggregates to transport lies in the interface between its surfaces with the hydrated paste, a region known as the 'aureole de transition' or the interfacial transition zone (ITZ). The idea of ITZ originated from optical microscopy observations made by Farran [1956] about 50 years ago. Since then, a vast number of researches have been dedicated to studying the nature of the ITZ and its influence on concrete properties. The ITZ has been reviewed in numerous articles, for example, by Struble et al. [1980], Larbi [1993], Ollivier et al. [1995], and Scrivener et al. [2004b]. The ITZ has also been

the subject of two technical committees of RILEM, which have published state-of-the-art reports [Maso, 1996; Alexander et al., 1999.]

2.1.2 Interfacial Transition Zone

The conventional view of the ITZ is that it is a region of the cement paste, approximately 20 to 50 μ m wide around each aggregate particle, where its microstructure is ‘disturbed’ by the very presence of the aggregates. The result of this is a ‘zone’ surrounding each aggregate particle where the microstructure is significantly different from the cement paste located farther away, i.e. the ‘bulk cement paste’.

The main reason for the formation of the ITZ is that during mixing, cement particles are unable to pack closely against the much larger aggregate particles; this is known as the particle-packing effect or the wall effect. Consequently, there are fewer cement particles present near the aggregate particles compared to paste regions farther away. Also, bleed water tends to accumulate on the aggregate surface during compaction. Both factors create a w/c ratio gradient that decreases from the vicinity of the aggregate particle to the bulk paste, causing an initial higher porosity at the ITZ than in the paste farther away.

Apart from the particle-packing effect, the higher porosity at the ITZ is also contributed to by the one-sided growth effect, as noted by Garboczi & Bentz [1991]. In the bulk cement paste, the pore space is filled with hydration products by migration of species from all directions. At the interface however, hydrates can only migrate from the paste side. According to De Rooij et al. [1998], the syneresis effect in a colloidal system, that is the expulsion of water from the hydration gel in its early formation, could also be a factor in the formation of a water-rich zone near aggregate particles.

Evidence for the existence of ITZ came from many early observations made using the scanning electron microscope in the secondary imaging mode on fractured surfaces. However, care should be taken in the interpretation of early studies because fractured surfaces may not be representative of the actual interface since they only reveal, selectively, planes of weaknesses. Such studies are also limited by their qualitative characteristic.

The development of the use of backscattered electron (BSE) imaging on flat-polished samples of cement-based materials and subsequent quantitative image analysis, a technique pioneered by Scrivener and co-workers in the 1980s [Scrivener & Pratt, 1984; Scrivener et al., 1987; Scrivener & Gartner, 1988], has finally allowed for proper and unam-

biguous quantitative characterisation of the microstructure. The examination of flat polished samples enables volume fraction measurement of each phase in the microstructure, as well as their spatial distribution to be assessed in two dimensions.

The variation of anhydrous cement, porosity and CH content with distance from aggregate particles in the ITZ can be assessed by using a series of interfacial strips extending from the aggregate boundary. Scrivener & Gartner [1988] showed that the porosity near the aggregate surface can be up to three times the value of the bulk porosity. The quantity of anhydrous particles was found to be very low at the interface and increases almost linearly with distance. The amount of CH at the ITZ was marginally higher than at the bulk paste [Crumbie, 1994]. However, studies by Diamond & Huang [1998, 2001] using a similar technique, found that the deficiency of cement grains near the aggregate surface was only statistical, and many cement grains close to or touching the aggregate were shown to present. Also, it was observed that the excess in mean porosity at the ITZ was much less than that reported in previous investigations. In a recent review of the ITZ, Scrivener et al. [2004] emphasised that the ITZ is a zone of gradual transition not drastically different from the rest of the cement paste and is highly heterogeneous. Nevertheless, the average microstructural features in the ITZ can be measured by image analysis of a large number of images.

The ITZ is often accepted as the ‘weakest link’ in concrete with respect to strength performance. Studies have shown that microcracking initiates at the ITZ before propagating to other areas [Hsu & Slate, 1963; Slate & Olsefski, 1963]. The deleterious effect of ITZ on mechanical properties is clear, for example, the compressive strength of a paste can be 30% higher than that of a mortar and up to 50% higher than that of ordinary concrete [Gilkey, 1961]. This is partly due to the differences in elastic behaviour between the aggregate particles and cement paste as well as the higher porosity at the ITZ, which significantly increases the probability of microcracking at the ITZ during loading. Studies of stress-strain behaviour of concrete under uniaxial compression show that microcracks that exist in the ITZ remain stable up to about 30% of the ultimate load, then begin to slowly increase in length, width and number; this is known as the slow crack propagation stage. Between about 70% and 90% of the ultimate load, fast crack propagation occurs when cracks begin to bridge and form a continuous link until failure occurs [Mehta & Monteiro, 1993]. However, at a constant w/c ratio, it is known that increasing the aggregate content generally increases compressive strength. This is thought to be due to a lower total porosity in the leaner mix.

For ordinary concretes, the hydrated cement paste is weaker than the aggregate particles so the ITZ will be the limiting factor in determining the ultimate strength. For ‘high-

performance' concretes containing very low w/c ratio and various microfiller pozzolanic materials, the situation is reversed; the strength of aggregate particles become the limiting factor in determining the ultimate strength. Bentur & Cohen [1987] showed that by using silica fume, increase in concrete strength in the order of 25-30% over plain cement concrete can be achieved, without any corresponding strength increase in the paste sample. Scrivener et al. [1988b] found that the ITZ for silica fume concretes was much denser, with porosity level similar to that of the bulk paste. This suggests that most of the strength enhancement is the result of an improved aggregate/matrix bond at the ITZ.

Since ITZ is more porous than the bulk paste, then it is also likely that it will have an effect on penetrability [Struble et al., 1980; Young, 1988]. By penetrating Wood's metal into concrete samples while being subjected to mechanical load testing, Scrivener & Nematì [1996] found in subsequent microscopic observation that the ITZ is permeated preferentially to the bulk paste. This suggests a higher connectivity of the pore structure at the ITZ and hence, its importance to mass transport. Considering that the mean spacing between aggregate particles in ordinary concrete is only about 75 to 100 μ m [Diamond et al., 1982], and an ITZ thickness of approximately 50 μ m, most of the cement paste lies in the ITZ. Therefore, it is believed that at high aggregate content, the ITZ will overlap and become interconnected, forming a continuous path of high porosity that acts as 'short circuits' for transport. Indeed, using mercury intrusion porosimetry, Winslow et al. [1994] found that mortars with a sand volume exceeding 48% showed extra-intruded pore space at pressure less than the threshold pressure. This was attributed to the percolation effect of the overlapping ITZs.

The idea of percolation through overlapping ITZ has received much support in terms of computational modelling and development, for example the hard core/soft shell model [Snyder et al., 1993]. Such models predict a threshold aggregate content above which mass transport should increase significantly. However, experimental transport testing does not always provide clear evidence in support for this prediction.

In fact, there is a lack of conclusive laboratory data to verify the deleterious effect of ITZ on transport. Early work by Valenta [1961, 1969] found that the permeability of the ITZ was much greater than the aggregates or the hardened cement paste. Watson & Oyeka [1981] observed that the oil permeability of concrete specimens is about 100 times greater than for cement paste specimens, while Norton & Pletta [1981] and Nyame [1985] found an increase in permeability of mortars with increasing aggregate volume fraction. However, later work by Wakely & Roy [1982], Mindess [1986], and Malek & Roy [1988] found that the ITZ does not seem to play any significant role in determining the permeability of concrete.

Due to inherent difficulties in investigating the influence of the ITZ on transport, some studies have resorted to using model specimens where the random paste structure is approximated by simpler geometries by casting cement paste onto a large piece of aggregate. Using such simplified sample geometries, Xie & Tang [1988] found that the electrical conductivity of the ITZ is higher than the bulk paste matrix. Costa et al. [1990] and Ping et al. [1991] found increases in permeability and electrical conductivity due to ITZ and calculated that the conductivity of the ITZ is ten times greater than that of the bulk paste. Studies by Breton et al. [1992] and Bourdette et al. [1995] indicated that the effective chloride diffusivity is 6 to 12 times greater in the ITZ than in the bulk paste. Whilst such studies show that the ITZ is indeed more penetrable than the bulk paste, they offer limited information as regard to the overall performance of the composite since the mass transport path in real mortar and concrete is certainly more complicated than in the model specimens.

Houst et al. [1993] studied the influence of aggregate fraction on gas diffusivity of mortar. Their results showed that as the sand content increased from 0% to 50%, both CO₂ and O₂ diffusivity decreased, but increased significantly at a higher sand content (55%). The authors explained that the steep increase in diffusivity at 55% sand content is due to an interconnected ITZ. However, the authors did not verify this phenomenon by repeating measurements at higher sand contents (only one point in their graph showed increase in transport). In another study, Halamickova et al. [1995] found that increasing sand content from 0% to 55% volume fraction resulted in a higher chloride diffusivity and water permeability for mortars at w/c 0.4, but this was less evident at w/c ratio of 0.5. This paper, together with the one by Winslow et al. [1994] is most often cited as direct evidence for percolation of interconnected ITZ.

Hornain et al. [1995] investigated the chloride diffusivity of cement pastes and mortars with and without limestone filler at a fixed w/c ratio of 0.55. Their results showed that the chloride diffusivity was reduced with addition of sand and limestone filler. Using impedance spectroscopy, Tumidajski [1996] found that the electrical conductivity of ITZ was not much different from that of the bulk paste and that the presence of aggregates decreased the overall conductivity. In another study using impedance spectroscopy, Shane et al. [2000] found a significant difference in conductivity between the ITZ and the bulk paste when a localised area was examined, but the presence of ITZ did not affect the global electrical conductivity of the mortar.

Delagrave et al. [1997] measured the chloride diffusivity of mortars with w/c: 0.25, 0.38 and 0.45, and sand volume fraction of 0%, 19%, 30%, 50% and 57%. In a subsequent

study, Delagrave et al. [1998] measured the tritiated water diffusivity of mortars with w/c ratio 0.25 and 0.45, and sand volume fraction of 0% and 50%. Both studies did not detect a critical sand volume threshold at which the bulk transport property increases rapidly, in fact, a decrease in diffusivity was observed. Carcasses et al. [1998] also found a consistent reduction in gas permeability of mortar specimens (w/c 0.5 and 0.35) with increase in sand volume fraction (10% to 60%). In another study, Buenfeld & Okundi [1998] found a steady reduction in various transport properties (O_2 diffusion, O_2 permeation, water absorption, electrical conduction, chloride diffusion and carbonation) in concretes when the cement content was reduced from 450 to 300kg/m³ at constant w/c ratio. Reducing cement content at a constant w/c ratio equates to increasing aggregate content.

The disagreement between experimental data from various sources suggests the difficulty in quantifying the effect of ITZ on mass transport. This is partly because different compositional parameters are varying together when the aggregate volume fraction is changed. Transport testing also requires some form of sample drying and severe drying treatments may cause microcracking at the weaker ITZ. At a high aggregate content, these artificially induced microcracks could significantly alter transport measurements. Nevertheless, most recent studies have consistently show that the ITZ has an insignificant influence on the bulk transport property. Aggregate particles act as obstacles to transport by reducing the overall porosity and increasing the tortuosity of the transport path. Also, because of water conservation, a higher initial w/c ratio at the ITZ will inevitably result in a lower w/c ratio and a denser bulk paste. These factors appear to predominate over the resultant porous ITZ in influencing mass transport.

2.1.3 Hollow-shell hydration grains

Another distinct pore type that can be found in cement-based materials is the hollow-shell hydration grain, also known as Hadley grain [1972], after its discoverer. In his Ph.D. thesis, Hadley observed that a shell of hydration products forms on hydrating cement grains at early ages. As hydration continues, a progressively larger void space develops within the shell. Most of the hydration shells will eventually become completely hollow, while some contain remnants of anhydrous particles. This observation appears not to agree with early hydration models [Powers, 1961] that predicted the deposition of hydration products both inside the original cement grain boundary (inner product) and outside in the original water-filled spaces between cement grains (outer product).

Barnes et al. [1978] showed that hollow-shells are not only confined to interfaces, but they exist throughout the bulk paste. Later observations using BSE detection confirmed that hollow-shells are indeed a characteristic feature of cement hydration [Scrivener, 1989; Kjellsen et al., 1996 & 1997; Kjellsen & Atlasi, 1999]. According to Diamond [1999], cement grains form a shell of hydration products around themselves during the first few hours of hydration. The shell is approximately $1\mu\text{m}$ thick, and is composed of C-S-H gels with some CH, and occasionally extensions of ettringite needles or thin calcium monosulphate plates [Diamond, 1987]. During subsequent hydration, the shell may either deposit dense layers of inner hydration products, forming what is known as a ‘Williamson grain’ [Williamson, 1970], or, empty out in a hollow-shell mode and precipitate hydration products in the capillary voids between adjacent shells. Diamond [1987] suggested that whether a cement grain develops into a Williamson or a Hadley grain depends on the amount of pore-solution filled space in the vicinity. Hollow-shells mode appears to be favoured where pore-solution filled spaces are available, for example near the ITZ, while the Williamson grain development appears to predominate in dense areas, for example in closely-packed cement grains.

It has been shown that hollow-shells are not an artefact caused by drying or particle pull-outs during specimen preparation [Kjellsen et al., 1996]. Kjellsen et al. [1997] observed that smaller cement grains, for example alites and aluminates, will hydrate completely by one day and leave completely hollow-shells, but inner products may increasingly form at later ages and fill up the empty spaces. Belite grains may also hydrate according to the hollow-shell mode, leaving a partially hollow-shell with a characteristic striated structure [Kjellsen et al. 1997]. Large cement grains may leave hollow-shells with a remnant anhydrous core. It has been argued whether or not a hollow-shell had to be completely hollow to qualify for the designation, but generally, any void space within the original boundaries of the cement particle is considered a hollow-shell [Hadley et al., 2000]. However, it is possible that some of the apparently completely hollow-shells are, in fact, corners of larger hollow-shells containing remnant anhydrous cores that have been sectioned. Since the formation of hollow-shells is related to cement hydration, they have a size in the order of cement grains ($25\mu\text{m}$) but smaller ones ($<5\mu\text{m}$) may still be observed due to the edge effect. At low w/c ratios, hollow-shells can be larger than capillary pores by more than two orders of magnitude [Kjellsen et al. 1997].

The question pertinent to this study is whether hollow-shells are relevant to transport. Scrivener [1989] measured the total porosity of a cement/silica fume paste using image analysis on BSE images and found that the value is similar to that of plain cement pastes, despite a significantly lower permeability of the blended paste. On examination, it was ob-

served that most of the remaining large pores in the blended paste were in fact hollow-shells, indicating that these may have little contribution to transport. Kjellsen et al. [1997] examined silica fume pastes of low w/b ratio to estimate the hollow-shell content. Since most of the non hollow-shell pores especially for mature pastes were below the detection limit for the image analysis system, Kjellsen et al. [1997] reported that the pores derived from hollow-shell grains (which constituted all the pores detected) ranged from 1-9% in different mixtures. The authors assumed that the capillary pores are too small to be detected after 1-day hydration in the low w/b ratio pastes. The quantity of hollow-shells was found to decrease with increasing age and decreasing w/b ratio.

According to Kjellsen & Atlasi [1999], capillary porosity is reduced and hollow-shells are 'preserved' when silica fume is added. The reason for this is unclear, but the preservation of hollow-shells results in reduction in capillary porosity because hydration products are preferentially deposited into the capillary pore space rather than inside the original cement grain boundary. They hypothesise that the reduction of capillary porosity due to the formation and preservation of hollow-shells is an important reason why silica fume is so efficient in reducing penetrability. Hollow-shells are enclosed in cement gel, but connected to capillary pores via fine gel pores; hence the large 'enclosed' hollow-shells will presumably not contribute much to transport. Kjellsen & Atlasi [1999] also observed that hollow-shells seem to remain saturated and smaller capillary pores desiccate before the larger hollow-shells, apparently because the hollow-shells are not drained until their smaller entryway pores (gel pores) are drained.

Hollow-shells are ubiquitous in hydrated cement paste, but their nature, process of formation and influence on bulk properties of cement-based materials is imperfectly understood. Whilst they are visually distinct from other pores, segmentation of hollow-shells in a backscattered electron image is not a straightforward task, making quantitative analysis difficult. Since hollow-shell pores appear to be enclosed by a layer of dense hydration products, it is generally assumed that transport does not occur through these voids, although no conclusive experimental evidence exists. However, our recent work using laser scanning microscopy for three-dimensional imaging of sub-micron pores [Head et al., 2005] found that many of these hollow-shell pores are in fact, connected to the capillary pore structure. The size and degree of connectivity between the hollow-shell and capillary pores increases with w/c ratio and for young samples. Therefore, hollow-shell pores may play a role in mass transport, particularly for very porous or high w/c ratio systems.

2.2 Methods for characterising the pore structure

It is common to describe pore structure by its porosity, specific surface area and size distribution. Porosity is defined as the fraction of the bulk volume of the porous material that is occupied by voids, while specific surface is defined as the interstitial surface area of the pores per unit bulk volume [Dullien, 1992]. Porosity is a parameter that is relatively easy to measure, but it does not provide information of the geometry, spatial distribution or the size distribution. Specific surface is related to the refinement of the pore structure, for example, given a certain porosity value, the material with a higher specific surface will have a finer pore structure. The definition for pore size, however, is ambiguous and is subject to the measurement technique. For random porous materials such as cement-based materials, it is extremely difficult to assign a parameter that adequately characterises the pore size due to the inherent complexity and irregularity of the pore structure [Scheidegger, 1974]. Therefore, the parameter pore size is usually an intuitive simplification of reality.

The pore structure can consist of interconnected pores that form a continuous phase within the porous medium, dead-end pores or ‘blind’ pores that are interconnected only from one side, and non-interconnected pores or isolated pores [Dullien, 1992]. Only the interconnected pores can contribute to transport, while dead-end pores have a negligible contribution. For mass transport, the shape, tortuosity and connectivity of the pore structure are also of fundamental importance, but are harder to define and to measure. Whilst these parameters can be used to describe simple pore configurations effectively, their application to complex pore structure has generally achieved limited success.

There exists a wide range of techniques for pore characterisation, but none of these can adequately determine all aspects of the pore structure. Each method has its own limitations in terms of resolution or its ability to describe specific features of the pore structure. There are several complications involved in characterising pores in cement-based materials. The pores have sizes ranging over many orders of magnitude with a large proportion having dimensions of less than $10\mu\text{m}$. The pores are random and have very complex geometries. Another difficulty arises from the fact that the pores contain a large amount of moisture. These can be in a state of ‘free water’ in large pores, or physically adsorbed water at the pore walls, or chemically bound water within the hydration products. Since most measurement techniques require the removal of pore moisture, the obtained results may be affected by changes or artefacts in the microstructure depending on the severity of the drying treatment.

Experimental pore characterisation techniques can be divided into either indirect or direct methods. Indirect methods are those that detect the presence of pores and thereby deduce their properties from measurements of a secondary or a derived property [Haynes, 1973]. Examples of commonly used indirect methods for characterising cement-based materials include D-drying for evaporable water content, resaturation using water or alcohol, solvent exchange using alcohols or organic solvents, nitrogen adsorption, helium pycnometry, mercury intrusion porosimetry (MIP), nuclear magnetic resonance, small angle X-ray scattering and quasi-elastic neutron scattering [Day & Marsh, 1988; Thomas et al., 1999].

Some indirect methods can give a misleading picture of the pore structure because their interpretation often requires assumptions on the mechanism of the test involved and on the pore geometry. The validity of some of these assumptions is questionable [Diamond, 1989]. As would be expected, different indirect methods can give varying views on the pore-structure, for example, different fluids differ in their abilities to penetrate the pore system. The microstructure may also be altered from severe sample drying, which is a requirement of many indirect methods, and by the action of the fluid subsequently introduced. This can be particularly critical for cement-based materials because the microstructure is sensitive to temperature and unstable upon removal of moisture. Changes to porosity, surface area and other properties have been shown to occur when the material is dried using rigorous methods [Parrott et al., 1980; Parrott, 1981; Moukwa & Aitc n, 1988]. Changes in the microstructure occurring on drying, particularly for the smaller pores, may not be reversible upon rewetting [Pratt, 1988].

MIP has been the most widely used method for studying the pore structure of cement-based materials because of its ability to cover a wide range of size. In this method, mercury is forced into the sample by gradually increasing the applied pressure. The volume of intruded mercury is recorded at each discrete pressure increment; this intruded volume is equivalent to the pore volume and the pore-size distribution is calculated from the Washburn [1921] equation. However, MIP does not provide information concerning spatial distribution because the pores are not imaged and, due to the high pressures and sample drying treatment, is destructive [Beaudoin, 1979; Feldman, 1984; Day & Marsh, 1988; Olson et al., 1997]. Other inherent weaknesses of MIP include the cylindrical pore shape assumption in the Washburn equation, the ink-bottle effect and uncertainties in the true contact angle [Shi & Winslow, 1985]. MIP results should only be interpreted qualitatively as it is not a true reflection of the actual pore sizes [Diamond, 2000]. Studies using image analysis have found that the pore diameters estimated from MIP are at least two orders of magnitude smaller than the actual value [Lange et al., 1994; Diamond & Leeman, 1995].

Direct methods are those that involve optical or scanning electron microscopy, which produce an image of the microstructure and revealing the morphology of the pore structure together with its spatial distribution [Pratt, 1988]. Direct imaging methods have advantages over indirect methods because they are capable of producing an unambiguous characterisation of the microstructure. Quantitative measurements on a two-dimensional image can be achieved by image analysis, and the results can be related to the three-dimensional structure by using stereology [Underwood, 1970; Russ & Dehoff, 2001].

However, an inherent drawback of quantitative microscopy is its size range limitation. This presents two complications: first, the ability to resolve the smallest features present, and second, the size of the field of view necessary to obtain a statistically valid representation of the microstructure. Increasing the magnification can improve resolution to a certain extent, but a high magnification will result in a small field of view, and hence, a larger number of images must be analysed to obtain statistical significance. A small field of view also limits the size of the largest feature that can be quantified accurately, regardless of the total number of images analysed. Transmission electron microscope gives a much higher resolution than the electron or optical microscope, but the sampling area is very limited and the sample preparation is difficult and time consuming.

The ideal method for characterising pores would not only be of high resolution, but also would cover the size range of pores relevant to transport, measure them in a relatively undamaged state, provide spatial location relative to the surrounding phases and allow 3D aspects of the pore geometry to be measured. The pore parameters that are needed for transport modelling include global information (porosity, specific surface), morphology (shape factor) and topology (tortuosity, connectivity, constrictivity). Application of stereology on 2D images can conveniently provide global information, but is inadequate when it comes to quantifying pore morphology and topology. 3D imaging can overcome this, but this area is relatively new and largely unexplored on cement-based materials. Nevertheless, recent developments in the application of various forms of 3D imaging to cement-based materials, for example, synchrotron X-ray microtomography [Gallucci et al., 2005], focus-ion beam nanotomography [Holzer et al., 2005] and laser scanning confocal microscopy [Head & Buenfeld, 2005b] is promising and opens up new possibilities for accurate 3D characterisation of the pore structure. All of these methods have their advantages and disadvantages in terms of the limitation in resolution and sampling volume, or the level of effort, time and resources required. However, with further technological advancement associated with these methods, it is foreseeable that a complete description of the pore structure by a combination of various forms of microscopy techniques is within reach in the near future.

2.3 Backscattered electron imaging of cement-based materials

The development of scanning electron microscopy (SEM) has enabled a vast amount of research on the microstructure of cement-based materials. Early SEM studies were carried out using the secondary electron (SE) imaging mode on fractured surfaces, which offers high resolution, but qualitative data. Beginning in the early 1980s, the application of backscattered electron (BSE) imaging mode on epoxy impregnated flat-polished samples, as pioneered by Scrivener & Pratt [1984], began to supersede the SE mode in most SEM studies. Despite its lower resolution compared to the secondary mode, examination in the backscattered mode has been extremely useful for quantitative studies. As opposed to fractured surfaces, a flat-polished surface represents a random cross-section of the microstructure, allowing unbiased quantitative characterisation of the various phases present. The basic working principle of the SEM is available in standard texts such as Goodhew et al. [2001] and Goldstein et al. [2003]. A review of SEM applied to cement and concrete research is available in a book chapter by Richardson [2002]. The use of the BSE imaging mode on cement-based materials has also been recently reviewed by Scrivener [2004] and Diamond [2004b].

When the electron beam strikes the sample in the electron microscope chamber, the incident electrons interact with the sample and their energy is dissipated by a series of scattering events. The region into which the electrons penetrate the sample is known as the interaction volume, and throughout it, various radiations are generated because of elastic and inelastic scattering. For cement-based materials, the lateral dimension of the interaction volume has been reported to be approximately 1-2 μm [Diamond, 1972; Detwiler et al., 2001; Scrivener, 2004] and the volume of material analysed by the electron probe approximately 1-2 μm^3 [Jensen et al., 1996]. The types of radiations that are emitted from a sample are differentiated depending on whether they are photons or electrons, and their associated energy level; these include auger electrons, secondary electrons, backscattered electrons, X-rays and cathodoluminescence. Secondary and backscattered electrons are usually used for imaging, X-rays are primarily used for chemical analysis, while auger electrons have very low energy such that they require an ultra high vacuum system and specialised equipment for their efficient use. The volume of material contributing to any emitted signal is known as the sampling volume; for X-rays, this is of the same order as the interaction volume. The electron-solid interactions in cement-based materials will be studied in detail in Chapters 5 and 6.

Secondary electrons, caused by inelastic scattering, originate from the smallest sampling volume, giving a better spatial resolution than other signals. Secondary electrons have much lower energies than the incident electrons and their intensity depends on the local inclination of the specimen surface. Therefore, secondary electrons are used for generating topographical images. On the other hand, backscattered electrons are incident electrons that have been elastically scattered through a wide-angle and re-emerged from the sample. The sampling volume of backscattered electrons is larger, and thus, they produce a lower spatial resolution when compared to secondary electrons at the same accelerating voltage. The intensity of backscattered electrons depends primarily on the local atomic number of the specimen and its topography, but the contribution from the latter is negligible for a reasonably well polished flat specimen.

Since the intensity of the backscattered electron increases monotonically with the atomic number, different phases in a composite material will have different brightness depending on their mean atomic number. Thus, the detection of a backscattered electron signal as the incident beam is scanned across the entire sample surface can be used to generate an image that contains compositional information about the sample. Individual phases will have different grey values in the image depending on their chemical composition. For a hydrated cement paste, the anhydrous cement particles will have the highest brightness intensity, followed by calcium hydroxide, calcium silicate hydrates and the resin-filled pores, which will appear as the darkest phase. This feature of backscattered electron imaging allows for segmentation and quantitative analysis of the various phases that exist in the microstructure.

The unreacted cement usually gives a distinct peak on the brightness histogram and therefore can be segmented rather easily and reproducibly by choosing the grey level corresponding to the minima between peaks as the threshold value. The peak for calcium hydroxide tends to overlap with C-S-H, making segmentation more difficult. The C-S-H phase is also hard to segment because it tends to have a range of grey levels due to varying CaO/SiO_2 ratio and microporosity [Famy et al., 2002]. Pores, the subject of interest in this study, are also hard to segment accurately despite being visually distinct. The appearance of a pore peak in the grey level histogram is not consistent and depends on its volume fraction. If the brightness and contrast setting of the microscope is calibrated and standardised for all images, selecting an arbitrary grey level threshold in the lower region of the histogram may provide a consistent measure of pore structure. However, if an accurate quantitative analysis of the pore structure is required, then a more precise definition of the pore-solid threshold must be developed. The issue of pore segmentation will be explored in detail in Chapter 4.

Examination of flat-polished samples by BSE mode enables the discrimination of individual phases as well as the assessment of their spatial distribution. The images can be subsequently digitised and analysed by image analysis. When sufficient images are analysed over different locations, the obtained results will be representative of the sample. In a study by Scrivener et al. [1987], the absolute volumes measured by image analysis on BSE images were compared with those determined by indirect methods for OPC pastes with a range of w/c ratios and hydration times. It was observed that the anhydrous cement volume fraction from image analysis agreed well with that determined by loss on ignition. The porosity measured by image analysis was found to be lower than by methanol adsorption, particularly at younger ages. This was possibly due to the limited resolution of the BSE images ($> 0.5\mu\text{m}$) compared to methanol adsorption ($> 36.8\text{nm}$), as well as the presence of large pores ($> 20\mu\text{m}$) that were not properly sampled by image analysis. Nevertheless, there was a good correlation between both sets of measurements. However, the measurement of the CH phase did not compare as well with the amount determined by thermogravimetry analysis. This was attributed to the inhomogeneous distribution of CH within the microstructure, hence a greater number of fields must be analysed in order to obtain a more accurate measurement [Scrivener et al., 1987].

2.4 Stereology

Stereology is a branch of science that determines the geometric relationships between an object that exists in three-dimensions and the images of that object that are in two-dimensions [Underwood, 1970; Russ & Dehoff, 2001]. Stereology provides a set of tools that relate measurements made on two-dimensional images to the actual three-dimensional structures that are represented and sampled by these images. These images are normally obtained from random cross-sections or projections of the particular object. The most intensive use of stereology has been in the field of materials science, in conjunction with microscope images such as from light and electron microscopes, for quantitative analysis of microstructures. Nevertheless, stereology has found wide-ranging applications in other fields including astronomy, geology, botany, anatomy and other life sciences. Reviews of modern stereological methods can be found in textbooks by Howard & Reed [1998] and Russ & Dehoff [2001], while classical methods are described in Dehoff & Rhines [1968]; Underwood [1970]; Weibel [1979] and Russ [1986].

All stereological methods are based on the requirement to sample the object of interest using various probes, make sufficient number of measurements and obtain a representative average value. A fundamental necessity is that the sampling method must be random with respect to the feature of interest. The object can be sampled with a population of points, lines, planes, disectors or other probes [Russ & Dehoff, 2001]. Events that result from the interactions of these probes with the feature of interest are tallied. Normalised averages of these counts are used to estimate the corresponding average for the entire population of probes. Fundamental stereological relationships are then applied to relate these values to a geometric property of the structure being sampled. Unbiased stereological measurement requires that the probes employed be chosen isotropically, uniformly and randomly from the corresponding population [Howard & Reed, 1998; Russ & Dehoff, 2001].

The two most common stereological measures, and indeed the two mainly used in this thesis, are volume fraction and surface area per unit volume. Consider a multi-phase material, in which the different phases can be discriminated by their brightness intensity or colour, in an image taken on a random section of the material. If the image is representative of the whole, then the volume fractions of each phase in the material (V_V) can be estimated from its area fraction (A_A) obtained from the random section. This is the most fundamental and oldest stereological rule that was first discovered more than 150 years ago by a geologist [Delesse, 1847] who studied polished rock sections.

Subsequent developments in this field established that further simplifications to this rule exists; that other simple fractions such as the fractional linear intercept (L_L) and the point count fraction (P_p) are also equal to the area and volume fractions. The fractional linear intercept can be obtained by drawing many random lines on the image and measuring the length that intersects the phase of interest, divided by the total line length. The point count fraction is determined by superimposing a random distribution of points on the image and counting the number of points, which happen to hit the phase of interest. Thus, the complete relationship can be written as:

$$V_V = A_A = L_L = P_p \quad \text{Eq. 2.1}$$

Note that the nomenclature indicates a fraction of the total amount for volumes (V), areas (A), line lengths (L) and point counts (P).

The second fundamental property that can be easily determined using stereology is the surface density (S_V) or the total surface area of the phase of interest contained in a unit

volume of the material. The surface area is a parameter of interest because it is a valuable indicator of the capacity of a surface-limited process such as diffusion across the surface, efficiency of gas exchange in a mammalian lung or a catalytic system [Howard & Reed, 1998], or to quantify the pore geometry in an oil bearing sandstone [Scheidegger, 1974]. The surface density is the surface area of the interface per unit volume of the reference space, thus having the dimensions of L^2/L^3 , which simplifies to L^{-1} . In a planar section, surfaces are represented as phase boundaries so are seen as lines, and the total length of these lines is proportional to the amount of surface area present in the three-dimensional structure. Therefore, it would be expected that the surface density is somewhat related to the boundary length per unit area of the random section (L_A) or the number of intersection points per unit length of the probe lines (P_L). The stereological equation for surface area density is:

$$S_V = 2P_L = \frac{4}{\pi} L_A \quad \text{Eq. 2.2}$$

Note that the factors 2 and $4/\pi$ appear in the above equation because the test lines and plane section do not intersect the phase boundaries at a right angle [Russ, 1986].

The basic stereological relationships shown in Eq. 2.1 and Eq. 2.2 are deceptively simple yet very powerful. The mathematical derivations of these apparently simple equations have been discovered several times independently and can be found in traditional texts in the field of stereology such as by DeHoff & Rhines [1968]; Underwood [1970]; and Weibel, [1978]. These relations do not make simplifying assumptions about the details of the geometry of the structure [Russ & Dehoff, 2001]. For the purpose of this study, it is only necessary to note that the accuracy of these equations depend only on the randomness of the sampling probe with respect to the material investigated, and not on the way in which the individual phases are shaped, dispersed or organised in the matrix [Russ, 1986]. These stereological equations are valid for simple as well as for complex materials exhibiting microstructural gradients and anisotropies, as long as the sampling procedure ensures that the population is uniformly sampled to yield representative data that do not produce bias in the result [Russ & Dehoff, 2001]. However, it is important to address the statistical problem of sampling, which is to say that many images must be taken from different fields of view, spread across the sample in an unbiased way, and analysed. The average measurement will approach the true value as more measurements are made.

2.5 Image Analysis

Image analysis forms a part of a wide-ranging field of image acquisition, processing and analysis, the main objective of which is to capture information in a digital image that is subsequently enhanced, analysed and measured. An image is a representation of an object. The human eye is a biological device for creating and capturing images, but human vision is primarily qualitative and comparative, rather than quantitative [Russ, 2002]. In addition, the human eye relies solely on the visible portion of the electromagnetic spectrum (wavelengths between 400-700nm) to create an image, while electronic sensors are now available that can detect and create images from infrared and ultraviolet radiation, X-rays and radio waves. Even signals other than electromagnetic radiation can be used to form an image, for examples, the atomic-force microscope that measures the topography of a specimen by using an atomic-scale probe and the acoustic microscope that detects acoustic waves. Developments in such devices have enhanced and increased our imaging capability tremendously.

Image analysis is a means of obtaining quantitative information from an image. It consists of image acquisition, signal treatment, mathematical morphology, stereology, pattern recognition and even three-dimensional reconstruction from a set of two-dimensional images. The first step is to acquire a digital image by using an input device such as a digital camera, video camera, flatbed scanner or microscopes equipped with a charge-coupled device (CCD). The subsequent steps involve an image processing software that may be first used to enhance the image and to prepare the image for quantitative measurements, by correcting for any defects and by increasing contrast between different features if necessary.

The feature of interest is then extracted by using a segmentation algorithm that may involve brightness or colour thresholding, edge or even motion detection. Thresholding refers to a user-selected grey level range in which every pixel that has a grey value within the threshold range is painted white, and all other pixels are painted black. The threshold is selected to separate the features of interest from their background. This step is usually the most crucial, but also the most difficult to implement accurately. A binary image is created after feature segmentation, and this image can be further processed by Boolean (arithmetic) operations and morphological operations to correct for segmentation errors.

Global measurements such as surface area, number of features and size distributions, and feature specific measurements such as brightness, size, perimeter, orientation, location or shape, can then be performed easily by counting pixels corresponding to the phase

of interest in order to extract required quantitative information. Application of image analysis can be found in various fields, including space research, satellite imaging, medical and life sciences, biotechnology, exploration and mining, navigation, surveillance, remote-sensing, forensic research, robot vision, artificial intelligence and even food technology [Russ, 2002].

In cement and concrete research, the rising use of image analysis since the mid-1980s is closely related to the development of optical microscopy as a petrographic tool for quality control in clinker production, identification of phases and diagnosis of concrete damage and deterioration, as well as the development of backscattered electron microscopy for quantitative characterisation of cement-based materials. Comprehensive reviews on the subject of concrete petrography are available in an article by French [1991] and in an inaugural textbook on the subject by St. John et al. [1998].

Visual assessment using a microscope is purely qualitative and subjective, making reliable comparison with other findings difficult. Although it is possible to measure feature size on microscopes fitted with calibrated reticules, and to determine the frequency or spatial distribution of features by manual point-count techniques, such procedures are time consuming and labour intensive. The ease with which precise feature quantification can be done by image analysis has led to the growing number of applications in cement and concrete research. These include: quantification of phases in cement clinker [Stutzman, 2004] and in hydrated cement paste [Scrivener et al., 1987; Zhao & Darwin, 1992], studies of the pore structure [Scrivener, 1989; Lange et al., 1994; Diamond & Leeman, 1995]; microstructural gradients at the ITZ [Scrivener et al., 1988], determining the degree of hydration [Mouret et al., 1997; Feng et al., 2004], estimation of the w/c ratio [Mayfield, 1990; Jakobsen et al., 1998], entrained air content and dispersion [Pleau et al., 2001; Dequiedt et al., 2001], micro-cracking [Ringot, 1988], aggregate particle shape and distribution [Mora et al., 1998; Fernlund, 2005], fire damage assessment [Short et al., 2001], alkali-aggregate reactivity potential [Sims et al., 1990], surface roughness [Lange et al., 1993]; deformation and shrinkage [Neubauer et al., 1997] and 3D particle shape analysis [Garboczi, 2002].

The references provided above are not meant to be exhaustive, but represent only a small selective sample of existing studies. These and many other studies that have applied quantitative microscopy have contributed immensely to the field of cement and concrete science. Nevertheless, there is still a lack of progress on relating the observed or quantified microstructural features to the bulk properties of interest, notably ion/molecular transport properties, and therefore, it is hoped that the present study will make a valuable contribution towards this area.

Chapter 3

Methodology

This chapter presents the approach and experimental procedures used in this thesis. Details of the materials, sample preparation, test methods and instrumentation are given.

3.1 Sample preparation

3.1.1 Materials

The ordinary Portland cement used was supplied by Lafarge Blue Circle Cements, which complies with the BS EN 197 - 1 - CEM 1. Its oxide and Bogue compositions are given in Table 3.1. The Blaine specific surface area and specific gravity of the cement were 342m²/kg and 3.15 respectively. An undensified Elkem Microsilica® Grade 940 was used as a pozzolanic micro-filler in some mortar samples. The silica fume contained more than 90% SiO₂, had a loss on ignition of less than 3%, a BET specific surface area greater than 15m²/g and a specific gravity of 2.2

A sulphonated naphthalene-based superplasticising admixture with a trade name Conplast SP430 by Fosroc was used to improve the workability of low w/c and stiff mixes. The admixture complied with BS 5075 Part 3 and ASTM C494, had a specific gravity of 1.20 and contained no chloride.

Composition (%)									
CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	Cl	SO ₃	LOI
65.0	20.5	5.0	2.7	0.9	0.19	0.73	0.008	3.1	1.36
Bogue composition (%)									
C ₃ S	C ₂ S	C ₃ A	C ₄ AF						
56.5	16.1	8.7	8.2						

Table 3.1 Composition of cement

Thames Valley sand and gravel were used as fine and coarse aggregates respectively. The particle size was less than 5mm for sand and ranged between 5 and 12mm for gravel. The sand complied with the BS 882 medium grading while the coarse aggregate complied with the BS 882 graded aggregate. The aggregates were kept in hoppers within the laboratory and hence, were relatively dry. The particle size distribution and physical properties of the Thames Valley aggregates are given in Fig. 3.1 and Table 3.2 respectively.

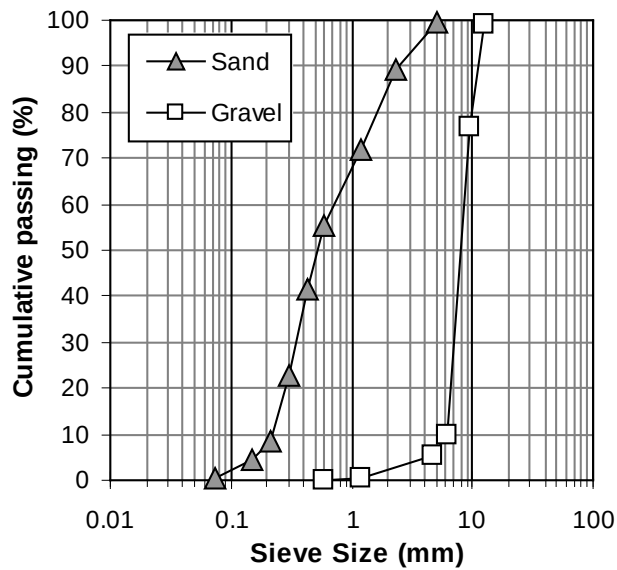


Figure 3.1 Grading curves for Thames valley sand and gravel.

Property	Sand	Gravel
Specific gravity (SSD)	2.6	2.5
Moisture content (%)	0.2 to 0.3	0.4
24-hr absorption	0.9 to 1.3	2.0

Table 3.2 Specific gravity at saturated and surface dry condition (SSD), moisture content and absorption values for aggregates.

3.1.2 Mix proportions

Mix proportions were designed based on the absolute volume method, which assumes that the volume of a compacted sample is equal to the sum of the volumes of all ingredients [Neville, 1997]. Tap water was used as the mix water. Since the aggregates were relatively dry, it is essential to consider the amount of mix water absorbed by the aggregates in the fresh state. The aggregate moisture content was determined prior to casting and the water required to bring the aggregates to ‘saturated-surface dry’ condition, that is the absorption minus moisture content, was added to the water needed to achieve the target free w/c ratio. The mix water was also corrected for additional water brought in by any admixtures used.

For low w/c mixes or stiff mixes, e.g. mortars with high sand content, trials were made to determine the superplasticiser content required to achieve sufficient compaction. The slump for mortars and concretes were all in the range of 30 to 100mm. High w/c ratio mixes, particularly pastes, showed visible signs of bleeding in the fresh state. However, no efforts were made to quantify the amount of mix water lost to bleeding. This provided another source of heterogeneity on the pore structure, which was detected in subsequent transport measurements. The samples prepared for this study are as follows:

1. OPC mortars at w/c 0.35 and 0.7, and cured for 28 days. These were used in an initial study to determine the feasibility of the experimental programme and to test the newly developed pore segmentation method [Chapter 4].
2. OPC mortars at w/c ratio 0.4 and 0.6, with 50% sand volume fraction and cured for 28 days. These were used to investigate the phenomena of ‘patch microstructure’ in cement-based materials [Chapter 7].
3. OPC concrete at w/c ratio 0.4 and OPC mortar at w/c ratio 0.6 (60% sand volume fraction), and cured for 3 and 28 days respectively. These were used to investigate microstructural gradients at the interfacial transition zone using the Euclidean Distance Mapping approach [Chapter 8].
4. OPC pastes at w/c ratio 0.3 and 0.5, OPC-silica fume blended pastes at w/c ratio 0.3, OPC mortars at w/c ratio 0.5 and 0.3, and OPC-silica fume blended mortars at w/c ratio 0.3. The mortars contained between 10 and 70% sand volume fraction.

These were used to investigate the effect of varying ITZ content on molecular transport properties [Chapter 8].

5. OPC mortars at w/c 0.35 and 0.7, and cured for 3 and 28 days. These were conditioned in various ways to produce a range of pore structure characteristics. The samples were then used to establish the feasibility of image analysis to quantify the pore structure for transport modelling [Chapter 9].

The actual mix proportions of these samples will be given in the following chapters where results pertaining to the particular samples are presented. Throughout this thesis, samples will be designated using the approach shown in Fig. 3.2.

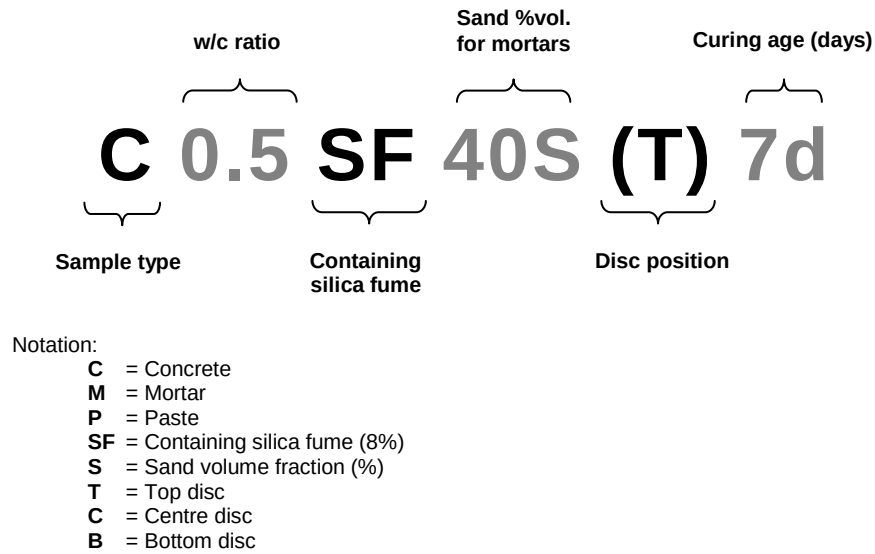


Figure 3.2 Sample designation

3.1.3 Mixing and curing

Materials were batched by weight and mixed in a pan mixer. First, the cement together with any supplementary cementitious materials was added and dry-mixed, followed by sand and gravel. Water was added next. If superplasticizer was used, this was added together with the mix water. The total wet mixing was no more than five minutes.

Cylindrical samples (100mm diameter, 250mm length) were cast in steel moulds. The samples were compacted in three equal-depth layers using a vibrating table. The intensity of the vibration was adjusted according to the workability of the mix; a stiff mix was compacted

at higher intensity than a wet mix. Care was taken during compaction to ensure that the layer did not ‘roll’ when being vibrated because this can result in air entrapment. For each layer, compaction was assumed sufficient when no significant amount of air bubbles escaped the surface. The compacted samples were covered in damp hessian and polythene to reduce evaporation. The samples were demoulded after 24 hours, labelled, then wrapped in a generous amount of cling film and finally sealed in polythene bags. The sealed samples were kept in the laboratory for curing. The ambient temperature and relative humidity of the laboratory was approximately 20°C and 60% respectively. Periodic weighing of the samples found no significant mass loss during curing, indicating the efficacy of the sealed curing.

After a pre-determined curing period, the samples were unwrapped, then sectioned to produce discs for microscopy and molecular transport testing. Each cylinder was cut to give two 10mm thick discs for microscopy and three 50mm thick discs for molecular transport testing. The end discs, approximately 30mm thick, were discarded. For pastes, 20mm thick discs were made for transport testing.

The sectioning was done using a Buehler Delta automatic abrasive cutter. This cutter features an ‘orbital-cutting’ action that minimises the area of contact between the blade and the sample, giving a constant high unit force to enable fast, deformation-free cutting for large and difficult to cut samples. This is achieved by the eccentric rotation of the wheel. A 350mm diamond cut-off blade, which is specifically designed for hard, brittle materials like composites and ceramics, was used. The samples were cut at a feed rate less than 0.3mm/s and water was used as a coolant. Fig. 3.3 shows the surface quality of various cut samples using the Buehler Delta automatic abrasive cutter.

3.1.4 Sample conditioning

Samples for microscopy need to be thoroughly dried before impregnation with epoxy because the pore moisture impedes epoxy intrusion and interferes with its hardening process. In addition, samples that have not been dried thoroughly will outgas when subjected to the high vacuum environment of the scanning electron microscope, which may cause contamination of the microscope and cracking of the sample. However, removing moisture from the hydrated cement paste will inevitably cause some form of alteration to its microstructure, particularly the fine gel pores, depending on the severity of the drying process. Nevertheless, damage occurring to the fine gel pores in the C-S-H phase will not be visible since they are well below the resolution limit of the electron microscope.



P 0.3 (C) 3d



M 0.5 – 50S (C) 3d



C 0.4 (C) 3d



Buehler Delta automatic abrasive cutter

Figure 3.3 Paste, mortar and concrete samples sectioned using the automatic abrasive cutter.

The gaseous diffusivity and permeability, and water sorptivity are also affected by the moisture content of the sample. Therefore, samples must be conditioned to a standard moisture state prior to transport testing. Experimental studies on cement pastes [Chapter 9] showed that the oxygen diffusivity, oxygen permeability and water sorptivity are strongly dependant on the conditioning humidity when the relative humidity is greater than 50% at 20°C. At this conditioning humidity and temperature, it appeared that most of the pores relevant to transport were emptied so further drying resulted in a negligible increase in transport properties. Thus, all samples were conditioned to this level prior to transport testing.

However, the conditioning time necessary for samples to reach moisture equilibrium with 50% relative humidity at 20°C is long; typically, at least a 6-months period is required. In order to lessen the time needed, samples were conditioned at temperatures higher than 20°C. However, to ensure that this was not damaging, care was taken to avoid a high thermal gradient in the sample and excessive moisture loss, particularly during the initial stages of drying. Upon reaching the pre-determined curing age, the discs were first weighed, then placed in an incubator containing soda lime and a saturated $\text{Na}_2\text{Cr}_2\text{O}_7$, giving a relative humidity of around 55% at 20°C. A motorised fan was placed inside the incubator to generate air circulation. The discs were kept in the incubator for 7 days, and then transferred to an oven set at 35°C. Silica gel was used to absorb the evaporated moisture, and as a result, the humidity inside the oven was generally higher than 30%. After 7 days at 35°C, the temperature was gradually increased up to 50°C and the samples were conditioned until equilibrium.

The vapour density at 50°C has to be the same as the vapour density at 20°C and 50% relative humidity in order for the samples to achieve similar equilibrium moisture state at the end of the conditioning regime. Since the saturation vapour density increases with temperature, the oven has to be maintained at a relative humidity lower than 50%, according to the definition:

$$RH = \frac{\rho_v}{\rho_{vs}} \times 100 = \frac{P_v}{P_{vs}} \times 100 \quad \text{Eq. 3.1}$$

where ρ_v , ρ_{vs} , P_v and P_{vs} are the vapour density, saturation density, vapour pressure and saturation vapour pressure.

The relationship between saturation vapour pressure and temperature over a flat surface for liquids or solids is given by the Clausius-Clapeyron equation:

$$P_s = P_o \exp \left[\frac{L_w}{R} \left(\frac{1}{T_o} - \frac{1}{T} \right) \right] \quad \text{Eq. 3.2}$$

where P_s and P_o is the saturation vapour pressure at temperatures T and T_o (in Kelvin) respectively, L_w is the molar heat of water vaporisation ($= 40.7\text{kJ/mol}$) and R is the ideal gas law constant ($= 8.3145\text{J/mol.K}$). Given that the saturation vapour pressure of water at 100°C is known to be 101.325kPa, the saturation vapour pressures at 20°C and 50°C are thus 2.82kPa and 13.29kPa respectively. Therefore, the vapour pressure at 20°C and 50% relative humidity

is 1.41kPa and in order to achieve this at 50°C, the oven must be held at approximately 10.6% relative humidity.

The next step is to find a suitable means to maintain the oven at this humidity level. According to the data compiled by O'Brien [1948], the saturated salt solution giving the closest relative humidity to 10.6% at 50°C is ZnCl_2 (10.0%). Therefore, for the final conditioning stage, samples were kept in the oven at 50°C over saturated ZnCl_2 solution until equilibrium was achieved. This was taken to be when the rate of mass loss was no more than 0.01%/day.

The centre disc of each cylinder was periodically weighed over the entire conditioning regime. Fig. 3.4 shows the mass loss curves for paste, mortar and concrete samples, after having been cured for 3 days. The time taken to achieve equilibrium was around 90 days, and was observed to be approximately the same for all samples regardless of mix proportions and curing age. The shape of the mass-loss curve was also found to be similar for most samples. Generally, a continuous drop in mass was observed in the first 30 days of conditioning followed by a plateau stage where a less gradual drop was recorded.

It is important to note that since the discs were to be tested at room temperature (20°C), care was taken to ensure that the moisture content did not increase when the temperature was reduced from 50°C to 20°C. To ensure this, the discs were kept in the oven until one day before testing, then transferred to a vacuumed desiccator containing silica gel and allowed to cool naturally to room temperature overnight. The discs were taken out of the desiccator only when required for testing. Checks by weighing the discs before and after cooling in the desiccator found negligible mass increase.

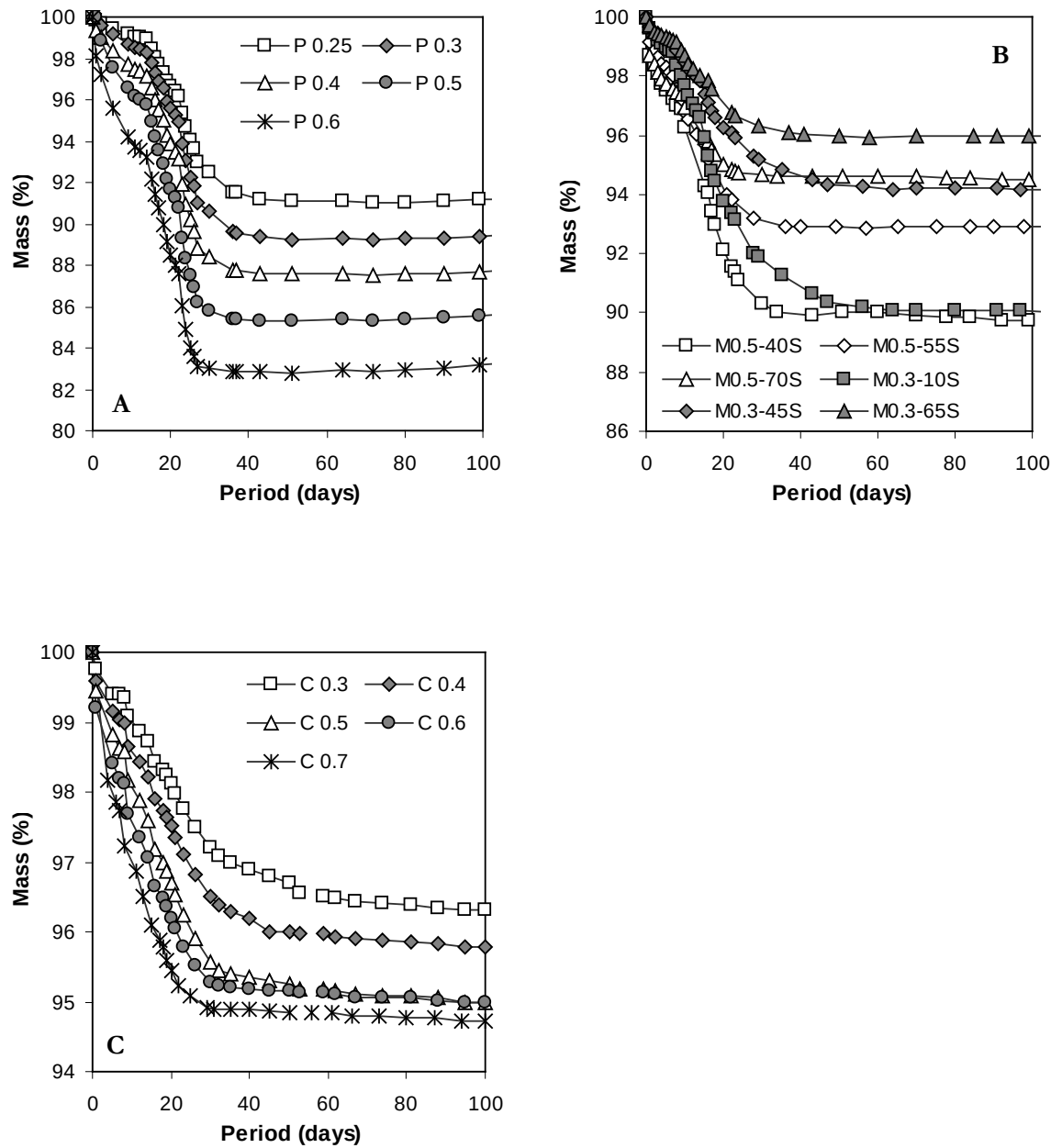


Figure 3.4 Characteristic mass loss curves for A) pastes; B) mortars; and C) concretes during conditioning, after curing in cling film for 3 days. The period is measured from the end of curing.

3.2 Backscattered electron microscopy

3.2.1 Sample preparation for microscopy

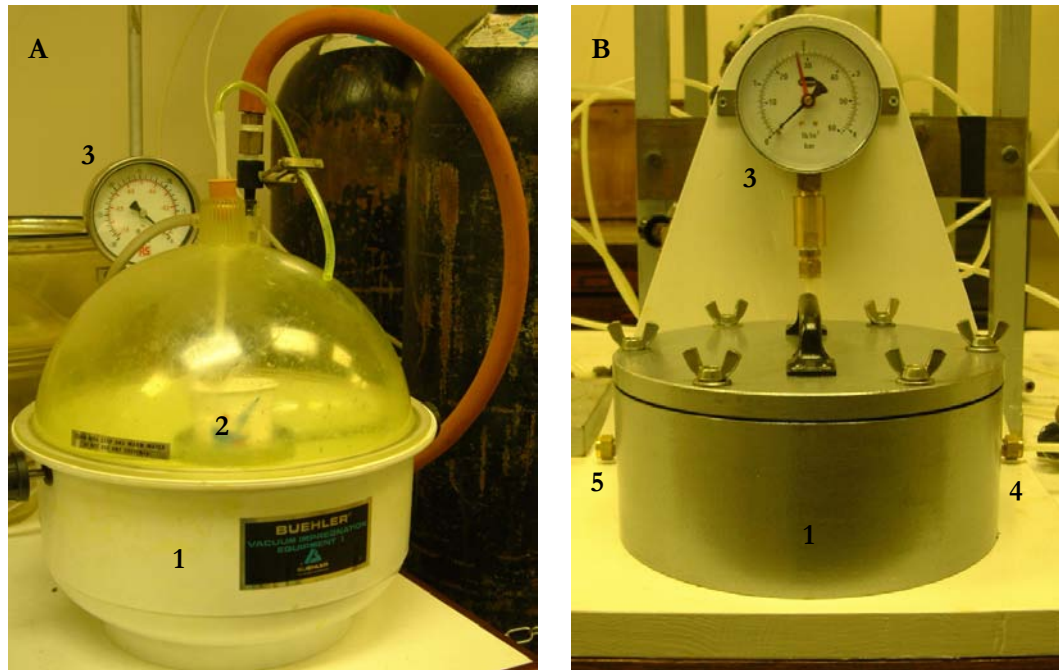
The sample preparation procedures adopted in this study generally follow, in principle, those developed over the last two decades for quantitative microscopy of cement-based materials [Scrivener & Pratt, 1984; St. John et al., 1998; Stutzman & Clifton, 1999; Crumbie, 2001; Detwiler, 2001; Kjellsen et al., 2003]. This involves drying the block sample, embedding with epoxy resin, followed by grinding and polishing at successively finer grades to achieve a flat and well-polished surface. The epoxy supports and protects the microstructure from damage during grinding and polishing, reduces particle plucking and provides atomic contrast so that the pores are visible in BSE images. The sample needs to be well polished because surface roughness as produced from saw cutting interferes with the signal generation/collection process, and compromises image quality by reducing contrast and feature definition. The surface also needs to be planar so that measurements made in 2D can be related to 3D using stereology [Underwood, 1970; Russ & DeHoff, 2001].

The 10mm-thick discs prepared for microscopy (Section 3.1.3) were trimmed using a diamond saw to produce block samples with a dimension of 40 x 20 x 10mm at mid-distance from the centre to the edge of the discs. Then, the blocks were dried by the conditioning approach outlined in Section 3.1.4, or if a rapid preparation was required, by freeze drying using a Lyotrap freeze drier. Freeze-drying is a gentler process of removing moisture by sublimation and desorption. This was done by first immersing the sample into liquid nitrogen (-196°C) for a few minutes until thermal equilibrium was reached. The super-cooling will rapidly freeze the pore moisture, which prevents the formation of large ice crystals that may be destructive to the microstructure. Then, the sample was allowed to dry at very low pressures, about 3 to 5Pa at -40°C . Under these conditions, the ice crystals will sublime, i.e. convert from a solid to a gaseous state without an intervening liquid phase. This process normally took about a week to achieve constant sample mass. Since the drying process does not involve a liquid state, it is less damaging due to the absence of capillary stress effects from a retreating liquid interface. Previous studies using mercury intrusion porosimetry have suggested that freeze-drying is an efficient and a less damaging method for drying cement-based material [Day & Marsh, 1988; Moukwa & Aitcin, 1988; Gallè, 2001].

The dried sample was then vacuum-impregnated with a low viscosity fluorescent epoxy resin. The fluorescent resin was first prepared by adding a fluorescent dye (Struers Epodye) into the resin (Araldite AY103) at 5g/litre resin, and mixed with a magnetic stirrer for several days to ensure uniform dispersion. The fluorescent dye helps to monitor the penetration of the otherwise clear resin into the sample, and ensure that the surface remains saturated with resin after the subsequent grinding and polishing steps. Next, the sample was fitted into a rubber silicone casting mould and evacuated in the impregnation kit (Fig. 3.5 A) for several hours; this is important to ensure that the pores are completely de-aired. Then, the fluorescent resin was mixed with a resin-hardener (HY 951) at a mass ratio of 10 to 1. The resin can be heated up to about 50°C prior to mixing with the hardener to reduce its viscosity. However, a higher temperature will increase the rate of polymerisation between the resin and hardener, resulting in a reduced usable lifetime. Thus, allowance should be made for this.

The resin-hardener mixture was de-aired in a separate vacuum chamber. As soon as the mixture had completely out-gassed, and without breaking the vacuum of the impregnation kit, the resin was poured onto the sample, covering its entire surface. The vacuum was then gradually released to force the epoxy into the pore structure of the sample. We have developed a slight modification on the conventional vacuum impregnation technique in order to achieve a deeper epoxy penetration. This will be further elaborated in Chapter 7. In essence, two additional steps are involved: 1) adding a small amount of toluene (5% wt) to the fluorescent resin to reduce the viscosity further, and; 2) applying a small overburden pressure (2.5 bars) on the sample following vacuum release, in a specially made pressuring device (Fig. 3.5 (B)). The pressure was maintained for at least 30 minutes. Pressuring the sample at this level is routinely used in permeability testing and is not known to cause damage. The sample was then allowed to cure at room temperature for 24 hours before demoulding, and for several days to achieve sufficient hardness.

Following epoxy impregnation, the sample was ground and polished in a series of steps using progressively finer abrasives. Each step successively removes the deformation and damage produced by the previous stage of the preparation; hence, a smoother surface is obtained after each operation. Three types of grinding/polishing media were used for the entire process. Firstly, diamond-impregnated grinding discs at 120 and 220 grit size (Struers MD-Piano 120 and MD-Piano 220) were used to remove excess resin from the surface and for plane grinding. This was followed by fine grinding using dry silicon carbide papers (Struers) of grit sizes 500, 1000 and 1200. Finally, polishing was done using non-woven cloths (Struers MD-Pan) embedded with diamond abrasives of sizes 9, 6, 3, 1 and $\frac{1}{4}\mu\text{m}$.



Notation: 1 = Sample; 2 = Epoxy resin container; 3 = Pressure gauge; 4 = Gas inlet; 5 = Gas outlet.

Figure 3.5 Apparatus for A) vacuum impregnation, and B) for subsequent pressuring.

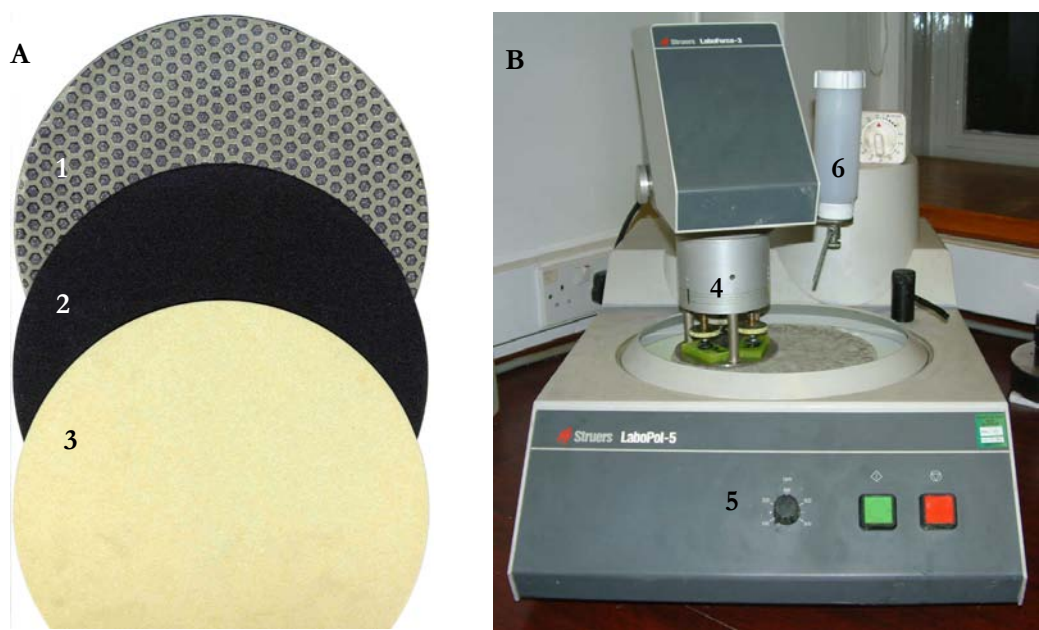
Grinding refers to the process of removing material using fixed abrasive particles that produce chips of the sample as it slides along the grinding plate. Polishing is based on the same mechanism, but uses smaller abrasives to produce smaller chip sizes. By applying successively smaller abrasives, polishing can remove all the deformations and scratches left from grinding. In order to achieve proper grinding and polishing, the pressure between the sample surface and the abrasive must be high enough to generate a cutting force able to produce a chip. The abrasive grains must also be fixed in the horizontal position while the sample passes over to obtain sufficient cutting force, and supported in the vertical direction to obtain the desired chip size. These three factors control the chip size and material removal rate. For fine grinding, the force on the sample should be relatively high to obtain a large chip size. For polishing, a smaller chip size is desirable to achieve a sample surface without scratches or deformations so a lower force on the sample along with smaller grain size is used. Sufficient lubrication between the sample surface and grinding/polishing media is necessary to reduce friction and excessive heat, and to enhance the cutting process.

The grinding/polishing step was performed using a Struers LaboPol-5 machine with variable rotational speed (50-500rpm) fitted with a LaboForce-3 sample mover that rotates at

250rpm. The grinding/polishing media was secured onto the magnetic platen and rotated at a speed of 70rpm, with an approximately 10 to 20N force applied onto each sample. A non-aqueous solution (Kemet lubricating fluid, Type OS) was used as a coolant and lubricant during polishing. Fig. 3.6 shows the polishing/grinding media and equipment used. Each grinding/polishing stage was generally carried out for no longer than 5 to 10 minutes. Polishing time was kept to the minimum to reduce surface relief. To avoid cross-contamination, the sample was cleaned ultrasonically in acetone so that grit and abrasives were removed after each grinding/polishing step.

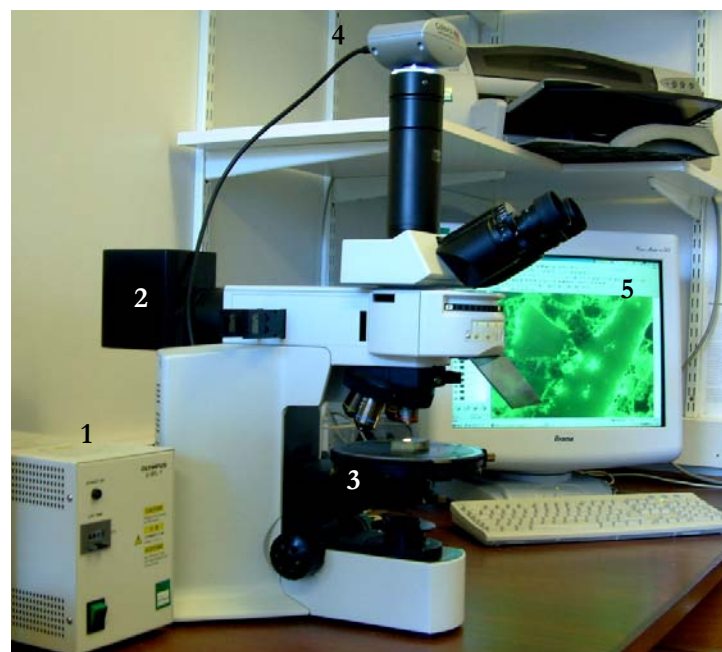
At each stage, the surface quality was monitored using a petrographic microscope in ordinary light and ultraviolet light (for fluorescent imaging) in reflected mode (Fig. 3.7). The sample was processed until no significant change on the surface quality was visible, before moving on to the next stage. Fig. 3.8 is a series of optical micrographs taken using reflected light, showing the evolution of the surface quality after each preparation step. Surface damage such as scratches, pullouts, cracks, lapping tracks and 'comet tails' appear dark in the reflected light mode due to light scattering. On the other hand, a well-polished surface is bright and reflects like a mirror, with sharp phase boundaries and good feature definition. Fig. 3.9 shows scanned images and fluorescent micrographs of the final surface finish for paste, mortar and concrete samples. It is clear from the scanned images and fluorescent micrographs that there is a good resin retention and the sample surface remains saturated with epoxy resin after all the grinding and polishing steps.

If the samples were to be imaged under high vacuum in the electron microscope, then the flat-polished blocks were coated with a layer of carbon using an evaporative coater (Emitech K450). This was necessary to avoid build up of excessive negative charge on the sample. Excessive charging can produce instabilities in the signal level and abnormal contrast, and may even deflect the incident beam, causing distortion in the recorded image [Goldstein et al., 2003]. However, if the imaging was to be done under low vacuum, it was not necessary to coat samples with a conductive layer since the presence of gas molecules in the microscope chamber helped to overcome the problem of charging. The interaction between the incident electron beam and the gas molecules results in the production of positively and negatively charged ions, which will neutralise any charge imbalance on the sample.



Notation: 1 = Diamond-impregnated grinding disc; 2 = Silicone carbide paper; 3 = Cloth for diamond polishing; 4 = Sample holder; 5 = Rotational speed controller; 6 = Lubricant dispenser.

Figure 3.6 A) Grinding and polishing media used, and B) Struers LaboPol-5 with sample holder LaboForce-3.



Notation: 1 = Mercury lamp for fluorescent imaging; 2 = Halogen lamp for normal reflected light; 3 = sample; 4 = CCD camera; 5 = Image analysis system

Figure 3.7 Olympus BX-51 petrographic microscope.

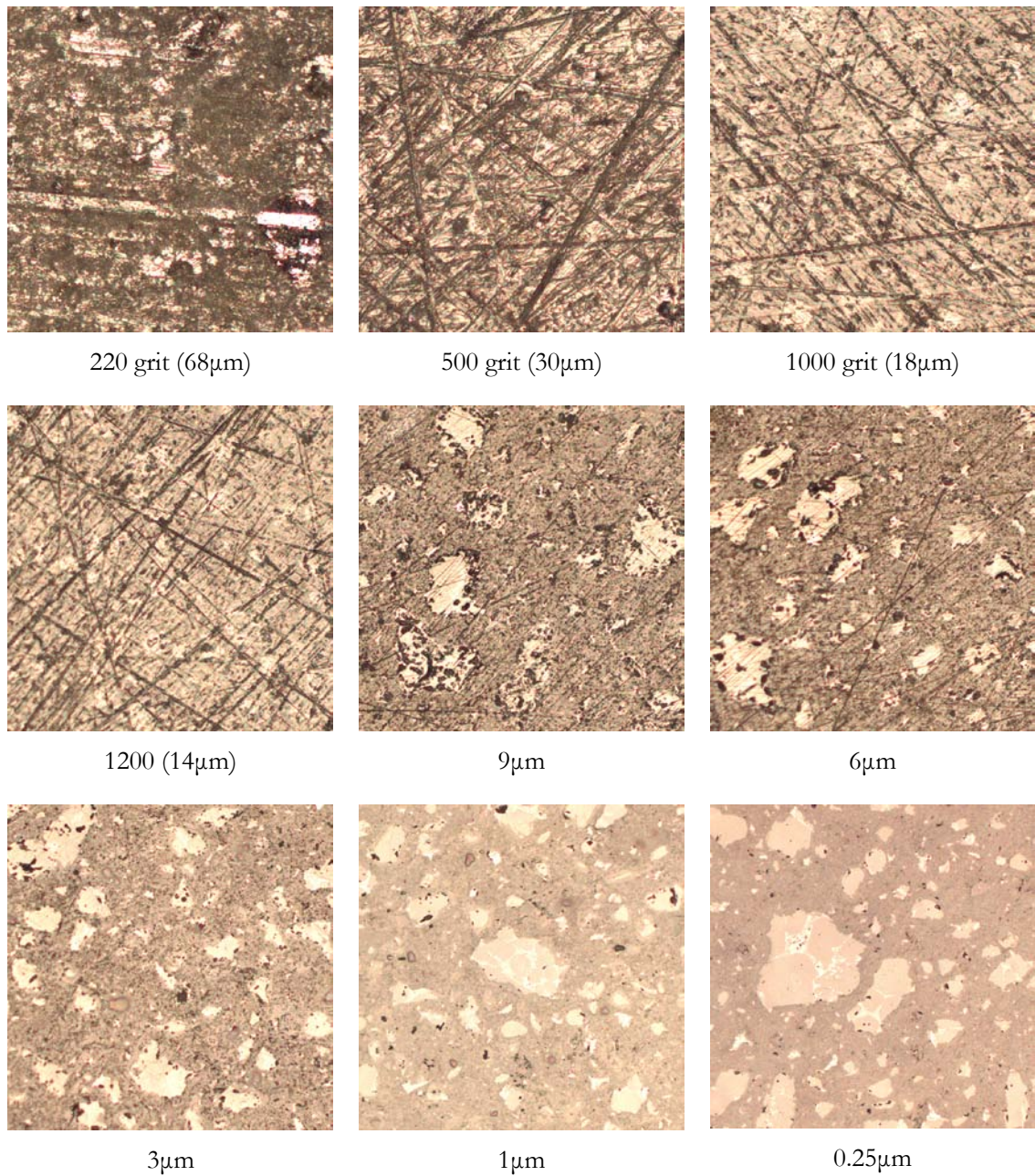


Figure 3.8 Surface quality of the cement paste as the sample is ground and polished at successively finer grit sizes. Note that the images are not from the same area. Images are captured in ordinary reflected light mode, field of view is 300x300 μ m. The sample is P 0.35 – 3d.

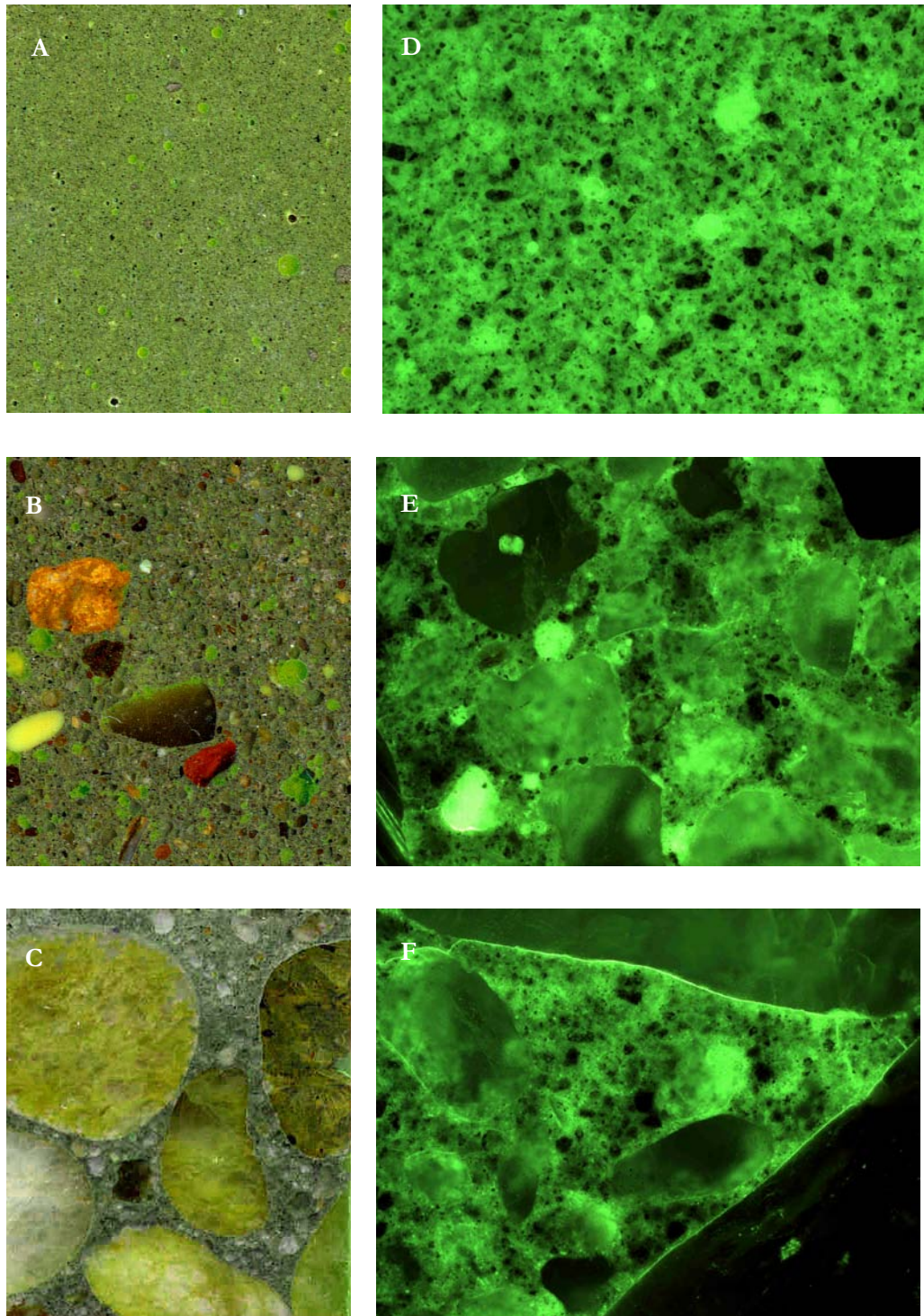


Figure 3.9 Images of the final polished surfaces of paste, mortar and concrete samples, captured using an ordinary desktop scanner (A-C) and a petrographic microscope in fluorescent imaging mode (D-F). Field of view is approximately 15 x 17mm for the scanned images and 1832 x 1374 μ m for the fluorescent micrographs.

3.2.2 Sample preparation damage and artefacts

The quality of the sample surface finish is crucial for backscattered electron imaging. The aim of preparation is to reveal the true microstructure of the sample and to ensure that the attained results are reproducible. Ideally, the finished sample preparation should not contain any foreign induced elements or damage such as deformation, scratches, pullouts, smearing, surface relief or rounded edges. For quantitative studies, it becomes more important to ensure that the measured features are inherent features of the microstructure, and are not artificially introduced during the preparation stages.

Whilst every possible effort was taken in this study to avoid artificially induced features or damage during the sample preparation stages, it is not always possible to guarantee a perfectly flat, scratch-free and artefact-free sample. Cement-based composites are one of the more difficult materials to prepare for microstructural analysis because of their heterogeneous nature. Their phases differ in micro-mechanical behaviour, hardness, and some components are water-soluble or may be damaged by water or by the removal of the pore solution. There will always be slight damage that remains even after all the necessary precautions and thus, it is important to recognise and to differentiate artefacts from the true microstructure during imaging. Examples include occasional bond failures between aggregate particles and adjacent cement pastes due to differential shrinkage, and characteristic drying shrinkage cracks with a triple-branch morphology. In Chapter 7 of this thesis, another form of artefact observed in BSE imaging is presented; this is known as ‘patch-microstructure’ and is a result of grinding beyond the epoxy intrusion depth.

As mentioned in the previous section, damage induced during the grinding and polishing stages such as scratches, pull-outs, cracks, lapping tracks and ‘comet tails’, is easily detectable using an optical microscope in reflected light mode since it will appear dark due to light scattering. Therefore, it is possible to monitor the extent of surface damage at every stage of the preparation process, and to ensure that the damage induced in the previous step is removed prior to progressing to the next preparation step (Fig. 3.8). However, it is often harder to isolate and to treat damage that has occurred prior to the epoxy impregnation step, for example from the saw cutting and drying process, as these would have been filled with epoxy and be ‘preserved’ in the microstructure.

The precautionary steps taken to minimise sample preparation damage are summarised below:

- a) Use of the right cutting tools for hard and brittle materials to ensure minimal deformation and good edge retention. The diamond-impregnated blades were dressed to expose fresh diamonds prior to the start of each cutting process. Silicon carbide abrasive blades were avoided as they produce poor quality, uneven cuts and tend to damage surfaces [St. John et al., 1998]. A slow feed rate was used to avoid cracking.
- b) Thickness of the block samples was no less than 8mm to ensure sufficient mechanical strength to allow for subsequent handling and processing.
- c) Samples were dried using mild conditioning methods that avoided excessive thermal or moisture gradients, except in situations where there was an intention to artificially induce cracks.
- d) Ensuring proper epoxy resin impregnation (Chapter 7) into the pore structure of the samples. A fluorescent dye was added to monitor the presence of resin in the sample surface. The dye also helps to highlight original cracks and pores and differentiate them from any damage, which may occur in subsequent preparation steps. The resin was allowed sufficient curing to achieve the needed strength to withstand mechanical preparation without fracturing and particle plucking.
- e) Use of proper grinding and polishing media, high resilience and low nap cloths for hard and brittle materials, the appropriate choice of applied pressure, rotational speed, amount of abrasives, lubricant and preparation time needed. These have been determined largely from experience through trial and error. Small intervals from one grain size to the next were chosen to effectively remove damage caused by previous steps. A non-aqueous solution was used as lubricant for cutting, grinding and polishing to avoid dissolution and etching of the hydrated phases.
- f) Scratches are grooves caused by the cutting action of the abrasive particles. To ensure their effective removal, the sample should show a uniform scratch-pattern over the entire surface prior to advancing to the next grit size; otherwise, the preparation time should be increased. The sample and holder were cleaned with acetone in between every preparation steps to remove grinding abrasives and grit from the previous step to avoid contamination.
- g) Pullouts are cavities left when particles are torn out of the sample surface during abrasion, while lapping tracks are distinct indentations made by free-rolling abrasive

particles on the surface. These are visible as dark spots or holes under reflected light. To avoid these defects, the smallest possible size was used as starting abrasive for plane grinding and fine grinding. The intervals between each grain size and the next were kept small to shorten the needed preparation time. Low nap and low resilience cloths were used as they have smaller tendencies to pluck particles out of the matrix and provide higher material removal rates.

- h) Checks with the optical microscope were conducted after every grinding/polishing step to ensure that it had removed the damage from the previous one, and had introduced as little damage as possible on its own.
- i) Surface relief is difficult to avoid entirely in mortars and concrete samples because of the inherent differences in hardness between the aggregate particles and the cement paste. However, this can be reduced by using low-resilience polishing cloths and by keeping polishing time as short as possible.
- j) Finished samples were checked using fluorescent microscopy to ensure a proper resin saturation and retention on the surface. Samples were then kept in conditioning boxes at 55% relative humidity that were CO₂ free until required for imaging.
- k) Prior to BSE imaging, samples were observed using secondary electron mode and topographical BSE mode to check for the extent of surface relief and particle pull-outs, and for the overall quality of the surface finish.

3.2.3 Scanning electron microscope

A JEOL 5410LV scanning electron microscope (Fig. 3.10) was used for imaging in the backscattered electron mode. It is equipped with a paired semiconductor backscatter electron detector, arranged symmetrically with respect to the electron optical axis and placed directly above the sample. BSE imaging can be conducted either under high vacuum (10^{-4} Pa) or under low vacuum (6 to 270Pa). The microscope can be operated at accelerating voltages from 0.5 to 3keV (variable in 0.1keV steps) and from 5 to 30keV (in 5keV steps), probe currents of between 10^{-12} and 10^{-6} A, and a large range of magnification is possible, from 15 to 200,000x. The spot size controls the size of the electron beam and is adjustable from 01 to 24 in arbitrary units, with a larger spot size value indicating a larger probe diameter. Three choices of objective lens apertures are available: 40 μ m (high-resolution), 60 μ m (normal resolution) and 120 μ m (large current for energy dispersive x-ray analysis).

The microscope is also equipped with a standard secondary electron detector and an x-ray detector for energy-dispersive x-ray imaging (Oxford Instruments). Scanning speed ranges between 0.27 and 9.6s per frame for normal observation, and a slower scanning speed of 86.4s per frame for image capture. The captured images are digitised using either Link ISIS (Oxford Instruments) or SemAfore (JEOL), offering maximum image resolutions of 1024 x 798 and 1940 x 1455 pixels respectively. Digitised images are stored in either bitmap or .tiff format for subsequent processing and analysis.

The microscope stage has a traverse movement of 40mm and 80mm in the Y and X-axis directions respectively, and the movement in the Z-direction gives a working distance of between 8 and 48mm. The stage movement is electronically controlled and fully programmable via a Deben Research stage controller with an accuracy of 1 μ m. Coordinates can be set, stored and recalled for future use, and the stage can be programmed to move in a sequence or in a grid fashion across pre-defined limits.

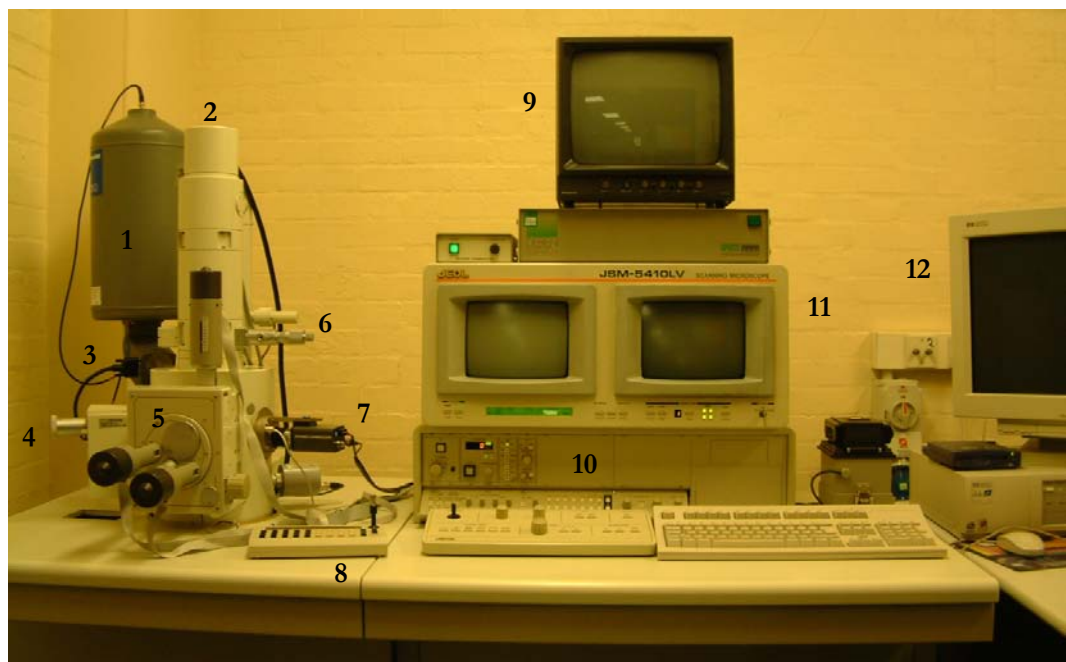
The electron microscope was set up for optimal BSE imaging of pores in cement-based materials. This requires the use of the lowest possible accelerating voltage and a sufficiently large probe current so that a high signal/noise ratio is attainable at a small signal sampling volume. More details on this will be given in Chapters 5 and 6, where a Monte Carlo code was used to simulate the electron-solid interactions in cement-based materials and the BSE signal generation across pore-solid boundaries under various imaging conditions.

At the beginning of every image capture session, the filament heating current was set up to ensure that the tungsten hairpin electron gun was operated at near-saturation point. This gave the highest emission current and brightness, while maintaining a relatively long service life of the filament. The electron gun was aligned to the electron optical axis by adjusting the tilt and shift correction knob, and the objective lens aperture position was centred to allow the electron beam from the filament to be most effectively collected on the sample surface. All the necessary video signal calibration and scan configuration of the image digitiser was checked prior to image capture to ensure a correct grey level reproduction. Distance calibration of the recorded images was performed using two SIRA standardised mesh grids at 19.7 and 2160 lines/mm. The mesh grid was also used to check for stage tilt and to correct for distortion in the image field.

We found that the lowest possible accelerating voltage on this microscope that can give a sufficient signal level for imaging pores in cement-based materials is 10keV. An optimal imaging condition was achieved when a small working distance (10mm) and a large spot size was used (c. 15 to 20) in order to improve the signal-to-noise ratio. For low vacuum im-

aging, the chamber pressure was slowly increased from the smallest value until no charging occurred on the sample; this was normally between 10 and 20Pa. When the microscope was properly set up, no significant difference in terms of image quality and resolution was found between those captured under high vacuum and low vacuum.

Inevitably, the recorded images will contain some amount of noise, or random fluctuation in pixel brightness values that are not due to natural variations in the mean atomic number. Noise can take many different forms and arise from various sources. One unavoidable source of noise is counting statistics in the detector due to a small number of incident particles detected. Noise can also be due to instability of the light source and detector during the time required to scan or digitise the image, electrical interference and external vibration. To improve the signal-to-noise ratio for every image, scanning was done at least four times per frame, and averaged to give the final recorded image. Frame averaging enhances the signal-to-noise ratio because signal detail is constant and will add in successive frames, whereas noise is random and so variations in successive frames will tend to cancel out.



Notation:

1 = Devar for liquid N₂;
 2 = Electron gun chamber;
 3 = X-ray detector;
 4 = Backscatter electron detector;
 5 = Sample chamber;
 6 = Objective lens aperture;

7 = Infrared camera;
 8 = Auto stage controller;
 9 = Chamber monitor;
 10 = Control panel;
 11 = Viewing screens;
 12 = Image digitiser

Figure 3.10 JEOL 5410LV Scanning Electron Microscope.

3.2.4 Brightness and contrast

The digitisation process of the SEM image produces pixel brightness values ranging from 0 to 255. Grey level value 0 represents black pixels, 255 represents white pixels and the remaining grey values (1 to 254) represent increasing brightness intensities from pure black to white. For backscattered electron images, increasing pixel brightness is associated with an increase in the mean atomic number, or the backscatter coefficient of the phases. The properties of a digital image can be conveniently summarised by the image greyscale or brightness histogram, which is a frequency plot of pixels associated with every grey level. The greyscale histogram is a valuable tool for examining the brightness and contrast settings of a particular image. Varying the brightness control changes the dc level of the amplifier output and will cause the greyscale histogram to shift along the x-axis, while varying the contrast control will change the amplifier gain and cause the histogram to either be stretched or compressed.

Obviously, the brightness and contrast settings of the microscope need to be calibrated prior to any image capture. This, in practice, means calibrating the backscatter coefficients of the various phases in the sample to span the entire dynamic range of the available greyscale and allowing the lowest and highest backscatter coefficients to be located within the grey scale limits. More importantly, for quantitative microscopy, the grey value for a particular phase needs to be faithfully reproduced for every image in every image capture session over the entire range of samples investigated, so that meaningful comparison and quantitative data can be obtained. The pixel grey value is very important because all subsequent image analysis will operate based on this number.

Fig. 3.11 is a series of BSE images of an OPC cement paste sample captured at the same location, but at different brightness and contrast settings. The greyscale histograms are plotted below their respective BSE images. It is clear from the figure that the brightness and contrast settings can have a substantial effect on the quality and image detail of the captured image. The appearance of the microstructure, specifically its apparent porosity, can be significantly altered by changing the brightness and contrast.

Fig. 3.11 shows BSE images that were captured at insufficient brightness (A), excessive brightness (B) and insufficient contrast (A, B & C). These are characterised by a narrow range of recorded grey values, much smaller than the entire dynamic range, indicating that only a few levels are represented. A low contrast image contains many unused greyscale bins, hence lacks image detail and resolution.

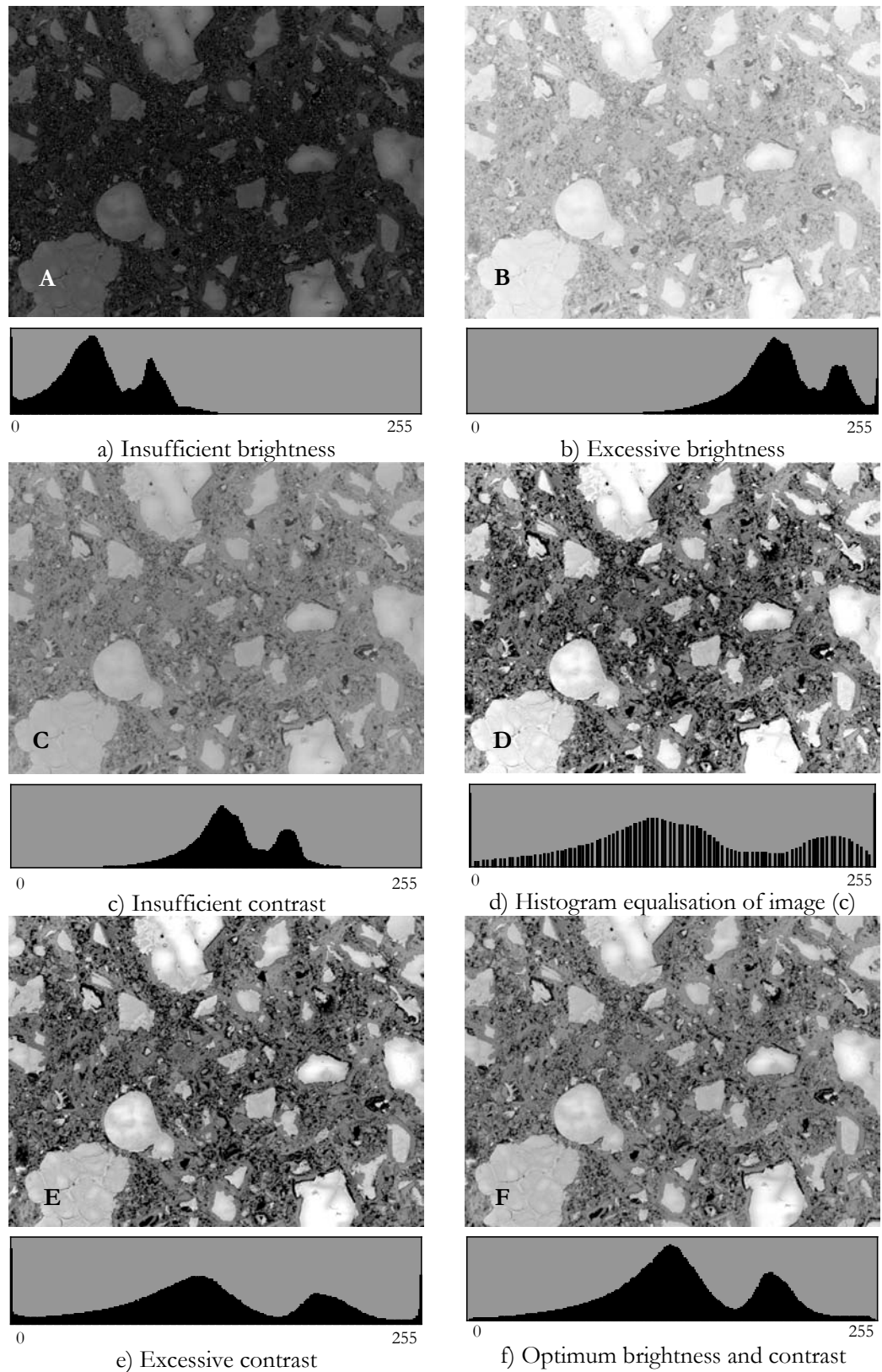


Figure 3.11 Effect of brightness and contrast settings on the appearance of the BSE image (sample is P 0.3 – 3d, images captured at 500x, field of view: 240 x 180μm).

The visibility of features can be improved by image post-processing. This involves some form of histogram equalisation that redistributes the intensity variation, as shown in Fig. 3.11 (D). The darkest pixels in the original image (Fig. 3.11 (C)) are assigned black, the lightest pixel assigned to white and the intermediate grey values are given new values, which are linearly interpolated between black and white. However, if the original image only covers a few of the available grey levels, then histogram equalisation will only spread these out to span the dynamic range, but will not add new ones, hence the new histogram contains the same number of grey values showing zero pixel counts (Fig. 3.11 (D)). The resulting image will look posterised, i.e. have discrete blocks of each brightness level, instead of varying smoothly [Russ, 2002]. Therefore, the histogram equalisation process has increased the visibility and the perceived contrast, but has not increased the ability to discriminate subtle variations in the greyscale that were not recorded in the original image [Russ, 2002].

Another form of image distortion arises from the excessive use of contrast, whereby the amplifier gain is driven so high as to force the signal at peak white or black level to reach the limits of the dynamic range, i.e. clipping or saturation occurs. Fig. 3.11 (E) shows an example of this. This leads to loss of image detail at the low and high ends of the greyscale and formation of artificial peaks at grey level 0 and 255 in the image histogram. The visibility of the image noise is also increased, resulting in a grainy and speckled appearance when the contrast level is set too high [Russ, 2002].

The ideal image is when every possible grey level is represented by some fraction of the pixels so that the entire dynamic range is fully utilised, but not saturated at both ends (Fig. 3.11 (F)). If the greyscale histogram shows that this is not being achieved, then the contrast and brightness controls should be adjusted until the histogram of the recorded image is centred and stretched to span the entire range (0 to 255) for each image. For cement-based materials, this usually means that the lowest grey value should correspond to the epoxy-resin filled pores and the highest to the iron rich ferrite phase. This generally requires trial and error adjustments before an optimum setting is achieved.

Calibration for brightness and contrast

Once the optimum brightness and contrast settings has been found, the same setting needs to be applied to all subsequent images for every sample in order to achieve a faithful reproduction of grey values. To ensure that the same brightness and contrast setting was applied, we used the help of a reference standard for x-ray microanalysis (MAC Ltd.) that contains a 1mm aluminium wire of 99.998% purity that was cast in epoxy and polished. Aluminium was chosen as the reference standard because its atomic number ($Z = 13$, $\eta = 0.153$) falls within the range of mean atomic number for cement based materials ($\bar{Z} \sim 9.4$ to 16.7 , $\bar{\eta} \sim 0.109$ to 0.186), and closely matches that of calcium hydroxide ($\bar{Z} = 14.3$, $\bar{\eta} = 0.162$). The reference standard is fitted into the sample holder and can be imaged together with the sample in the same image capture session.

BSE images of the Al standard were captured at the epoxy-Al interface, at 500x magnification, for several brightness and contrast settings. The greyscale histogram essentially showed a bi-modal curve, the lower grey value peak representing the epoxy phase and the higher grey value peak representing the Al phase respectively. The relative position of the peaks will depend on the brightness and contrast settings, as shown in Fig. 3.12 for three examples. We found that the optimum brightness and contrast settings for imaging cement-based materials was obtained when the epoxy peak and the Al peak were adjusted to correspond to grey values of approximately 45 and 180 respectively (Fig. 3.12 (C)). Hence, these values were used as a reference to calibrate the brightness and contrast settings of the microscope, for every new image capture session.

If the electron beam condition remains stable and the same brightness and contrast settings was used for a particular image capture session, then a common greyscale will be allocated to all images and any given phase will be represented by the same greyscale values. However, it was observed that the electron beam conditions tend to drift over time; this occurs even after a long warm-up time of the microscope. This will have an effect on the grey values as shown in Fig. 3.13, particularly for a long image capture session of a sample, if the beam drift is not corrected by readjusting the brightness and contrast settings. Therefore, during image capture, the brightness and contrast settings were recalibrated periodically to the greyscale histogram of the Al standard in order to correct for any beam fluctuation effects.

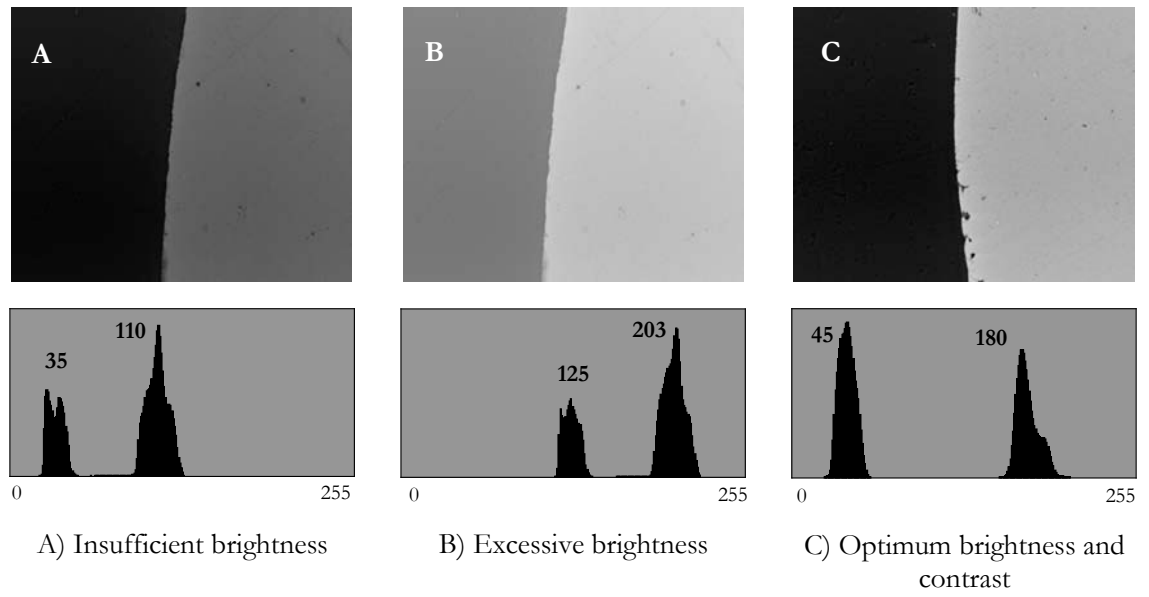


Figure 3.12 Calibration of the brightness and contrast settings using a pure aluminium standard cast in epoxy.

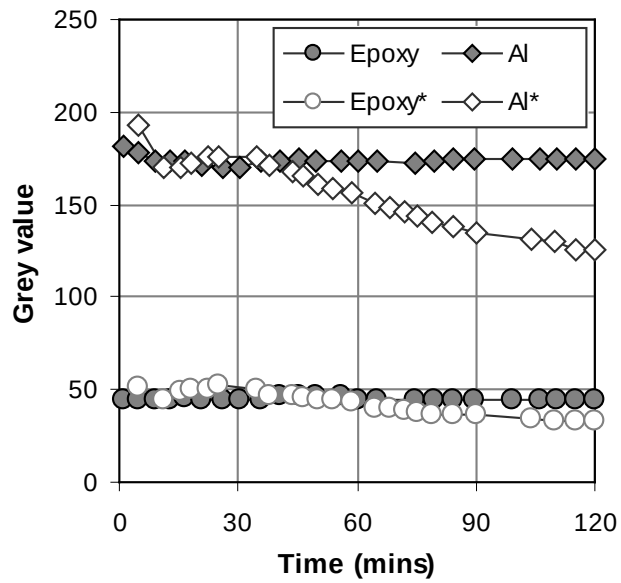


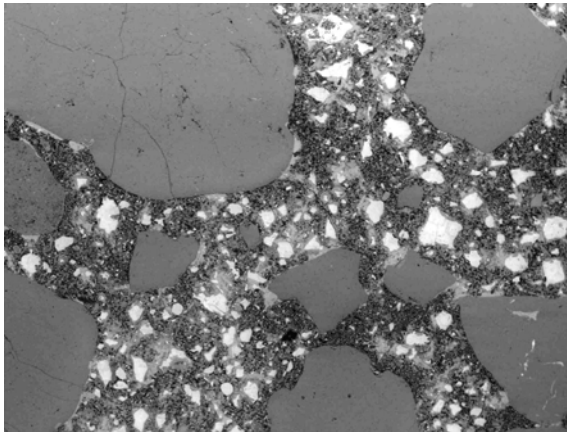
Figure 3.13 Effect of fluctuation of the beam condition on the position of the epoxy and aluminium peaks over a two-hour monitoring period. The curves marked * are not corrected for beam fluctuation and show a gradual decrease in peak grey values for epoxy and Al over time.

3.2.5 Choice of magnification and pixel spacing

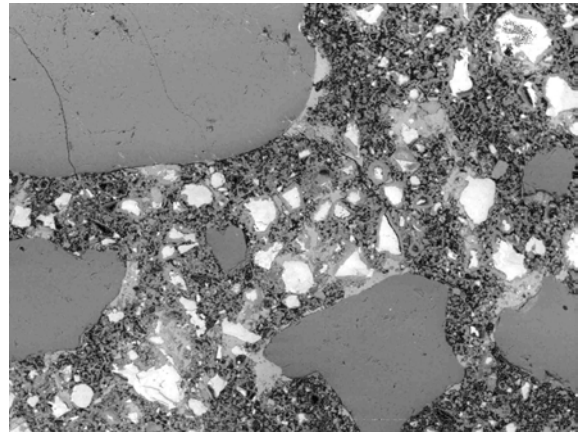
Fig. 3.14 shows the effect of magnification on the image resolution and field of view. The pixel spacing values at various magnifications are given in Table 3.3 for images digitised to 1024 x 768 pixels and 1940 x 1455 pixels. Images captured at a large magnification have a smaller pixel spacing, hence a higher potential image resolution. However, a large magnification gives a small field of view and so more images need to be analysed to obtain a statistically significant measure of the feature of interest. In addition, features with a large particle size will not be sampled accurately using a small field of view due to edge effects. Therefore, in choosing the optimal magnification for quantitative analysis of a particular phase, considerations for the need of adequate resolution and a representative sampling area must be given. The chosen value reflects a compromise between these two factors.

Although the magnifying power of the electron microscope can go up to 200,000x the useful range of magnification for BSE imaging of cement-based materials is typically no more than about 1000x. This is because beyond a certain magnification level, there will be no additional gain in information that can be acquired. This is known as hollow or blank magnification [Goldstein et al, 2003], and it occurs when there is a significant overlap of signal sampling volume or probe size between adjacent sampling points. If the signal sampling volume is substantially greater than the pixel spacing, then the area sampled will begin to overlap several picture elements, and be perceived as blurring at sharply changing features such as edges. If the probe size is greater than the pixel size, then the signal from adjacent pixels will be merged. Both effects will cause a reduction in the image resolution.

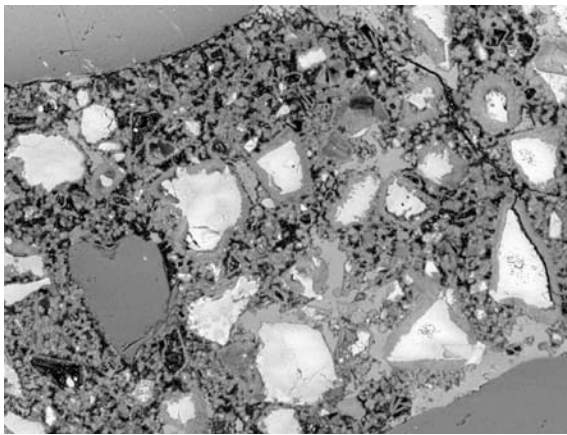
While the above-mentioned effects are true, this does not necessarily mean that the chosen pixel spacing should correspond as closely as possible to the probe diameter or the sampling volume. As will be shown in Chapters 5 and 6 using Monte Carlo simulation, the signal sampling volume in cement-based materials exceeds that of the pixel spacing even at the lowest magnification level. The size of the sampling volume does not represent in itself a limit to the spatial resolution because the visibility of a particular phase depends on the natural contrast from its surroundings. The pixel spacing should be considerably smaller than the image resolution; otherwise, spatial digitising errors will become the most significant error in quantitative analysis. In this study, BSE images for quantitative pore structure analysis will be captured at 500x magnification. The pixel spacing at this level is in the order of the effective probe size ($\sim 126\text{nm}$) as calculated for a 10keV accelerating voltage (Appendix I).



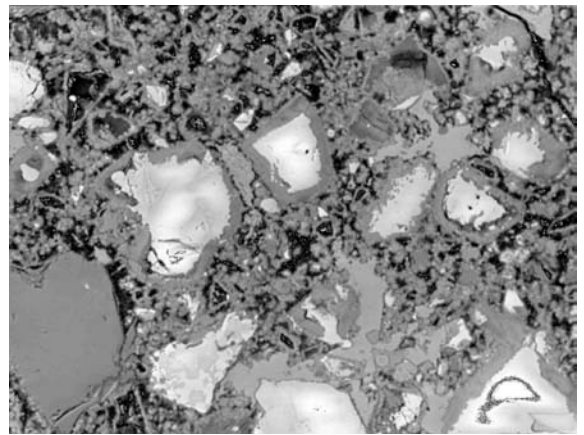
a) 100x (1220 x 915 μ m)



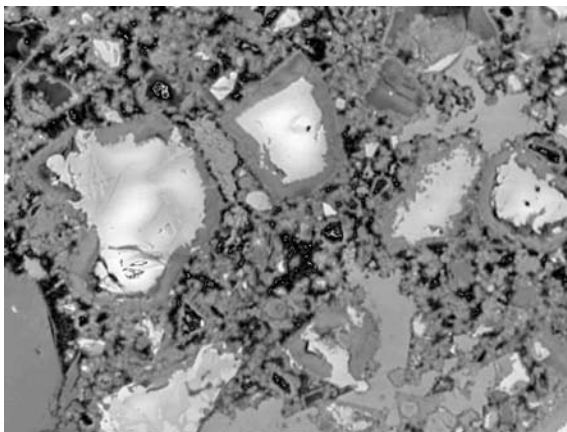
b) 200x (610 x 458 μ m)



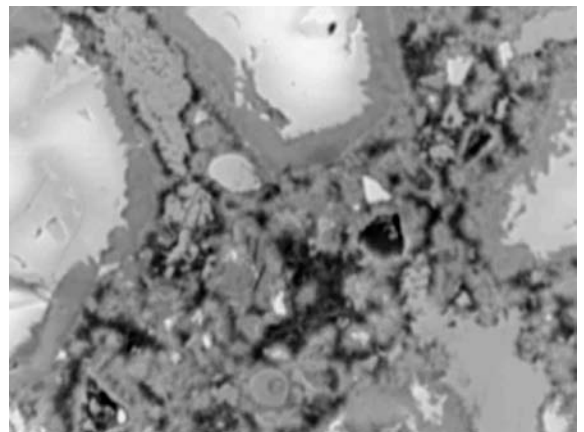
c) 500x (240 x 180 μ m)



d) 750x (160 x 120 μ m)



e) 1000x (120 x 90 μ m)



f) 2000x (61 x 46 μ m)

Figure 3.14 Effect of magnification on the resolution and field of view of the image.
Images are digitised to 1940 x 1455 pixels, sample is M 0.5 (50S) 3d.

Magnification	Link Isis (1024 x 768)		SemAfore (1940 x 1455)	
	Pixel spacing (μm)	Field of view (μm)	Pixel spacing (μm)	Field of view (μm)
50x	2.604	2667 x 200	1.237	2400 x 1800
100x	1.302	1333 x 1000	0.629	1220 x 915
200x	0.651	667 x 500	0.314	610 x 458
350x	0.372	381 x 286	0.175	340 x 255
500x	0.260	267 x 200	0.124	240 x 180
750x	0.174	178 x 133	0.082	160 x 120
1000x	0.130	133 x 100	0.062	120 x 90
2000x	0.065	67 x 50	0.031	61 x 46

Table 3.3 List of pixel spacing and field of view of images digitised to 1024 x 768 pixels and 1940 x 1455 pixels, captured at various magnifications up to 2000x.

3.2.6 Sampling issues

If a microscope is used to resolve fine features of interest, it is almost inevitable that only a tiny fraction of the original object will be analysed. Increasing magnification, while improving visibility, decreases the proportion of the original image being sampled. Consider that for a polished block sample with a dimension of 20 x 40mm obtained from a 100mm diameter cylinder, an image captured at 500x magnification gives a field of view of about 240 x 180 μm , which represents only a fraction of about a millionth of the cross-sectional area of the original cylinder. While such a small field of view may suffice to give a reasonable qualitative description of a particular feature, it is unsuitable for quantitative analysis. On the other hand, it is practically impossible to subject the entire specimen to the same measurement hence we are left with the choice of taking only a fraction of the material for analysis and making an estimate of the required value. The nature of this sampling process is most fundamental in determining the quality of the estimate and therefore the overall validity of the investigation. Assuming that the samples are representative of the population, the results of our measurements allow us to infer something about the entire population.

For the values estimated from a finite sample to be accurate and unbiased, three criteria need to be fulfilled: that is the sampling must be uniform, random and isotropic [Howard & Reed, 1998; Russ & DeHoff, 2001]. If the specimen itself is perfectly uniform, random and isotropic, then measurements performed in any area will suffice, subject only to the statistical requirement of obtaining enough measurements to get an adequate precision. However, very few real world materials fulfil this condition, so sampling strategies must be devised to obtain representative data that do not produce bias in the result [Russ & DeHoff, 2001]. For example, in cement-based composites, it is known that porosity gradients exist at the ITZ, so sampling only the ITZ would lead to a biased (non-uniform) estimate of the average paste porosity. If the sampling areas were always taken to include the ITZ, the results will also not be representative (non-random). For microstructures with aligned features, such as fibre composites, samples that are taken at the same orientation with respect to the fibres will result in a non-isotropic measurement.

A uniform, random and isotropic sampling method ensures that every member of the population has an equal chance of being selected and is equally represented (uniform), that there is no conscious or consistent placement of measurement regions with respect to the structure itself to select what is to be measured (random) and that all the directions of measurements are equally represented (isotropic) [Russ & DeHoff, 2001]. Once such a representative sample has been collected, it must be analysed in some way that avoids a systematic bias in the estimated value of the unknown quantity. The way to avoid a systematic bias is to use the correct ‘measurement tool’ that can guarantee accuracy and precision in the measurements [Howard & Reed, 1998]. Since image analysis relies on measurements on a thresholded image whereby the features of interest are segmented from the rest using grey-scale selection, the thresholding criteria used is a major source of systematic error or bias. More on this will be presented in Chapter 4.

If the specimen itself has no inherent periodicity or repetitive structure, a regular grid of points can be used as a systematic/structured random sampling method [Russ & DeHoff, 2001]. However, each point has to be independent, which is to say that the points should be separated from each other by enough distance so that they do not repeat the same measurement. The procedure to achieve a systematic random sampling is to first determine the number of points to sample (image) based on the desired level of precision, and then form a regular square grid and finally, generate a pair of random numbers that defines the (X,Y) coordinates for the placement of the first grid point within the sample. This is done by using either a computer random number generator or a random number table, the two numbers are typically decimal fractions between 0 and 1, and can be conveniently scaled to locate

first point. If the first grid point is randomised, then all other points are randomised with respect to the specimen. For each crossing point, a sample (i.e. an image) is taken and this collection of images represents a systematic random sample in 2D.

It has been shown that the systematic random sample is more efficient than ordinary random sampling in which grid points are independently placed on the sample. This is because, in the latter case, points will inevitably cluster in some areas producing over sampling, while being sparse in others producing under sampling [Russ & DeHoff, 2001]. It has also been observed that the variance is very much smaller for the systematic random approach than for the simple random sample [Gundersen & Jensen, 1987]. The systematic random sampling converges to the same answer, but more rapidly than the random sampling approach. Thus, applying the systematic random sampling strategy permits attainment of a given precision with fewer counts and with reduced effort, or for the same number of counts, increases the precision.

In this study, a systematic random sampling approach was achieved by programming the microscope stage to move in a grid fashion and stopping at a number of predefined, equally spaced coordinates. The number of points selected typically range between twenty and thirty depending on the precision required. Areas that are less than 5mm from the sample edge were not imaged to avoid the possibility of including areas that may have been saw-damaged. For mortar and concrete samples, occasionally a field of view may entirely consist of a large aggregate particle, so random numbers were used to select another location within the neighbouring grid for image capture. However, this may inevitably result in a higher amount of ITZ sampled. A set of twenty images typically required about 1.5 hours of microscope time.

3.2.7 Number of fields and estimates of error

The number of fields necessary to obtain a representative estimate of a particular measurement can be determined from a plot of moving average as the experiment is replicated, i.e. as more and more frames are analysed. As the number of analysed frames increases, the average of a series settles down to a steady value, which in the case of an unbiased estimator, is equal to the true value. The convergence point is taken as the true mean value and the point at which the successive average consistently falls within given limits of the true mean, is taken as the minimum number of fields. However, for the case of a biased estimator, the average settles to some other value, which is not equal to the true value.

This bias is invisible and undetectable within any one experiment [Howard & Reed, 1998]. Another approach to determine the number of fields required is by using the Student's *t*-distribution. This method, together with other statistical characterisation tools used to estimate the variability and reliability of a finite data are given in Appendix II. These include the coefficient of variation, standard error, relative standard error and confidence limits.

3.3 Image analysis

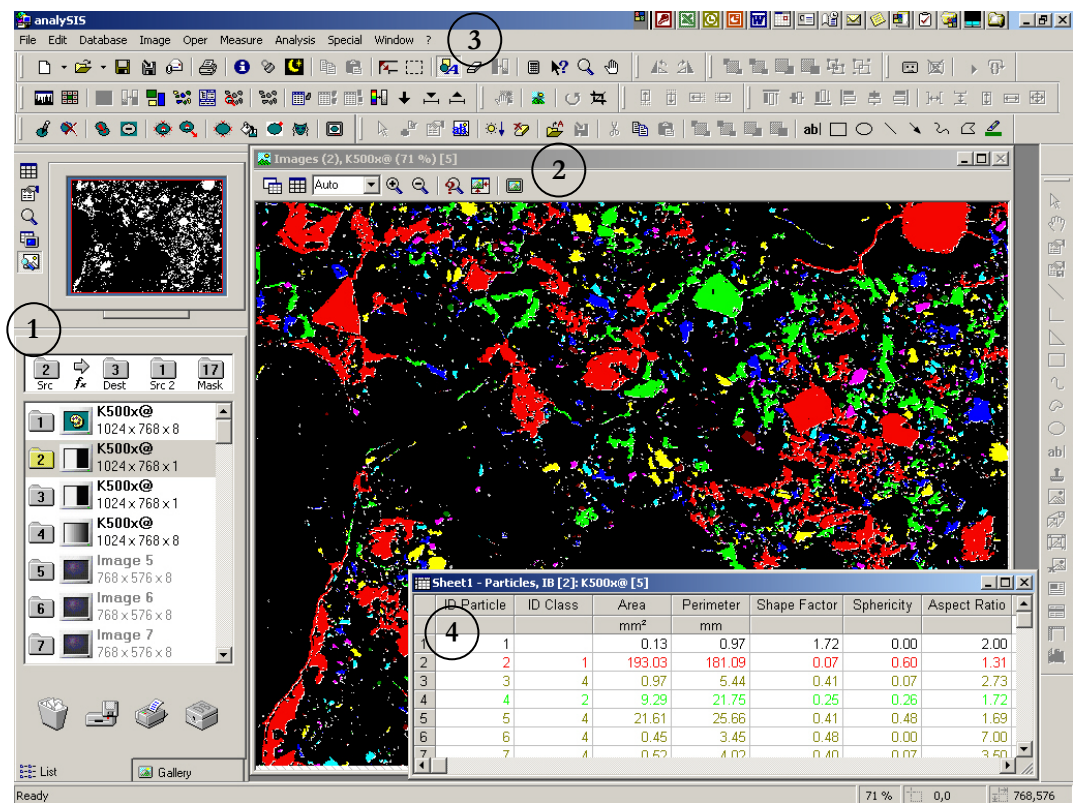
Once a representative sample of BSE images is captured in a digital format, a wide range of pixel-based operations and measurements can be made on the feature of interest. Measurements such as counting objects, distance or length, areas, brightness intensity, centre of mass, shape factors, et cetera can be performed automatically and very quickly. The images may be first processed or filtered to correct for defects and noise prior to quantitative measurements, however, for this study, most images were analysed in raw as-recorded form. More effort was placed on optimising the image capture so that high-quality and good resolution images were obtained in the first instance. This avoids the need for any post-processing to correct for defects or to 'enhance' the image later on. Use of filters such as histogram equalising, averaging and edge enhancement will change the pixel greyscale values, while morphological filters such as erosion and dilation on the binary image will remove small features or alter feature boundary, so these were avoided entirely for quantitative analysis.

An essential step in image analysis is to convert the greyscale image to a black and white binary image whereby the feature of interest is separated from other features, which are reduced to background. This is done by segmentation, or thresholding the image, which refers to the selection of a grey level range whereby every pixel in the image that has a grey value within that range is painted white (feature) and all other pixels are painted black (background). This step is of fundamental importance because all subsequent measurements will be carried out on the segmented image. Once the image has been thresholded, measurements can be made relatively trivially using image analysis software.

However, segmentation of the phase of interest is not a straightforward process and can never be a perfect one, even for a relative highly contrasted phase such as pores in cement-based materials. Hence, a key obstacle to achieving accurate and reliable quantitative measurements using image analysis is to develop an accurate and reliable segmentation method. Feature segmentation of a greyscale BSE image can never be error free due to vari-

ous reasons such as the finite-pixel size effect and the overlapping of sampling volumes. Nevertheless, as will be shown in subsequent chapters, errors can be reduced by using an objective and consistent thresholding rule.

In this study, all image processing and analysis were performed using the analySIS® software (Ver. 3.2, Build 744) developed by Soft Imaging System GmbH. This software can interface with a range of microscopes and cameras, and allows for image acquisition, archiving, processing and analysis. Development of new functions, customisation and automation of any image processing and measurement procedure can be done using the Imaging C programming language. A screenshot of analySIS® is shown in Fig. 3.15.



Notation:
 1 = Image buffer; 2 = Active image; 3 = Image capture, operation, measurement and analysis menus; 4 = Result sheet;

Figure 3.15 Screenshot of analySIS®

3.4 Molecular transport testing

3.4.1 Oxygen diffusion

Gas transport through porous media can be classified into four independent mechanisms [Carman, 1956; Mason & Malinauskas, 1983], as follows:

1. Molecular diffusion or ordinary diffusion: different species of a gas mixture move relative to each other under the influence of concentration gradients, temperature gradients or external forces (forced diffusion). In this case, the molecule-molecule collisions dominate over the collisions between gas molecules and the pore walls.
2. Viscous flow: the gas moves as a continuum fluid driven by a pressure gradient and the molecule-molecule collisions dominate over molecule-wall collisions. This is sometimes called convective or bulk flow.
3. Free molecule flow or Knudsen flow: this becomes significant when the gas density is low, i.e. its mean free path is of the magnitude comparable to the pore dimension so that molecule-wall collisions dominate over molecule-molecule collisions.
4. Surface flow or surface diffusion: occurs when there is significant adsorption of the gas molecules on the pore walls and the gas molecules move in the adsorbed layer.

In an isobaric and isothermal condition, the movement of gas through a porous medium occurs mainly due to ordinary concentration diffusion, Knudsen flow and surface diffusion. The contribution of surface diffusion is generally considered small and negligible [Mason & Malinauskas, 1983; Kobayashi & Shuttoh, 1991]. Cement-based materials are not known to have significant adsorption characteristics for oxygen and since the samples are thoroughly dried, dissolution of the gas in the pore solution is negligible, and therefore the above assumption is reasonable.

Whether ordinary diffusion or Knudsen diffusion predominates for a particular situation depends on the ratio of the pore size (d) to the mean-free path of the gas molecule (λ_o), i.e. the average distance a molecule travels before colliding with another. However, it is not possible to define a strict limit for d/λ_o that separates the two modes of diffusion. Generally, it is taken that when d/λ_o is $\gg 1$, ordinary diffusion is predominant, while Knudsen diffusion predominates when $d/\lambda_o \ll 1$.

There is also a transition region whereby both modes of diffusion are important and must be considered in describing the net flux. Eq. 3.3 gives the mean free path for gas at a particular pressure (P/Nm^{-2}) and temperature (T/K), where R is the ideal gas law constant ($= 8.3145\text{J/mol.K}$), N_A is the Avogadro number ($= 6.022 \times 10^{23}$) and d_o (m) is the diameter of a gas molecule.

$$\lambda_o = \frac{RT}{\sqrt{2} N_A \pi d_o^2 P} \quad \text{Eq. 3.3}$$

For oxygen ($d_o \sim 0.339\text{nm}$) at 20°C and 1 bar pressure, the mean free path is about 80nm . If the relevant capillary pores for transport in cement-based materials have size ranging from $0.1\mu\text{m}$ to $10\mu\text{m}$, d/λ_o will be approximately 1.25 to 125. Thus, it can be assumed that the oxygen diffusion in cement-based materials occurs in the transition region where both ordinary diffusion and Knudsen diffusion co-exist. This combined flow is described by the following equation [Mason & Malinauskas, 1983] for a binary gas system:

$$J_A = - \frac{1}{(1 - \alpha Y_A)/D_{AB} + 1/D_{KA}} \frac{\partial C_A}{\partial x} \quad \text{Eq. 3.4}$$

Where J_A = flux of Gas A ($\text{mol/m}^2.\text{s}$)
 D_{AB} = ordinary diffusion coefficient of Gas A (m^2/s)
 D_{KA} = Knudsen diffusion coefficient of Gas A (m^2/s)
 C_A = concentration of Gas A (mol/m^3)
 α = $1 + J_B/J_A$, where J_B is the flux of Gas B ($\text{mol/m}^2.\text{s}$)
 Y_A = mole fraction of Gas A
 x = distance (m)

Graham's law of diffusion states that the rate of gas diffusion is proportional to the square root of its molecular weight (m), thus:

$$-J_B/J_A = \sqrt{m_A/m_B} \quad \text{Eq. 3.5}$$

Therefore, in an oxygen-nitrogen binary system where both gases have almost similar weights, $J_B/J_A = -1.069$ and $\alpha = -0.069 \sim 0$, flow in the transitional region can be approximated by a simple diffusion equation based on Fick's Law [Lawrence, 1984; Kobayashi & Shutttoh, 1991]:

$$J_A \approx -\frac{1}{1/D_{AB} + 1/D_{KA}} \frac{\delta C_A}{\delta x} = -D \frac{\delta C_A}{\delta x} \quad \text{Eq. 3.6}$$

Where D is the diffusion coefficient (m^2/s) in the transition region [Carman, 1956; Mason & Malinauskas, 1983] that can be represented by:

$$\frac{1}{D} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}} \quad \text{Eq. 3.7}$$

Test method

The diffusion test was carried out by exposing one flat face of the sample to a stream of oxygen and the opposite face to a stream of nitrogen at equal pressure and temperature. The rate of diffusion of oxygen was determined by measuring the oxygen concentration in the nitrogen stream. The test set-up, shown in Fig. 3.16, involves fitting the sample into a silicon rubber ring in a diffusion cell. The curved surface was sealed by loading the top plate and silicone rubber ring, which expands laterally, providing an air-tight grip onto the sample. Note that the sample is not loaded directly. Blank tests on a steel disc with similar dimensions found no measurable flow when a load of 1.5 tonne was applied. This shows that the seal was effective and the only possible transmission path was through the sample.

The gas flow rates were adjusted to minimise the pressure difference between both streams. At steady state condition, the oxygen concentration in the nitrogen stream was measured using an oxygen analyser. The analyser consists of a zirconium oxide tube heated to 700°C , through which the gas stream to be analysed is passed. The zirconia ceramic sensor provides a measuring range of 0.25vpm up to 25% oxygen, which is sufficient for the samples tested. The measured oxygen concentration value, together with the gas flow rates, the pressure differential and the sample dimensions were used to calculate the oxygen diffusion coefficient, D (m^2/s), according to the method described by Lawrence [1984]:

$$D = \frac{Q \times L}{A \times (C_2 - C_1)} \quad \text{Eq. 3.8}$$

Where Q = Oxygen diffusion rate at 1 bar (m^3/s)

$$= \frac{R_1}{60 \times 10^6} \times \frac{(G_1 - G_0)}{100} \times (P_1 - P_2)$$

R_1 = Flow rate of nitrogen stream (mL/min)

R_2 = Flow rate of oxygen stream (mL/min)

G_1 = Percentage of oxygen in outflow stream

G_0 = Percentage of oxygen in the initial nitrogen stream (0.007%)

P_1 = Pressure of oxygen stream (bar)

P_2 = Pressure difference between the oxygen and nitrogen stream (bar)

A = Cross-sectional area of sample (m^2)

L = Thickness of sample (m)

C_2 = Concentration of oxygen in the oxygen stream at 1 bar (m^3/m^3)

~~$$= \left[100 - \left(\frac{R_1}{R_2} \times \frac{(G_1 - G_0)}{2} \times \frac{\sqrt{32}}{\sqrt{28}} \right) \times \frac{P_1}{100} \right] \left[100 - \left(\frac{R_1}{R_2} \times \frac{(G_1 - G_0)}{2} \times \frac{\sqrt{32}}{\sqrt{28}} \right) \right] \times \frac{P_1}{100}$$~~

C_1 = Mean concentration of oxygen in the nitrogen stream at 1 bar (m^3/m^3)

$$= \frac{(G_1 + G_0)}{2} \times \frac{(P_1 - P_2)}{100}$$

Samples were weighed before and after the test to determine if there was any mass change. The difference rarely exceeded 0.1g (~0.01%).

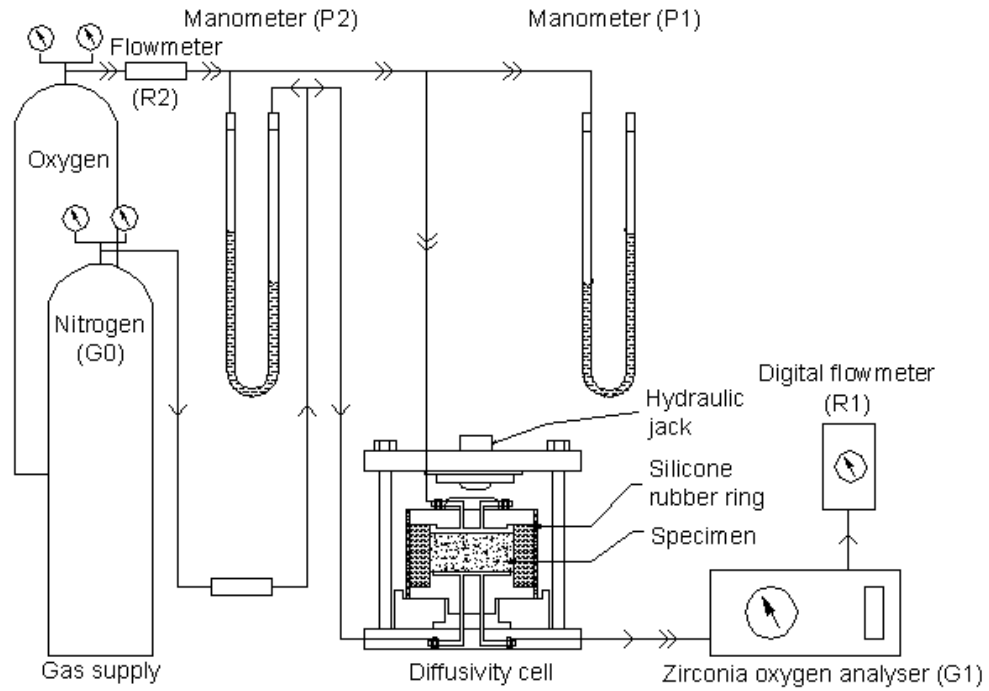


Figure 3.16 Oxygen diffusion test apparatus

3.4.2 Oxygen permeation

Permeation, or viscous flow, is the transport process occurring due to a pressure gradient. Darcy's law states that at steady-state conditions, the flow-rate Q (m³/s) is proportional to the pressure gradient $\Delta P/L$ (N/m³):

$$Q = -k \frac{A}{\eta_v} \frac{\Delta P}{L} \quad \text{Eq. 3.9}$$

Where k (m²) is the permeability coefficient, A (m²) is the cross-sectional area of flow, and η_v (Ns/m²) is the dynamic viscosity of the permeating fluid. Darcy's law is valid for incompressible fluids in the laminar and viscous flow regime, as long as the resistance to flow is entirely due to viscous drag and the fluid is inert to the porous medium [Carman, 1956].

Since gas is compressible, the volume and the rate of flow changes from point to point as the pressure decreases and therefore, Eq. 3.9 is no longer valid. The solution is to integrate the differential form of Darcy's law by considering that at isothermal and steady state conditions, the pressure-velocity product is constant throughout the sample [Carman, 1956, Dullien, 1992]. Thus, for gases, the following form of Darcy's law is appropriate:

$$Q = k_g \frac{A}{2\eta_v L} \left(\frac{P_1^2 - P_2^2}{P_2} \right) \quad \text{Eq. 3.10}$$

Where k_g (m²) is the gas permeability coefficient, A (m²) is the cross-sectional area of the sample, η_v is the gas viscosity (for oxygen at 20°C, $\eta_v = 2.02 \times 10^{-5}$ Ns/m²), L (m) is the sample thickness, P_1 and P_2 are the absolute pressures on the inlet and outlet faces respectively (N/m²).

Test method

The test set-up is shown in Fig. 3.17. The test involved applying pressurised oxygen to one face of the sample and measuring the outflow through the opposite face at steady-state. The sample was placed into a permeability cell similar to the one used in the diffusion

test. A confining pressure was applied to seal the curved surface of the sample by loading the top plate and silicone rubber ring with a hydraulic jack. No load was applied directly onto the sample. Blank tests on a steel disc with similar dimensions found no measurable flow at the highest operating pressure (2.5 bar) when a load of 1.5 tonne was applied. This confirmed that the seal was impermeable and that the only possible transmission path was through the sample.

Three input pressures of 0.5, 1.5 and 2.5 bars above atmospheric pressure were used. At each input pressure, flow was allowed to stabilise, which was normally achieved within 10 to 30 minutes, and the outflow rate was measured using a series of soap bubble flow meters. At least four readings were taken to compute the average flow for each applied pressure. The ratio of the maximum to minimum flow rate in each set of readings was no more than 1.02. Samples were weighed before and after the test to determine if there was any mass change. The difference rarely exceeded 0.1g (~0.01%).

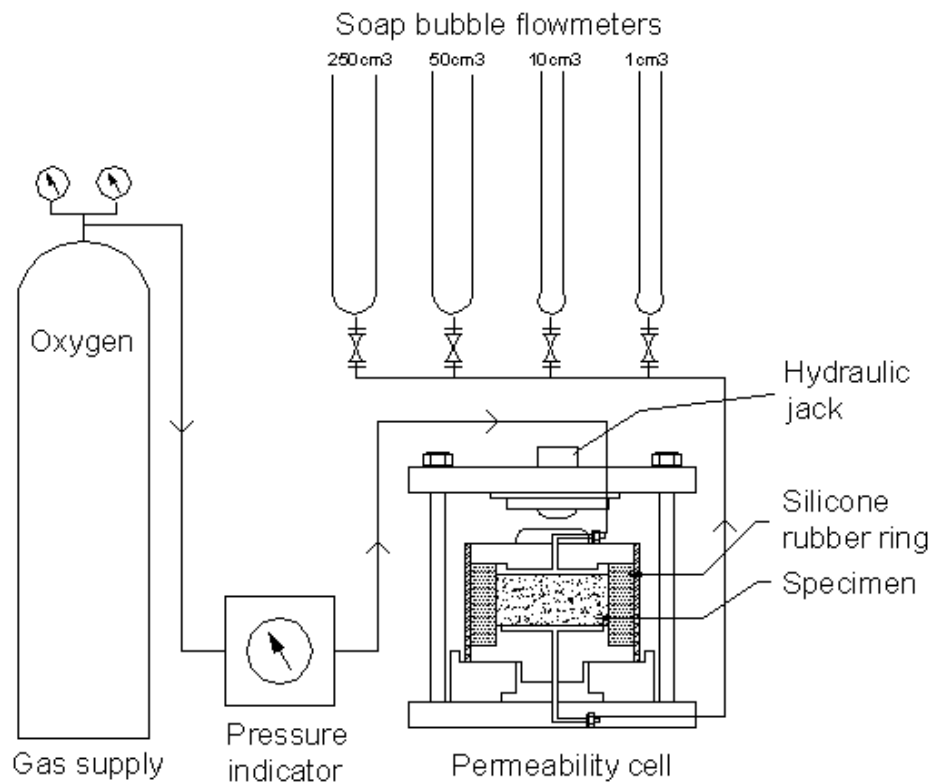


Figure 3.17 Oxygen permeability test apparatus

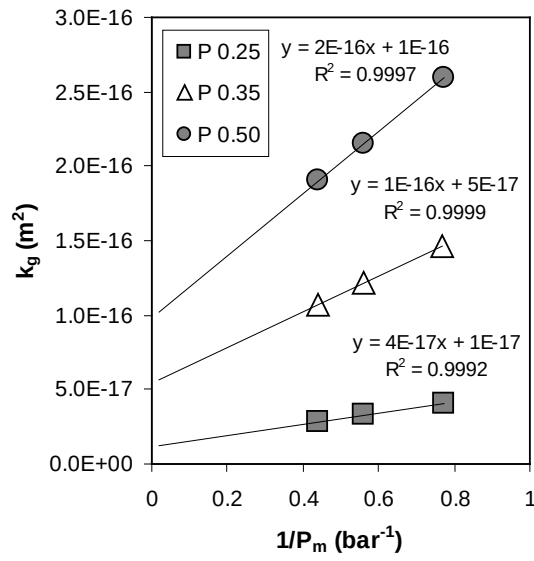
Klinkenberg correction for gas slippage

The coefficient k_g in Eq. 3.10 is an apparent permeability coefficient that is not pressure-invariant, but decreases with the applied pressure. This is due to gas molecules slipping (i.e. not being stationary) at the walls of the pore channels, a condition known as gas slippage. This effect becomes significant when the mean-free path of the gas molecules is of comparable magnitude to the pore size. In very fine capillaries, the gas molecules will collide more frequently with the pore walls than with other gas molecules, and flow will then take place via Knudsen diffusion, in contrast to a viscous mechanism. A consequence of this is that the quantity of gas flowing through a capillary pore is larger than would be expected and therefore, the calculated Darcy constant (Eq. 3.10) is overestimated. The most popular correction method for this non-viscous flow is the Klinkenberg method [1941], which introduces the concept of intrinsic permeability.

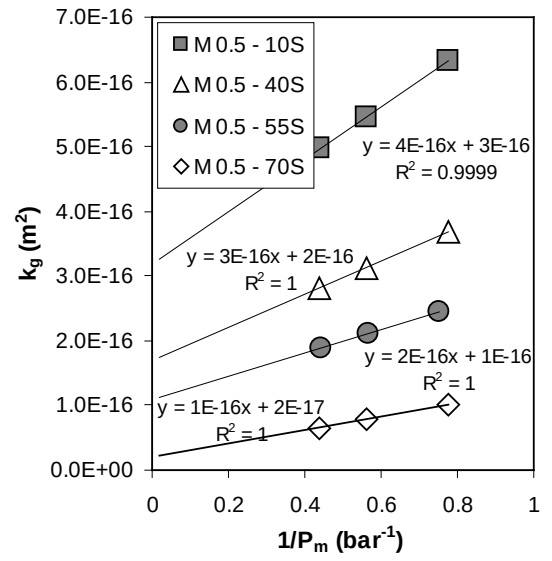
The Klinkenberg correction method is stated in Eq. 3.11, where k_{int} (m^2) is the intrinsic permeability coefficient, P_m is the mean pressure of the inlet and outlet streams ($P_m = \frac{1}{2} (P_1 + P_2)$) and β is a constant for a given material and gas. The intrinsic permeability coefficient depends purely on the pore structure and is independent of the fluid characteristics and applied pressure. The Klinkenberg correction gives the permeability coefficient when the sample is tested at an infinite input pressure ($1/P_m = 0$) so that at very high pressure, the mean free path approaches zero (Eq. 3.3) and thus, will be small compared to the pore size. Knudsen diffusion becomes negligible and thus, the flow is predominantly viscous.

$$k_g = k_{int} \left(1 - \frac{\beta}{P_m} \right) \quad \text{Eq. 3.11}$$

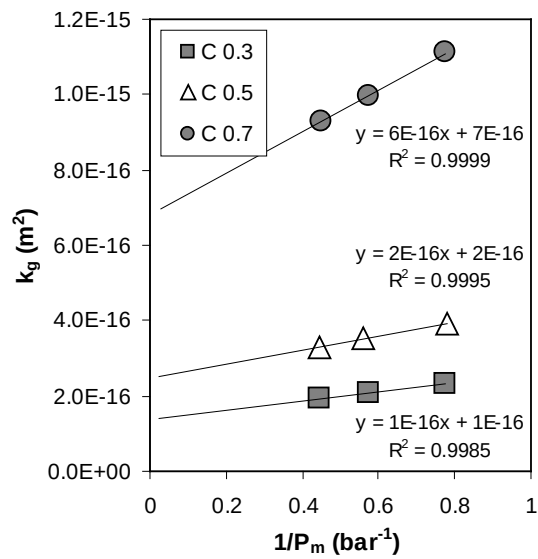
The apparent permeability is calculated from Eq. 3.10 for the three input pressures and plotted against $1/P_m$. The intrinsic permeability is obtained from the y-intercept of the best-fit line. Typical plots of k_g against $1/P_m$ are shown in Fig. 3.18 for several pastes (28-days), mortars (3-days) and concretes (7-days) at different w/c ratios. A linear relationship between k_g and $1/P_m$ was consistently observed for all samples tested in this study and the coefficient of regression for the least-squares fit was always greater than 0.99.



a) Paste



b) Mortar



c) Concrete

Figure 3.18 Typical plots for Klinkenberg corrections for paste (28-days), mortar (3-days) and concretes (7-days).

3.4.3 Water absorption

Water absorption is a form of non-saturated flow [Hall, 1977] whereby a wetting fluid moves within a porous medium under the action of a capillary force. The capillary transport results from unbalanced surface tension forces between the fluid-fluid and fluid-solid interfaces [Martys & Ferraris, 1997]. In the case of water absorption, the unbalanced surface tension forces create a pressure drop across the water-air interface, driving the water phase to move in the capillary pores. At saturation, the capillary forces are absent and transport occurs only in response to an externally imposed force, such as a pressure gradient or a concentration gradient [Hall & Yau, 1987]. However, the saturated transport state is uncommon because, except for submerged marine structures, most concrete structures have moisture contents that are below saturation. In addition, since concrete deterioration is largely mediated by water, non-saturated flow is an important transport mechanism in cement-based materials.

The strength of the capillary force is determined by the pore size, but also modified by the local moisture content. The local capillary force is inversely proportional to the pore diameter, therefore, the capillary force is strongest when the pores are small and the material is dry, and becomes zero at complete saturation. Smaller pores exert a larger capillary force, although the rate of mass ingress into a smaller pore will actually be less than that into a larger one [Hall, 1989].

The capillary rise test approximates the case of one-dimensional absorption into a semi-infinite medium. Non-saturated flow theory [Hall, 1977] shows that for a homogeneous porous material in which capillary forces are much larger than gravitational forces, a condition is satisfied by the capillary pores in the first states of capillary rise such that the cumulative absorbed volume per unit area of the inflow face, denoted as i , increases as the square root of elapsed time, $t^{0.5}$, that is:

$$i = S\sqrt{t} \quad \text{Eq. 3.12}$$

Where S is a constant known as the sorptivity coefficient.

The term sorptivity was introduced by Philip [1957], in the context of hydrology and soil physics, and could be defined for any porous medium in which unsaturated flow obeyed the extended Darcy equation. Sorptivity is a well-defined physical quantity that characterises

the tendency of a porous material to absorb and transmit water by capillarity [Hall, 1989]. From unsaturated flow theory, sorptivity is mathematically related to the hydraulic diffusivity [Hall, 1977; Gummerson et al., 1980]. Hydraulic diffusivity can be regarded as the fundamental water absorption and transmission property of a porous medium, but it is difficult to determine. Sorptivity on the other hand, can be easily determined from a simple capillary absorption test in the laboratory. However, sorptivity is dependent on initial moisture state, temperature and fluid properties [Hall, 1989].

Test method

The test was done by monitoring the amount of water uptake with time until a saturated state was achieved. Fig. 3.19 shows the test set up. Deionised water at 20°C was used as the test fluid. The sample was placed on two plastic rods (5 x 5mm) to allow free access of water to the inflow surface. The water level was kept at approximately 2 to 3mm above the base of the sample. The mass of absorbed water was measured at intervals: 5, 10, 15, 20 and 30 minutes, then every 15 minutes for the next hour, and then approximately every hour for the next 6 hours. Daily readings were taken until the sample reached saturation. An electronic balance accurate to 0.01g was used. Prior to weighing, surface water on the sample was wiped off with a dampened tissue. Each weighing was completed within 30s and the clock was allowed to run during the weighing operation. Loss of absorbed water by evaporation from non-immersed faces was prevented by covering the tray with a loosely fitting lid at all times. This shields the samples from air movement and creates a humid, but not saturated, environment. The relative humidity in the container was about 50-70% and approached 80-90% when the sample was near saturation. No particular care was taken to seal the curve surfaces, so as to avoid absorption from sides. Studies have shown that this effect is negligible [Hall, 1989] as long as the water level from the base of the sample is small in comparison to the entire sample depth. However, care was taken to ensure that condensates did not form on the underside of the lid, and drop on to the sample.

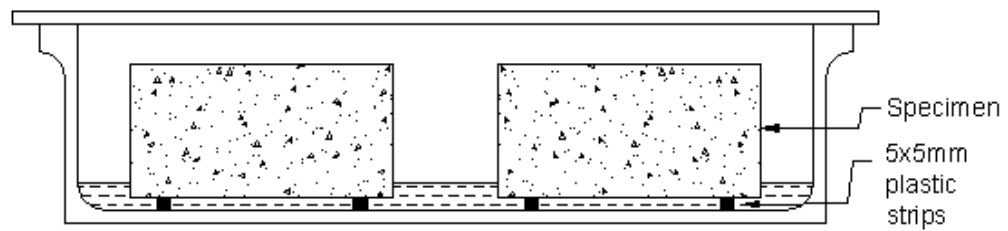


Figure 3.19 Water absorption test set-up

To determine the sorptivity coefficient, the cumulative mass gain per unit cross-sectional area of the inflow face, i , was plotted against the square root of elapsed time. Suitable units for i were g/m^2 and time was recorded in minutes; thus, giving the units $\text{g}/\text{m}^2 \cdot \text{min}^{1/2}$ for the sorptivity coefficient. All of the absorption tests carried out gave results obeying Eq. 3.12, with no discernible curvature in the i vs. $t^{0.5}$ plot. From this, a best-fit line was drawn across the first 10-15 readings (approximately 2-6 hours of measurement) and the slope of this is equivalent to the sorptivity coefficient. The coefficient of regression of the least squares fit was always greater than 0.99. Typical water absorption plots are bi-linear, as shown in Fig. 3.20 for pastes, mortars and concretes.

In practice, experimental data frequently show a finite (generally small, positive) intercept at time $t = 0$ (when extrapolated), therefore they are fitted to the equation: $i = S\sqrt{t} + A$. It has been said that this intercept arises from the rapid initial absorption due to filling of open surface porosity on the inflow surface and along the sides of the adjacent faces [Hall & Yau, 1987]. However, it was also observed that the intercepts are very variable, being as often negative as positive in mortars [Hall & Tse, 1986]. It is likely that the value of this intercept is largely dependent on the curve fitting process, i.e. how many points used and the period covered for the regression analysis, hence it is of no physical significance.

Another result that is obtainable from the capillary rise test is the total amount of water absorbed, which is related to the total volume of pores in the sample. After the capillary rise test, the samples were fully submerged in deionised water for another 72-hour period, after which, the samples were surface-dried and weighed. The total amount of water uptake from the initial condition to saturation point, after correction for the amount absorbed by aggregates, gives a first-approximation for the total porosity of the hydrated cement paste in the sample. Since wetting was from one direction during the capillary rise test,

the probability of non-water filled pores due to air entrapment is low. Indeed, checks by vacuum saturation over a period of 3 hours, after the samples had been submerged for 72 hours, found negligible increase in weight.

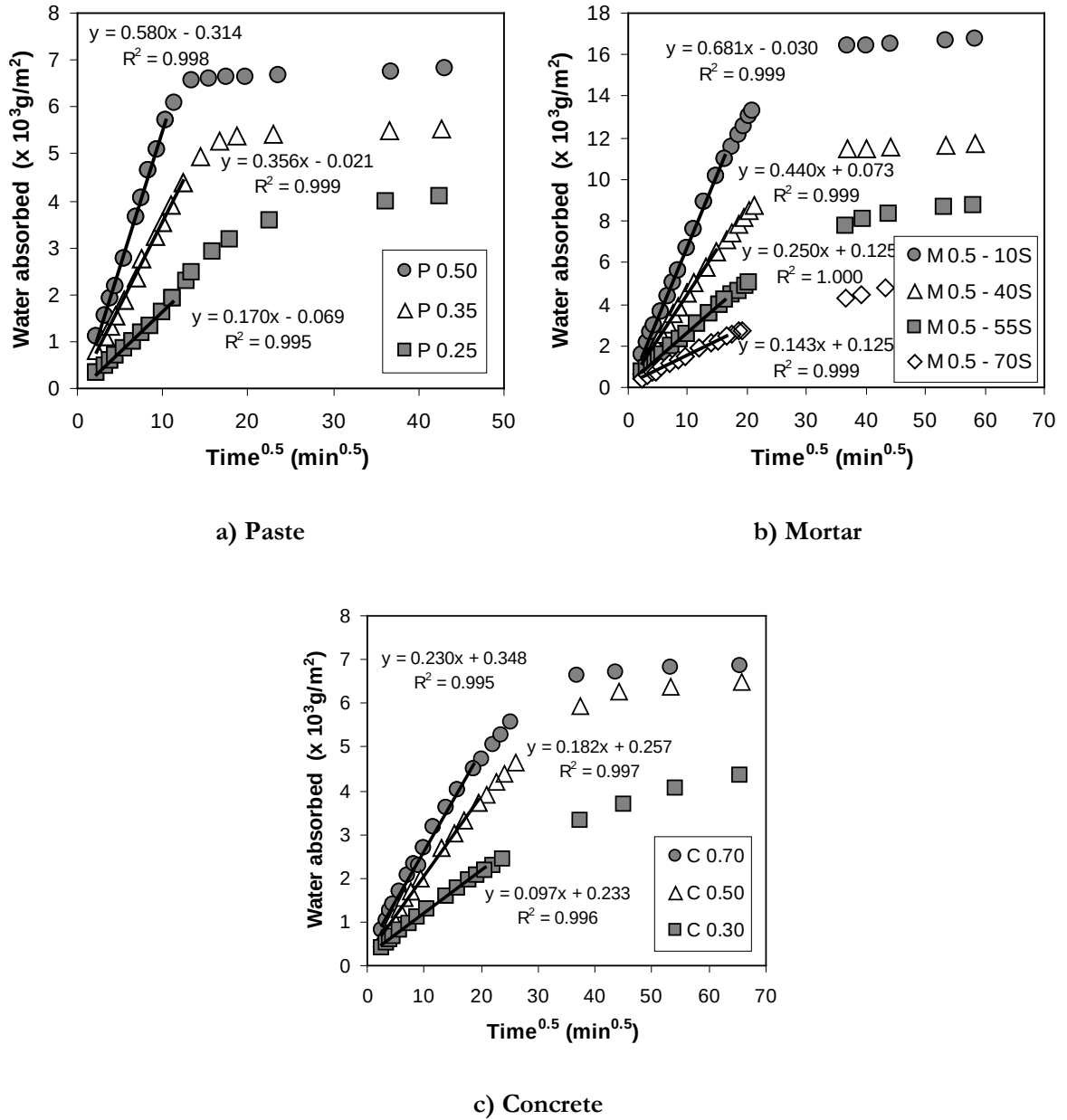


Figure 3.20 Water absorbed per unit area vs. square root of time plots for paste (28-days), mortar (3-days) and concrete (7-days) samples.

3.5 Chapter summary

In this chapter, the experimental procedures used in this thesis are presented. Details of the materials, sample preparation, test methods and instrumentation for backscattered electron microscopy and molecular transport testing are given. The molecular transport test methods used in this thesis are based on well-established procedures supported by sound transport physics and mathematical theories. However, the measured transport properties are strongly affected by pore moisture so samples need to be conditioned thoroughly to an equilibrium moisture state prior to testing.

Care must be taken whilst preparing samples for microscopy to avoid damage and artefacts. The appearance of the BSE image can be substantially altered by the brightness and calibration controls of the microscope hence these must be carefully calibrated. The BSE imaging approach is to use a low accelerating voltage and a sufficiently large probe current so that a high signal-to-noise ratio is attained at a small signal sampling volume. Nevertheless, a detailed study on the electron-solid interactions using the Monte Carlo method needs to be undertaken in order to understand the signal generation process better, and to optimise the microscope operating conditions, as well as to quantify its limitations. Discussions on the random, uniform and isotropic sampling procedure, choice of magnification, pixel spacing and the statistics for determining the variability and reliability of measured data are given. The segmentation process is a crucial step in quantitative microscopy, hence an objective and accurate segmentation procedure needs to be developed, as described in the next chapter.

Chapter 4

Pore segmentation

This chapter presents an image analysis technique to segment pores from a BSE image of cement-based materials. It is proposed that the upper threshold grey level for pores be determined from the inflection point of the cumulative brightness histogram of the BSE image. This represents a critical point where a small incremental grey value will cause a sudden increase in thresholded area, a condition termed as ‘overflow’. The proposed technique was found to be more consistent and reliable than existing methods. Significantly fewer images are required to achieve a satisfactory level of statistical confidence for quantifying porosity.

4.1 Introduction

Quantification of features via image analysis requires, firstly, good specimen preparation and imaging technique to produce representative images (Section 3.2), and secondly, a feature-segmentation algorithm that is objective, precise and reproducible. When features can be segmented with accuracy and consistency, only then can meaningful quantitative data be obtained, that can be used for comparative studies and/or to formulate structure-property relationships. Since individual phases in a BSE image have brightness intensities that increase with their mean atomic number, the obvious way to segment features is by grey level thresholding.

Ideally, the grey level histogram would be composed of separate peaks corresponding to distinct phases with heights proportional to the relative fractions of each phase. However, as the size of a pixel in a digital image is finite and because of sampling volume effects, the brightness of each pixel does not necessarily represent a single phase alone. Pixels lying on inter-phase boundaries will display an intermediate grey level that averages those of the two sampled phases. This will have an effect of broadening the histogram peaks and depending on the degree of overlap between the broadened signals, it becomes increasingly difficult to ascertain the appropriate thresholds for feature segmentation.

In cement-based materials, the backscatter coefficient for several hydration products such as C-S-H, ettringite and monosulphate, are too close to be individually distinguished on

the brightness histogram; a single broad peak is usually observed in the histogram. The epoxy-filled pores are perhaps easiest to segment because the backscatter coefficient of epoxy is substantially smaller than other phases. For example, the backscatter coefficient for araldite ($C_{10}H_{18}O_4$) is about 0.07 (calculated after Reuter, 1972) compared to 0.12 to 0.19 for major hydration products and anhydrous cement phases. The lower threshold level for pores can be set to zero (i.e. black pixels) and the segmentation process is then reduced to only determining the upper threshold level. However, problems in defining the exact boundary between pores and the surrounding hydrated paste still exist. Apart from the inherent weaknesses associated with the imaging process, the pore boundary is indistinct due to the diffuse morphology of the C-S-H gel [Scrivener et al. 1987; Scrivener, 1989]. In addition, a separate pore peak does not always occur in the brightness histogram, particularly when the porosity is low [Scrivener et al. 1987; Scrivener, 1989].

Commonly used methods to select the upper threshold for pores include manual thresholding, the tangent-slope method and entropy maximisation. In manual thresholding, the operator iteratively selects the threshold value so that the segmented pixels correspond satisfactorily to the features of interest in the original image. This is highly subjective, inconsistent between different operators or even the same operator over a period or over a range of different samples. It is also affected by operator fatigue. Scrivener et al. [1987] found that the grey level at which the tangent to the upper portion of the hydration products (HP) peak intersected the initial tangent on the grey level histogram gave consistent results and was closest to the manual threshold. However, the tangent-slope threshold is difficult to ascertain if a pore peak exists in the histogram for a highly porous sample. In this case, the minimum point between the pore peak and the HP peak can be used for thresholding. This is expected to give the smallest error because it corresponds to the value that affects the fewest pixels [Russ, 2002]. Entropy maximisation is a classical thresholding method based on measuring the information content (entropy) of an image [Pun, 1980; Kapur et al, 1985; Pal & Pal, 1989]. The equations for thresholding by entropy maximisation are given Appendix III. This method has been used to segment microcracks and voids that are highly contrasted from the cement paste, for example, by impregnation with fluorescent dye [Ammouche et al., 2000 & 2001] and Wood's metal [Soroushian et al., 2003].

4.2 Resolution, brightness and contrast

A high quality original image is the prerequisite for accurate segmentation of features and subsequent quantification steps. For optimum performance, the electron microscope operating configuration (accelerating voltage, beam current and working distance) must be set depending on the particular contrast produced by the specimen/detector system. The threshold equation [Goldstein et al., 1981, 2003] can be used to determine the minimum beam current for a required level of contrast so that the smallest probe size is attained. The theoretical calculations for the electron gun brightness, probe current and probe diameter at different accelerating voltages for optimal imaging condition of cement-based materials are presented in Appendix I.

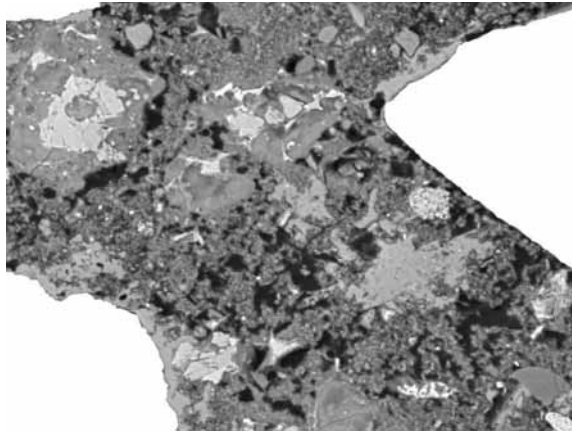
In most cases, however, spatial resolution is limited by the sampling volume from which the signal used for image formation is generated, whose effective size can be substantially larger than the electron beam. In a digital image, pixel spacing should ideally be smaller than the image resolution; otherwise, spatial digitising errors will become the most significant error in quantitative analysis. Aspects of the sampling volume and electron-solid interactions, optimum imaging strategy and resolution of BSE imaging for pores will be studied in detail using Monte Carlo simulation in Chapters 5 and 6.

As shown in Section 3.2.4, the brightness and contrast settings can have a significant influence on the appearance of the BSE image, in particular the amount of pore phase present. Some misinterpretation of BSE images arises from a lack of understanding of the need for a bright and properly contrasted image. A low contrast image contains many unused greyscale bins, hence lacks image detail and resolution. Therefore, inexperienced operators tend to ‘enhance’ the image during capture by increasing its contrast. However, if contrast is too high, image detail will be lost in the low and high regions of the greyscale, creating a distorted histogram with artificial peaks at both ends of the greyscale histogram. If all the phases are to be quantified, then ideally, the histogram should spread out as much as possible, but not beyond the greyscale spectrum. If the image is initially captured at too high contrast, it is meaningless to reduce the contrast later by image processing, as this will only compress the histogram, but not remove the artificial peaks. Any signal processing performed after image capture, although possibly improving visual appearance, does not increase the information content of the image.

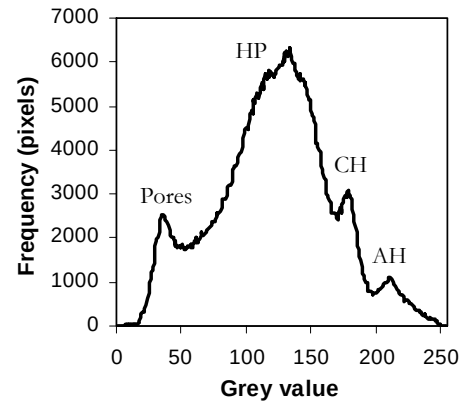
4.3 Development of a pore segmentation method

Fig. 4.1 shows two BSE images of different mortars taken at 500x magnification. Aggregates were removed from the original image and the brightness histogram of the remaining paste region is displayed. For the mortar with high w/c ratio, the brightness histogram consists of four distinct peaks representing pores, hydration products (HP), calcium hydroxide (CH) and anhydrous cement (AH) phases. For the mortar with low w/c ratio, only two peaks are visible; the larger peak is possibly made up of pixels from HP and CH phases, while the smaller peak from unreacted cement grains. There is no visible pore peak, apparently due to the low volume of pores in the sample. This observation suggests that a general segmentation method cannot only depend on the existence of feature peaks on the brightness histogram.

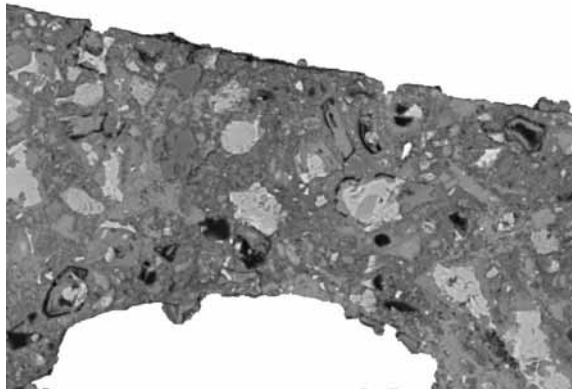
A single capillary pore extracted from Fig. 4.1 (c) is shown in Fig. 4.2 (a). The change in brightness along the mid-horizontal line indicates a gradual drop in grey value from approximately 100 to 20 over a distance of approximately $3\mu\text{m}$ near the pore boundary. Although the boundary may be atomically sharp, the gradual transition of the measured signal is a result of overlapping sampling volume at the boundary. This is schematically illustrated in Fig. 4.3. It can also be seen that this effect increases when the boundary is inclined towards the lower atomic number (Z) material (case b), for example, in the case of a shallow pore. The slightly higher signal recorded near the boundary of the high-Z material is due to an edge effect (see Section 6.3). The gradual drop in brightness near the boundary creates uncertainty regarding the true position of the pore edge. One may assume the pore threshold level to be either the upper, middle or the lower end of the ‘transition region’; in each case the measured pore size will be significantly different. However, as observed in Fig. 4.3, the grey value at the upper end of the transition region provides a closer estimate for the pore threshold.



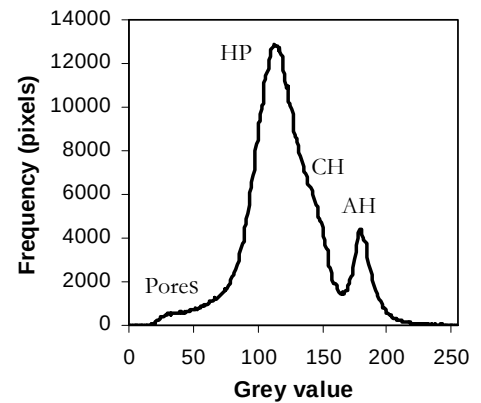
a) Mortar A (w/c: 0.70)



b) Brightness histogram for Mortar A



c) Mortar B (w/c: 0.35)



d) Brightness histogram for Mortar B

Figure 4.1 BSE images of paste regions from two different mortars at 28 days. The brightness histogram for the low w/c ratio mortar did not show a distinct peak for pores. Field of view is 267 μ m x 200 μ m.

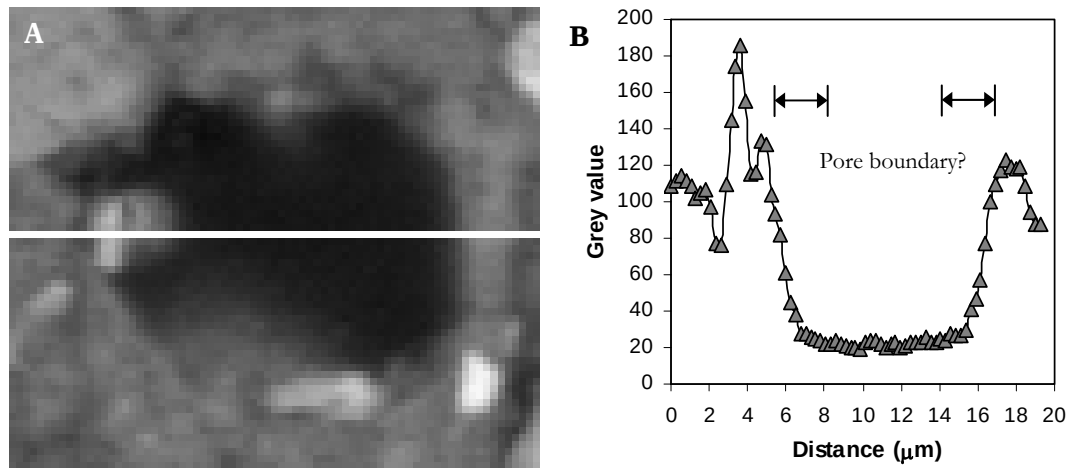


Figure 4.2 A) BSE image of a single capillary pore and B) variation of grey value along the horizontal white line shows ambiguity of the pore boundary. Field of view is approximately 20μm x 18μm.

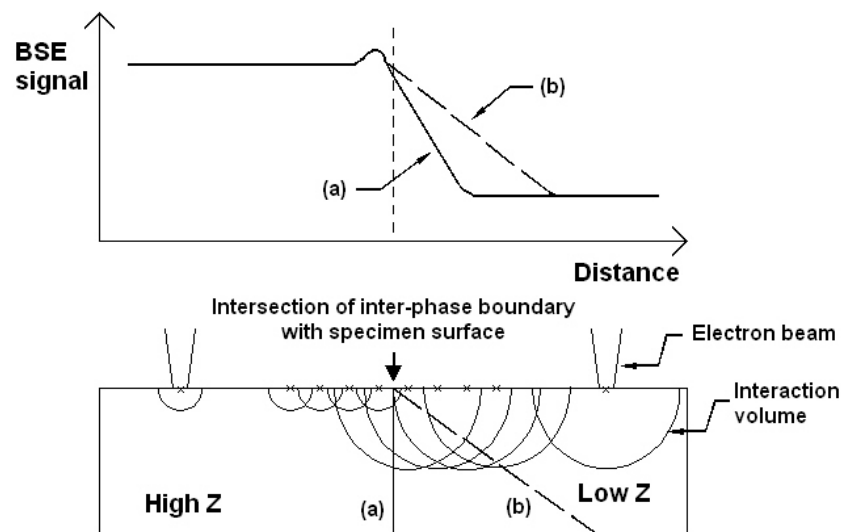


Figure 4.3 Schematic illustrating the influence of beam interaction volume on the BSE signal near the inter-phase boundary of a high and a low atomic number (Z) material when the hypothetical boundary is a) perpendicular and b) inclined to the specimen surface. Adapted from Goldstein et al. [1981]

Fig. 4.4 shows a series of images of the same pore with area segmented (white pixels) at different threshold levels. As the threshold is increased, pixels located in the pore centre are segmented first followed by pixels near the pore boundary. This figure demonstrates the ambiguity of the manual segmentation technique since the operator may select anywhere between 60 and 100 as the threshold. However, between 80 and 110, a sudden increase in area segmented can be observed when the surrounding solid phase is also selected. This is analogous to filling up a pore with a fluid. If viewed in plan, the area filled with the fluid will increase slowly as more volume is poured. As it arrives near the rim, a critical point is reached when the liquid will overflow to the surrounding areas and this will lead to a sudden increase of the area covered with the fluid. Therefore, the critical point where the area segmented starts to ‘overflow’ can provide a good estimate for the pore threshold level.

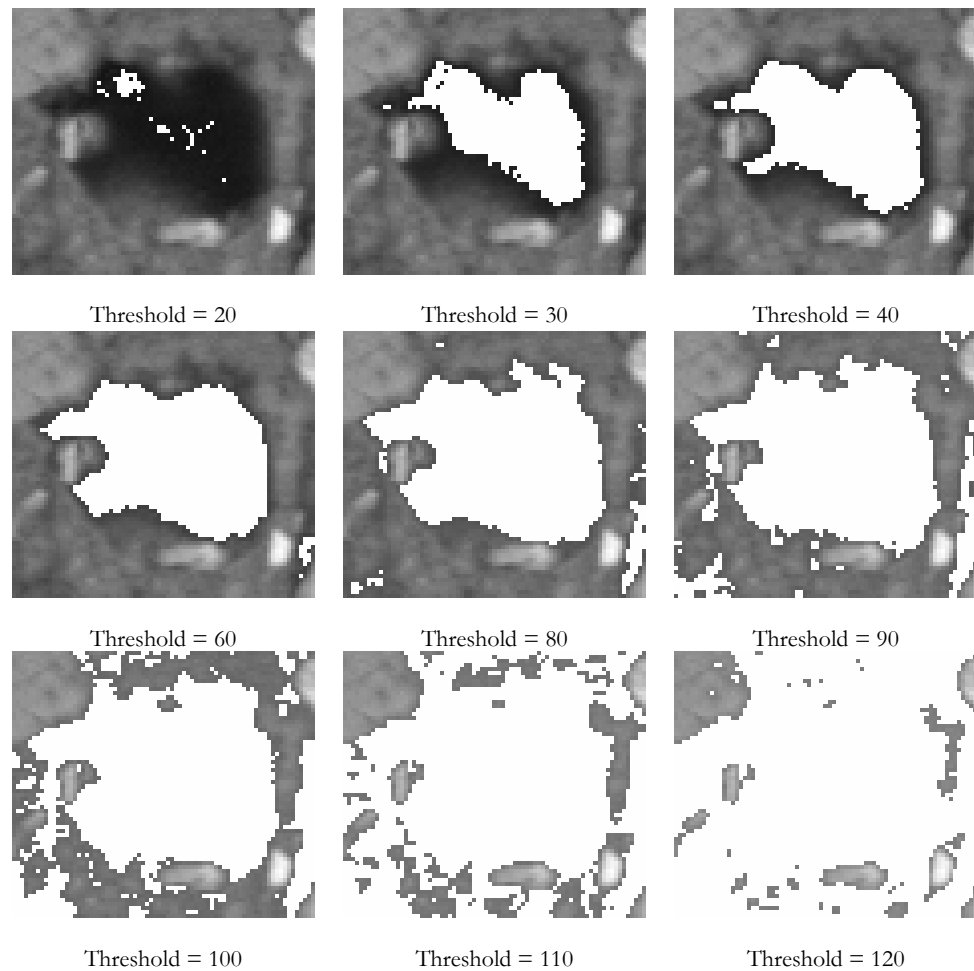


Figure 4.4 Change in area segmented (white pixels) at different threshold levels. Between thresholds 80 and 110, a sudden increase in segmented area is observed when the surrounding paste is also selected.

When the total area segmented is plotted against the threshold level in Fig. 4.5, the critical overflow point corresponds to the inflection of the cumulative curve, which can be estimated from the intersection between the two linear segments as shown in the figure. The grey value at this intersection can be used as the upper threshold level for porosity. However, this value may slightly overestimate the true overflowing point. A more conservative estimate may be obtained from the point where the curve begins to deviate from the first linear segment. This can be manually selected or approximated by multiplying the grey value obtained at the intersection by a factor of 0.9. Application of the proposed overflow criteria for pore segmentation is demonstrated on the full BSE image in Fig. 4.6.

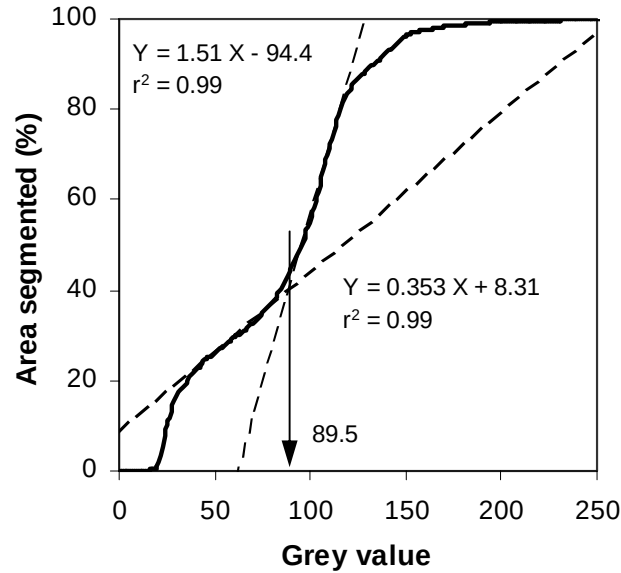
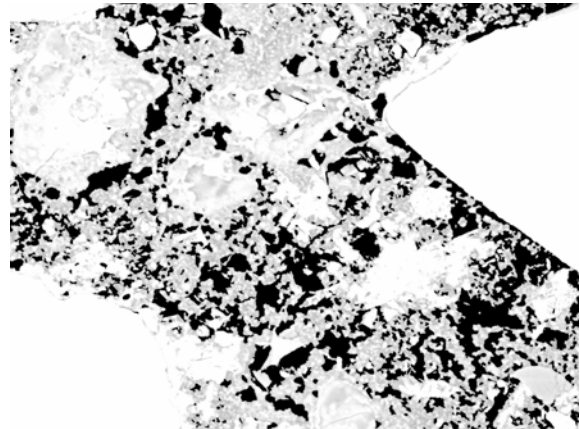
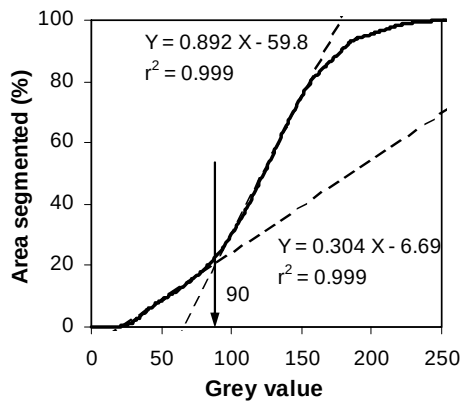


Figure 4.5 Change in area segmented with grey value for the pore in Fig. 4.3. The threshold value for porosity can be estimated from the inflection point.

4.4 Experimental

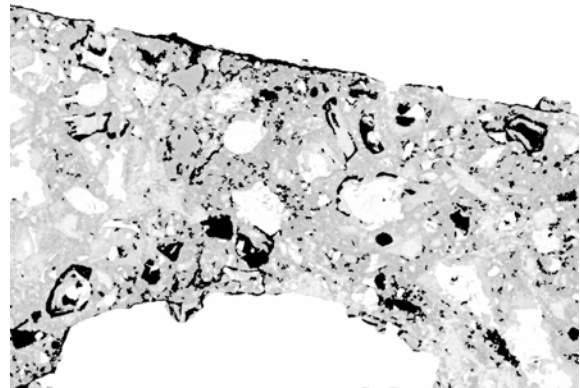
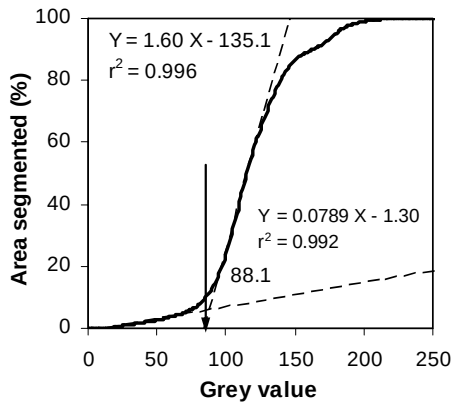
The proposed overflow method and several other existing pore segmentation methods were tested on mortars of w/c ratios 0.35 and 0.70. OPC and siliceous sand were used to prepare the mortars according to the proportions shown in Table 4.1. A naphthalene sulphonated type superplasticizer was used for Mortar B at a dosage of 0.5% by weight of ce-

ment. Cylindrical specimens (100 ϕ x 250mm) were cast, demoulded after 24 hours, wrapped in cling film and stored at 20°C (Section 3.1). After curing for 28 days, a 10mm thick disc was cut from each cylinder at approximately 100mm from the bottom cast face, from which a block specimen (40 x 20 x 10mm) for microscopy was prepared. The block sample was dried in an oven at 50°C, epoxy impregnated, polished using diamond paste down to 1/4 μ m (Section 3.2.1) and coated with carbon. A non-aqueous solution was used as lubricant for cutting and polishing. Acetone was used as cleaning fluid.



a) Cumulative greyscale histogram for Mortar A (Fig. 4.1 a)

b) Pores segmented (black pixels) from Mortar A at threshold level 90. Porosity of paste = 23.6%



c) Cumulative greyscale histogram for Mortar B (Fig. 4.1 c)

d) Pores segmented (black pixels) from Mortar B at threshold level 88. Porosity of paste = 11.5%

Figure 4.6 Application of the overflow criteria to determine a global threshold level for porosity

Mixture	Cement (kg/m ³)	Sand (kg/m ³)	w/c ratio
Mortar A	365	1635	0.70
Mortar B	550	1635	0.35

Table 4.1 Mixture proportions

Backscattered electron imaging was conducted under high vacuum. The microscope was operated at 20keV accelerating voltage and 15mm working distance. Thirty greyscale images were collected per sample at 500x magnification. Images were digitised to 1024 x 768 pixels at a pixel spacing of 0.26 μ m. In order to ensure a systematic random sampling, the microscope stage was programmed to move in a grid fashion, stopping at thirty predefined, equally spaced coordinates (Section 3.2.6). Sections near the specimen edge were not imaged to avoid areas that may have been saw-damaged. During image capture, the brightness and contrast setting was adjusted such that ten bins from each end of the greyscale were left empty, i.e. no pixel count is registered on the 0-10 and 245-255 grey values of the captured image. This was done to ensure that the brightness histogram is well spread out, but does not exceed the greyscale spectrum. It also indirectly calibrates the microscope so that the brightness and contrast for each frame is relatively similar.

4.4.1 Aggregate segmentation

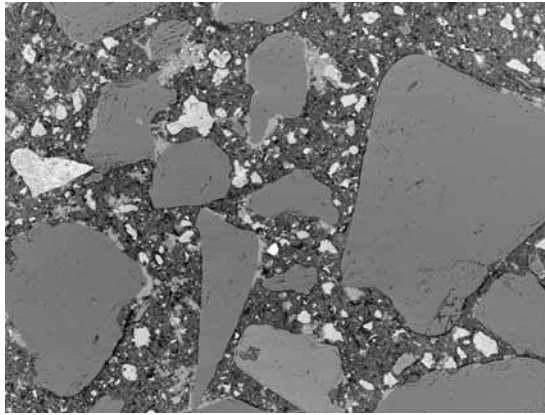
For mortars and concretes, an image captured at 500x magnification will most likely contain a considerable fraction of aggregate particles. These aggregate particles must first be removed from the original image before subsequent processing such as segmentation and measurement of the pore phase can be carried out. Since the greyscale values of the aggregate phase overlap with that of the hydrated cement paste, they can present an obstacle for greyscale thresholding of other phases. The aggregate particles themselves may contain some pores and these need to be isolated from other pores. In addition, measurements made on the pores (volume fraction and specific surface) are normalised to the cement paste. Therefore, an accurate and efficient method to segment aggregate particles must be established.

The aggregates used in concrete production typically contain silica-rich or calcium-rich minerals such as quartz and calcite, which share very similar BSE coefficients to the hydrated cement phases (Aft, C-S-H, CH). As such, a simple greyscale thresholding is not ef-

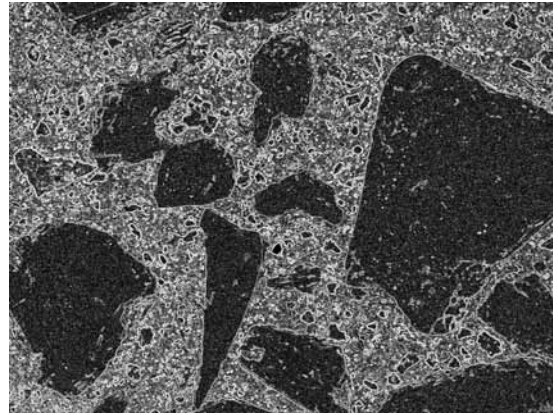
fective because more than one phase would be selected simultaneously. Early on, it was decided that methods employing energy dispersive x-ray dot maps collected in tandem with BSE images, which allows for elemental mapping to identify the aggregate phase based a priori knowledge of the aggregate mineralogy [Brough & Atkinson, 2000; Head & Buenfeld, 2005], are unsuitable because of the amount of effort and time involved. Clearly, a quicker yet reasonably accurate method is required so that analysing a large image dataset is practical.

The aggregates used in this study are siliceous and contained mainly one mineral, quartz. Hence, it would be expected that the variation of grey level within an aggregate particle is very small compared to the hydrated cement paste, where the grey level fluctuates substantially within a small area due to the presence of various phases of different mean atomic numbers. This forms the basis of an aggregate segmentation algorithm and Fig. 4.7 shows how this may be achieved. The sample is a mortar with w/c ratio 0.7, captured at low magnification. First, a sobel filter is applied to differentiate the ‘rough’ areas with high grey value variation from the ‘smooth’ areas with small grey value variation, the result of which is a highly contrasted image (Fig. 4.7 b). A suitable greyscale threshold is selected for the aggregate phase producing a binary image (Fig. 4.7 c). This inevitably contains small particles of other phases, so the larger aggregate particles are extracted using a size filter particle detection tool (Fig. 4.7 d) and a binary mask is created from the selected particles. Morphological closing and hole-filling operations are then applied to fill gaps within the aggregate boundary (Fig. 4.7 e) and finally, the aggregate mask is superimposed onto the original image (Fig. 4.7f).

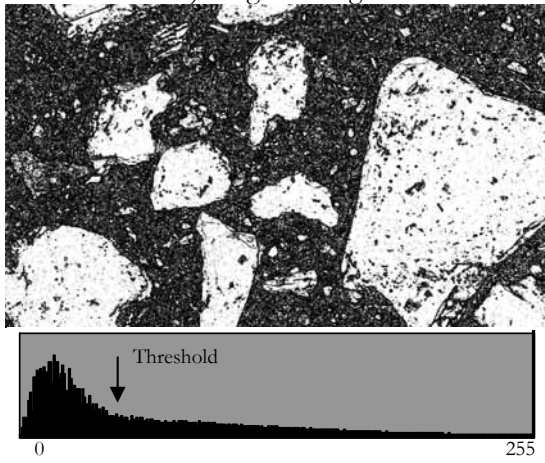
This approach is similar to the one proposed by Yang & Buenfeld [2001], which uses an edge detection filter to identify local gradients in grey values. Its advantage is that the entire process is operator-free and can be fully automated. However, as observed in Fig. 4.7(f), segmentation errors (arrowed) occur where pixels not belonging to the aggregate phase are also selected while some aggregate pixels are ignored. Such errors become obvious when the same operation is done on a 500x magnification image (Fig. 4.8). Segmentation errors normally occurred where the aggregate particle was in close contact with CH deposits, and where there was damage on the aggregate surface.



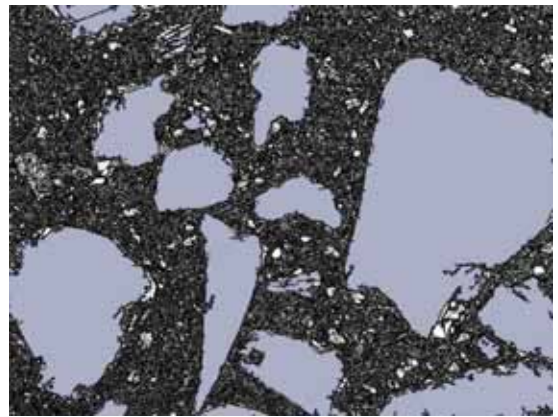
a) Original image



b) Sobel filter



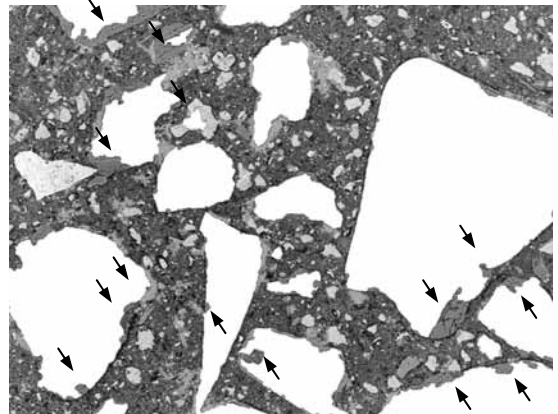
c) Greyscale thresholding



d) Particle selection



e) Aggregate binary mask



f) Final result

Figure 4.7 Using Sobel and morphological filters for aggregate segmentation. Sample is M 0.7 (63S) 3d, image captured at 150x, field of view is 800 x 600 μ m.

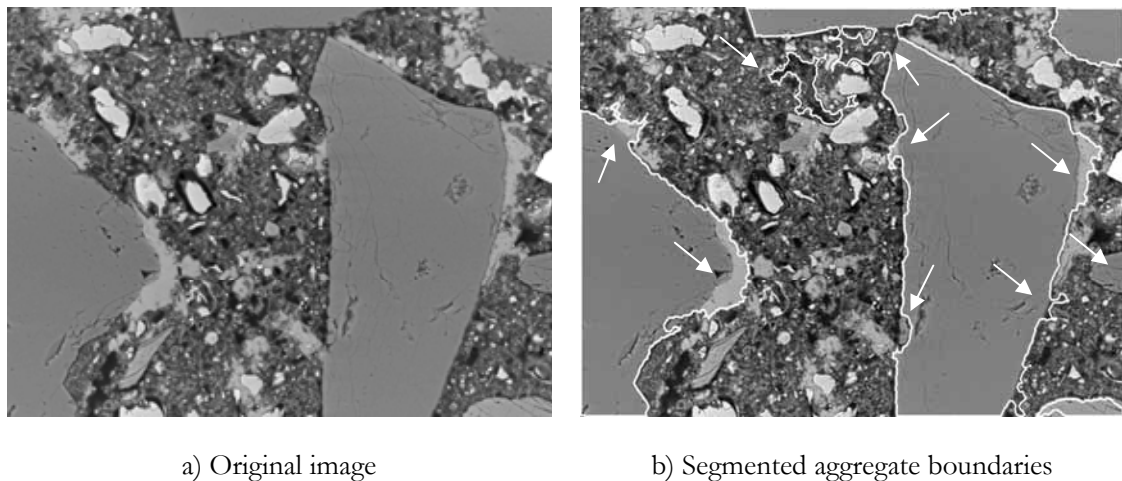
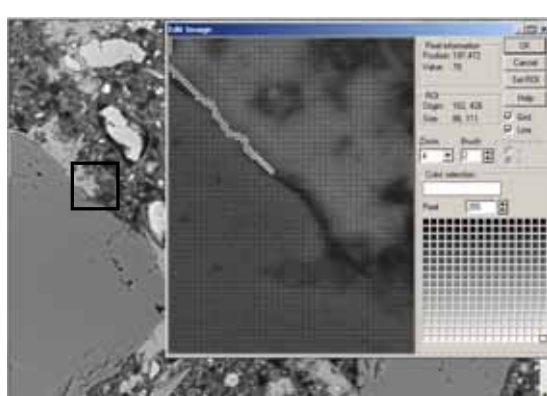


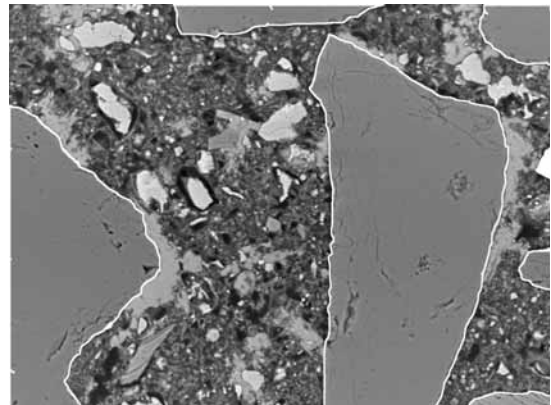
Figure 4.8 Errors generated from the aggregate segmentation method in Fig. 4.7. Sample is M 0.7 (63S) 3d, image captured at 500x, field of view is 240 x 180 μ m.

It appears that segmentation errors from a fully automated procedure based on a combined filtering, grey level thresholding and binary operation, are inevitable, and that the final image would consistently require manual checks and corrections, therefore defeating its purpose. A simpler and more accurate approach is to first manually trace out the aggregate boundary using a white line, threshold the white boundary, then carry out a particle detection and hole filling operation. This approach is shown in Fig. 4.9. Obviously, the first step is the most crucial, so the image needs to be enlarged sufficiently so that the aggregate boundary is clear and a fine pixel-wide line can be drawn on to it (Fig. 4.9 a).

This manual boundary tracing method may first appear to be a tedious process and prone to operator judgemental error, but in fact, it is not. The boundary marking is done at high magnification, which helps the operator to make an accurate decision on the location of the aggregate-cement paste interface, even where there are dense CH deposits. Another benefit is that the operator can simultaneously detect bond cracks between the aggregate and cement paste, and exclude them from the cement paste. Bond cracking is a form of sample preparation artefact and should not be taken as part of the original pore structure. It is not easy to design a procedure that automatically differentiates between bond cracks and other forms of cracks, because they do not always occur on every aggregate particle, so the most effective way to detect them is to do it manually. Once the aggregate boundary is accurately marked, subsequent operations are automated and guaranteed to be defect free. From experience, the manual segmentation method can process approximately one frame per minute, for images captured at 500x magnification.



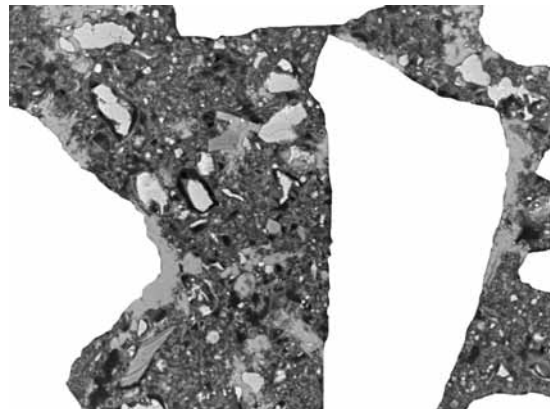
a) Manual tracing of the aggregate boundary



b) Completely traced out boundaries



c) Thresholding and particle detection



d) Final image

Figure 4.9 Using manual boundary tracing method to segment aggregate particles. Sample is M 0.7 (63S) 3d, image captured at 500x, field of view is 240 x 180 μ m.

4.4.2 Pore segmentation

Various methods for pore segmentation were tested. Manual thresholding was done by the same operator and prior to the other methods to minimise bias. An initial threshold corresponding to larger pores was first set by judgement. The pixels selected were colour coded and superimposed on to the original image to check if the selected pixels matched the pores in the original image. This visual comparison was made at higher magnifications to reveal smaller pores and detailed pore boundaries; the threshold was then adjusted until all pores were satisfactory covered by the coloured pixels. The tangent-slope thresholding

method was done according to Scrivener et al. [1987]. For mortar A, where a pore peak existed in the histogram, the minimum point between the pore peak and the HP peak was taken as the porosity threshold. This can be located by referring to the first-derivative curve of the brightness histogram. Thresholding by entropy maximisation was done according to Kapur et al. [1985] (see Appendix III).

For the proposed method, two values were tested: Overflow 1 is the grey value at the inflection point and Overflow 2 is a more conservative estimate obtained by factoring Overflow 1 by 0.9. Another method tested is the auto-threshold utility that is available in image analysis software. This method calculates thresholds based on the overall histogram of the image. A priori knowledge of the number of phases that exist in the image is required. In this study, the greyscale histogram after having the aggregate particles removed was assumed to consist of four phases: pores, HP, CH and anhydrous products. Thresholds are calculated using a statistical comparison of the grey values of the various parts of the image. The algorithm first selects a grey value randomly as the threshold for each phase. The average grey value and the standard deviation are then calculated for the grey value ranges both to the left and the right of this initial threshold. The system will then continue to adjust the randomly selected threshold until optimal averages and standard deviations have been attained.

Once the various pore thresholds had been determined, binary segmentation was performed on the images to separate pores from other phases. Based on principles of stereology (Section 2.4), the volume fraction of a particular phase in an isotropic material is equivalent to its area fraction observed on a random plane-section. Porosity was then calculated as a percentage of the segmented pore area to the total paste area. However, features smaller than 10 pixels were regarded as noise and excluded from the porosity calculation. This sets a lower size limit of the detected pores to 10 pixels, which have an equivalent circular diameter of $0.9\mu\text{m}$. The detected hydrated cement paste porosity from all frames was then averaged and the values from various segmentation methods were compared.

4.4.3 Averaging pore volume fraction

Although the volume fraction of a particular phase of interest is generally defined with respect to a unit volume of the reference space, i.e. the image field of view, this does not always have to be the case. For example, in a multi-phase material, the volume fraction of a certain phase can be defined as per unit volume of another phase, rather than per unit volume of the reference space. In the context of this study, when image analysis is used to

quantify the porosity of mortar and concrete samples, it is usually the case that the detectable pore area fraction is normalised to the cement paste area and not the image field of view. This is the correct approach because at the magnification level used in such analyses (500x for this study) the aggregate particles themselves are large with respect to the field of view and therefore would not be sampled representatively. Conversely, if the image is captured at very low magnification, in order to sample the aggregate particles adequately, its resolution would be insufficient for accurate pore characterisation.

In such cases, averaging the pore volume fraction of a dataset of images needs to be done carefully because now the reference space (i.e. the hydrated cement paste) varies from one field of view to another. If the reference space area varies then the unbiased estimator for volume fraction becomes an example of a ‘ratio estimator’ [Cochran, 1977] where both the numerator and the denominator of the ratio can vary from one field of view to the next. In these circumstances, it is not correct simply to average the individual pore volume fraction over all fields [Howard & Reed, 1998]. The unbiased way to deal with a ratio estimate is to sum all pixels of the phase of interest (pore pixels) over all fields analysed, then divide by the sum of all pixels of the reference space (cement paste pixels) over all fields analysed. For example, if A_i and B_i represent the number of pixels counted for the pore and cement paste respectively for frame i , then the unbiased average porosity, μ , which we term here as ‘cumulative average porosity’, after a total of n frames, is:

$$\mu = \frac{\sum_{i=1}^n A_i}{\sum_{i=1}^n B_i} \quad \text{‘Cumulative average porosity’ (Unbiased estimate)} \quad \text{Eq. 4.1}$$

Whereas, the ‘normal average porosity’ over n frames is:

$$\mu = \frac{1}{n} \sum_{i=1}^n \left(\frac{A_i}{B_i} \right) \quad \text{‘Normal average porosity’ (Biased estimate)} \quad \text{Eq. 4.2}$$

For mortar and concrete samples, where the image area covered by aggregates varies substantially from one field to another, as shown in several examples in Fig. 4.10, the cumulative average porosity (Eq. 4.1) should always be used. The difference between Eq. 4.1 and Eq. 4.2 is subtle, but the final result can have a substantial difference depending on which method is used. It is well-known that pores in the hydrated cement paste are not homogene-

ously distributed. Specifically, the paste region adjacent to aggregate particles, known as the ‘interfacial transition zone’ (ITZ), contains statistically more capillary pores than the ‘bulk paste’ located further away (Section 8.3). Therefore, in images containing a large portion of aggregate particles such as in the example shown in Fig. 4.10, a higher fraction of ITZs will be analysed and most likely, a higher pore fraction per unit paste area will be measured in this frame compared to another that contains less aggregate particles. Using Eq. 4.2 to compute the average porosity over a set of images will provide a result that is biased towards values from images with a higher ITZ fraction, since every frame is given equal weight. However, for cement paste samples, both equations will lead to the same answer because the denominator, B_i in this instance, is constant for every frame and equivalent to the field of view.

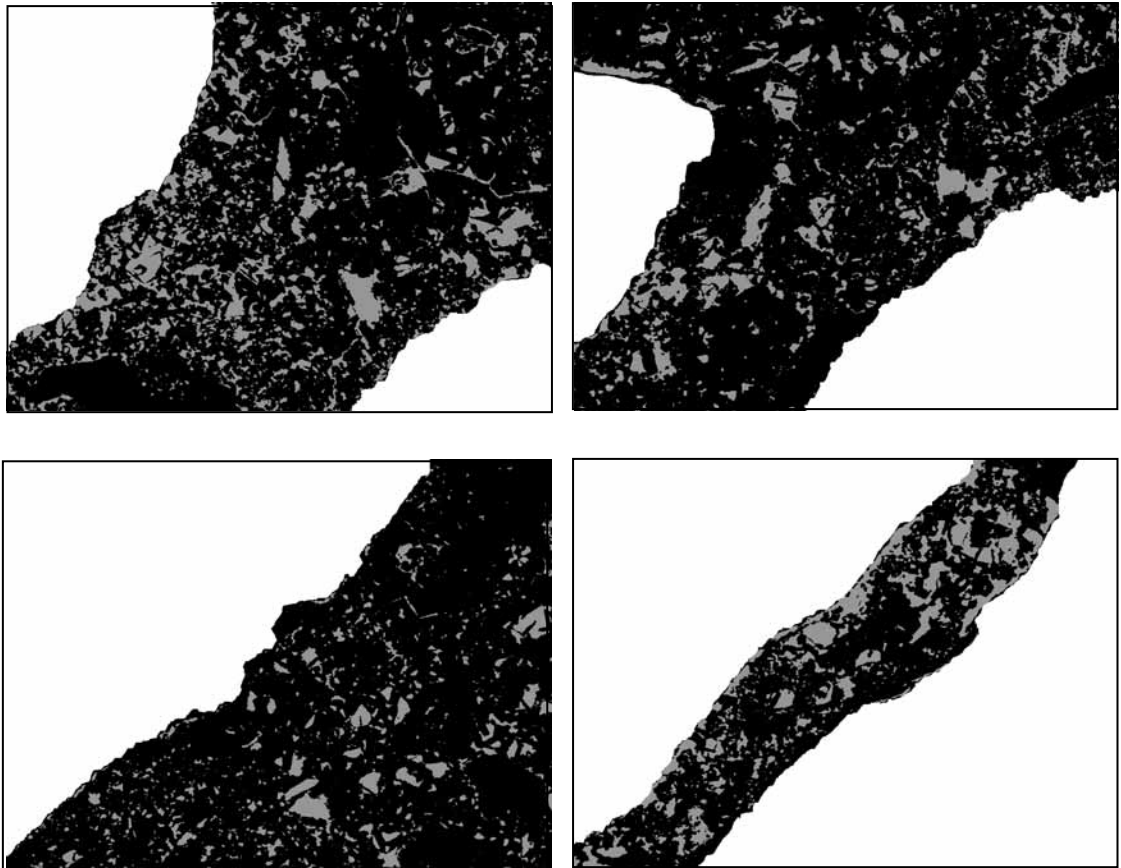


Figure 4.10 Four segmented BSE images showing the aggregate (white), pores (grey) and hydrated cement paste (black) phases. The cement paste area varies depending on the amount of aggregate present. Sample is M 0.7 (63S) 28d, images captured at 500x, field of view is 267 x 200 μ m.

4.5 Results and Discussion

Table 4.2 shows results of the cumulative average porosity μ and standard deviation s , after processing all thirty images using various segmentation methods. The minimum number of frames required to give a level of statistical confidence is also provided. The number of frames required per sample, n , such that the sample mean is within 10% of the true population mean μ , at 95% degree of confidence is calculated from Student's t-distribution (see Appendix II).

Entropy maximisation produced the most consistent thresholded porosity since only one frame was required to achieve a statistically significant result, but gave unrealistically high porosity values for both mortars. This method may only be suitable when the pores are highly contrasted. The auto-detection (analySIS®) method performed well for Mortar A, but also returned a high porosity value for Mortar B. The proposed overflow technique was found to perform better than other methods based on the coefficient of variation and the number of frames required to achieve a desired degree of confidence. It is worthwhile to note here that the two linear segments used to determine the critical overflow point can be found in each of the analysed images. For Overflow 1, less than 15 frames were needed compared to 30-100 frames for other methods. This highlights the importance of using an objective and reproducible threshold selection criteria. Near the critical overflow point, any subtle changes in the threshold value will create an enormous response in the total thresholded area. Hence, manual selection of the threshold value will most certainly lead to a high variance in the segmented porosity.

In Fig. 4.11, the cumulative average porosity is plotted against the number of frames. The cumulative average porosity after frame i give a pore fraction value that is measured over a larger combined area. The figure shows that the cumulative average porosity obtained from the overflow criteria stabilises after about 15 frames. This remains valid even when the order of the images is shuffled. It is also interesting to note that the manually thresholded porosity matches with Overflow 1 values and the tangent-slope values with Overflow 2. The manually thresholded porosity is slightly higher than Overflow 1, possibly because human bias tends to slightly overestimate the area of the features of interest [Russ, 2002]. When visually selecting a threshold, the operator is more tolerant of settings that include additional pixels from background region (solid) along with the features (pores), than they are at settings that exclude some pixels from the background.

Segmentation method	Mortar A (w/c: 0.70)				Mortar B (w/c: 0.35)			
	μ (%)	s (%)	$(S/\mu) \times 100\%$	n	μ (%)	s (%)	$(S/\mu) \times 100\%$	n
Manual	22.0	7.3	33.3	46	11.3	5.6	49.5	103
Minimum-point between peaks	13.2	5.0	37.8	60	-	-	-	-
Tangent-slope	-	-	-	-	6.3	2.4	37.6	59
Entropy maximisation	47.9	0.7	1.4	1	48.1	1.2	2.4	1
Auto (analySIS®)	23.4	3.3	14.0	8	21.5	5.8	26.8	30
Overflow (1)	21.2	3.8	17.7	13	10.6	1.5	14.2	8
Overflow (2)	15.9	4.2	26.6	30	6.7	1.4	21.9	20

Table 4.2 Statistical analyses

The mixtures investigated in this study represent very high and low porosity mortar, and the proposed technique performed well in both cases; therefore, it should also be applicable to samples with intermediate porosity values. Although only one magnification level was investigated in this paper, albeit a commonly used one, unpublished observations show that the critical overflow point can also be found in the cumulative brightness histogram of images taken at 350x and 750x magnifications. Another advantage of this method is that it can be applied to a BSE image of an ordinary polished sample without requiring any special techniques to highlight the pores, such as liquid metal intrusion.

It is difficult, if not impossible, to ascertain which segmentation method produces a more accurate porosity value. Possibly, by comparing results with other pore-quantification methods such as gas-adsorption or mercury porosimetry, an indication may be obtained, however, the fundamental differences and inherent weaknesses of these techniques must also be taken into account in making such comparisons. Another way is by correlating the image analysis porosity with some other physical characteristics such as mechanical strength and transport properties. Nevertheless, it must be stressed that classification of pixels into their respective phases based on grey level can never be a perfect process, although as shown in this study, errors can be minimised by using an appropriate thresholding rule.

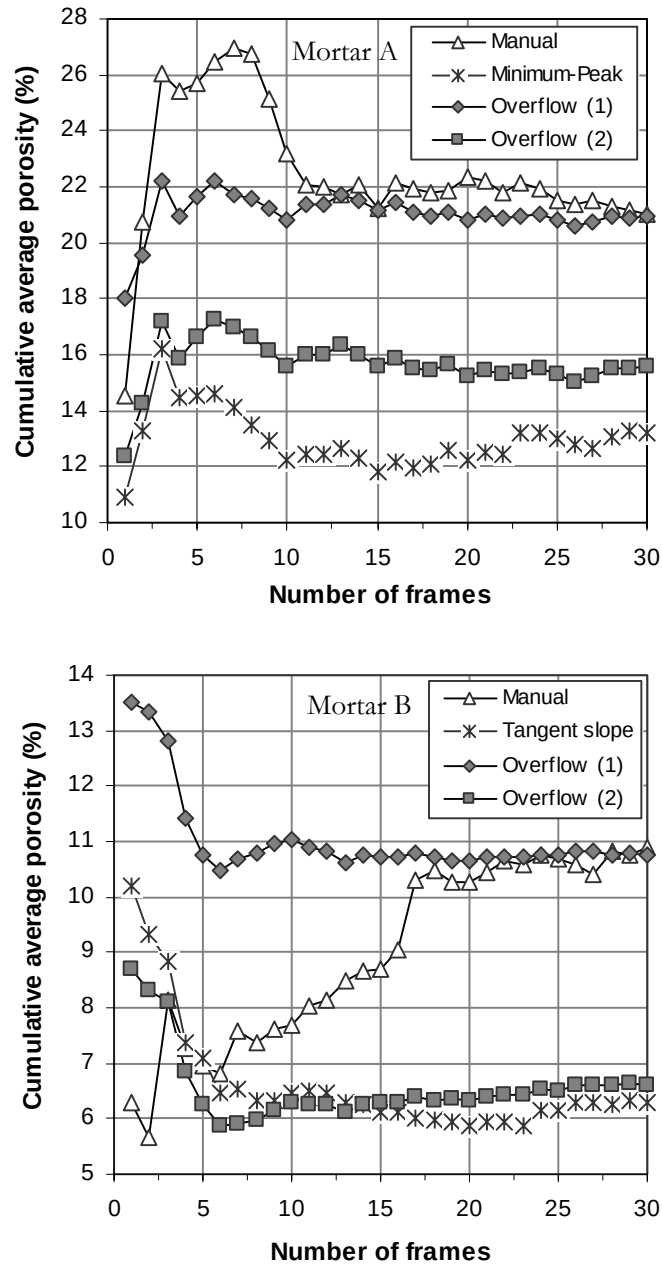


Figure 4.11 Cumulative average porosity for Mortar A and Mortar B. The proposed segmentation method requires fewer frames to achieve a stable porosity value.

In the late 1940s, Powers & Brownyard [1948] developed a model based on data obtained from water vapour adsorption isotherms, which can be used to estimate the volume fraction of all major phases in Portland cement pastes cured at room temperature. According

to the Powers' model, the capillary porosity (Φ_{cap}) is related to the w/c ratio and the degree of hydration (α) via the following equation [Hansen, 1986]:

$$\Phi_{cap} = \frac{w/c - 0.36\alpha}{w/c + 0.32} \quad \text{Eq. 4.3}$$

Using image analysis, the degree of hydration for Mortar A and Mortar B is estimated to be about 0.9 and 0.7 respectively. Thus, according to Powers' model, the capillary porosity for a cement paste at the same w/c ratio and degree of hydration as Mortar A and Mortar B is about 37% and 15% respectively. By comparing these values to those shown in Table 4.2, it is observed that all thresholding methods except for entropy maximisation gave porosity values smaller than the capillary porosity predicted by Powers' model. Assuming that Powers' model is correct, this underestimation of the capillary porosity is likely due to the finite image resolution. Nevertheless, the porosity values obtained from the manually selected threshold and Overflow (1) are closest to the Powers' model. A further study comparing the porosity values measured from image analysis for a range of samples to those obtained by other methods, including Powers' model, is presented in Section 9.4.1

4.6 Conclusions

The feature-segmentation stage is of prime importance for accurate quantitative image analysis of microstructures. A good segmentation method is one that is autonomous and objective, returning an accurate and reproducible result. In this chapter, a pore segmentation method for backscattered electron images of cement-based materials is presented. The method involves determining the porosity threshold from the inflection point of the cumulative brightness histogram of the grey level image. This value corresponds to the critical point where the segmented pore areas begin to 'overflow' to the surrounding paste. This technique was found to be more objective, reliable and economical than existing pore segmentation methods and resolves the difficulties in defining the true boundary of the pore phase, particularly for dense microstructures. The proposed segmentation method is able to produce a porosity value that is close to the one obtained by visual thresholding, but requires substantially fewer frames to achieve a statistically significant result. This technique facilitates future work on pore-structure characterisation via image analysis, which is an important subject in cement and concrete research since the pore phase controls not only strength and elastic properties, but also molecular transport properties and overall durability.

Chapter 5

Monte Carlo simulation of electron-solid interactions in cement-based materials

Knowledge of the size of the electron-solid interaction volume and the sampling volume of various signals within it is important for interpretation of images and analytical results obtained from electron microscopy. In this chapter, a Monte Carlo technique is applied to simulate electron trajectories in order to investigate the shape and size of the interaction volume and the spatial and energy distribution of backscattered electrons and characteristic X-rays in cement-based materials. It is found that the maximum penetration depth of the electron trajectories ranges from 0.75 to 1.5 μm at 10keV and from 2.5 to 5.0 μm at 20keV. For backscattered electrons, the maximum sampling depth is about 30% of the interaction volume depth and its lateral dimension is close to the interaction volume depth. The sampling volume size of characteristic X-rays is a substantial fraction of the interaction volume. For ettringite, the amount of material analysed in X-ray microanalysis is in the order of 1 to 100 μm^3 at conventional SEM accelerating voltages of 10 to 20keV.

5.1 Introduction

Electron microscopy, in particular the backscattered electron (BSE) mode coupled with X-ray microanalysis, is an important research tool in cement and concrete science. For many years, electron microscopy has been used for qualitative and quantitative studies of the microstructure and chemical composition of phases in cement-based materials. In the journal *Cement and Concrete Research* alone, an electronic search [ScienceDirect, 2005] using the keywords electron microscopy, SEM, EDS or EDX returned more than 500 articles within the abstract, title or keywords field and more than 1500 articles within the full-text field, dating from its first publication in 1971.

In the electron microscope, a high-energy electron probe with a size in the nanometre range is focussed onto a target sample. The interactions between the incident electrons and the sample produce various signals that can be used to form images or spectra, giving information regarding topography, structure and chemical composition of the sample. How-

ever, these signals are generated within a finite volume in the sample that can be substantially larger than the incident probe size. Therefore, knowledge of the shape and dimension of this interaction volume, the distribution of various signals within it and factors that control this, is critical for interpretation of the resulting images or spectra.

The shape and size of the interaction volume depends on the sample properties (chemical composition, atomic number, density) and the operating conditions of the electron microscope (accelerating voltage, probe diameter, surface tilt). For cement-based materials, the shape of the interaction volume is generally assumed to follow that of low density, low atomic number materials, i.e. pear shaped with a small entry neck where most secondary and backscattered electrons originate. As electrons penetrate deeper, the lateral spread of the electron-solid interaction region increases. This is shown schematically in Fig. 5.1, taken from Scrivener [2004]. Secondary electrons originate from the sample close to the surface, backscattered electrons emerge from slightly greater depths and characteristic X-rays are generated throughout the entire interaction volume. The lateral dimension of the interaction volume for cement-based materials has been reported to be around 1-2 μm [Diamond, 1972; Detwiler et al, 2001; Scrivener, 2004] and the volume of material analysed by the electron probe approximately 1-2 μm^3 [Jensen et al., 1996].

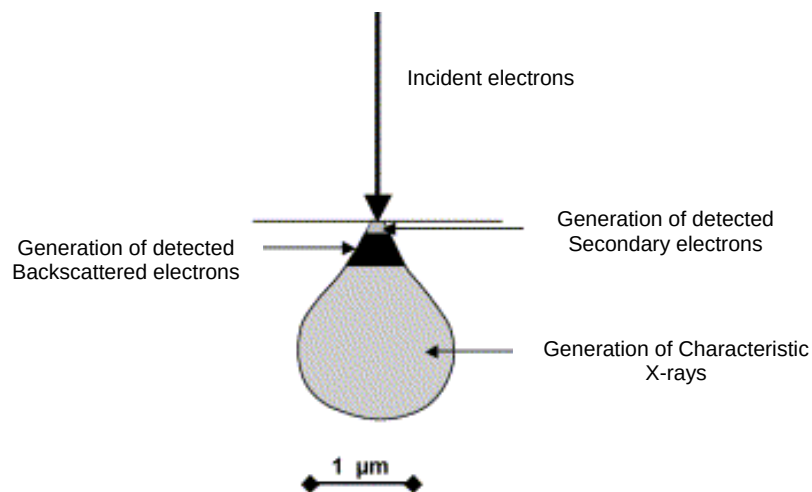


Figure 5.1 Schematic showing signal generation in the electron microscope for typical cementitious materials (from Scrivener [2004]).

In this chapter, a Monte Carlo technique is used to simulate the electron-solid interactions in cement-based materials. The aim is to investigate the shape and size of the interaction volume in cement-based materials under typical microscope operating conditions. The particular focus will be the region where backscattered electrons and characteristic X-rays are generated when a flat-polished sample is subjected to conventional beam energies (10keV to 20keV). It is hoped that this study will give a better understanding of the signal formation process, the performance and limitations of electron microscopy as an imaging and analytical tool for cement and concrete research. This can also assist in the selection of an optimal imaging strategy for a particular application and facilitate interpretation of results.

5.2 Physics of the electron-solid interactions

This section gives a brief overview of the physical processes that occur when an electron beam interacts with a solid target and how Monte Carlo methods can be used to simulate this. A detailed mathematical description is beyond the scope of this thesis, therefore, only a summary of important concepts is given here. A comprehensive treatment of the subject can be found in texts by Shimizu & Ze-Jun [1992], Joy [1995a], and Goldstein et al. [2003].

When a beam of high-energy electrons hits a solid target, the electrons will interact with the electrical fields of the target's atoms and undergo elastic and inelastic scattering events. In elastic scattering, the incident electron is deflected to a new trajectory with no energy loss. After several elastic scattering events, the electrons will spread out and some may escape the sample surface as backscattered electrons. The incident electrons will also gradually lose their energy with distance travelled via inelastic scattering. Kinetic energy is transferred to the sample, producing signals such as secondary electrons, auger electrons, cathodoluminescence, and characteristic and continuum X-rays. There are several mathematical models that describe the probability of an electron undergoing elastic scattering, most notably the Rutherford and Mott scattering cross-section [Mott & Massey, 1965]. For inelastic scattering, the Bethe's stopping power equation [Bethe, 1930] describes the rate of energy loss with distance travelled.

The probability of elastic scattering increases strongly with atomic number Z , approximately Z^2 , since heavier atoms have a stronger positive charge in the atomic nucleus. The probability of elastic scattering also decreases with increase in electron energy E , ap-

proximately as $1/E^2$. This process is described mathematically in Eq. 5.1, which calculates the probability of elastic scattering for angles greater than a specified angle Φ_o :

$$Q(>\phi_o) = 1.62 \times 10^{-20} (Z^2 / E^2) \cot^2(\phi_o / 2) \quad \text{Eq. 5.1}$$

Q is known as the cross section (cm^2) for elastic scattering, or the probability of elastic scattering. The mean free path λ (cm), i.e. the distance the electron travels between scattering events, is calculated from the cross section and density of atoms along its travel path:

$$\lambda = A_o / N_A \rho Q \quad \text{Eq. 5.2}$$

Where N_A is Avogadro's number, A_o is the atomic weight (g/mole) and ρ is the density (g/cm^3). As the electrons propagate through the sample, they will gradually lose its energy via inelastic scattering, transfer of energy to specimen atoms, producing signals such as secondary electrons, auger electrons, cathodoluminescence and X-rays. Bethe [1930] described the rate of energy loss dE (keV) with distance travelled ds (cm) as:

$$\frac{dE}{ds} = -2\pi e^4 N_A \frac{Z\rho}{A_o E_i} \ln\left(\frac{1.166E_i}{J}\right) \quad \text{Eq. 5.3}$$

Where E_i (keV) is the electron energy at any point in the specimen and J (keV) = $(9.76Z + 58.5Z^{-0.19}) \times 10^{-3}$, is the average loss in energy per event [Berger & Seltzer, 1964].

5.3 Monte Carlo simulation of the electron-solid interactions

Apart from low atomic number materials, such as polymethylmethacrylate that undergoes damage during electron bombardment, experimental observation of the interaction volume is not possible. As a result, the Monte Carlo simulation technique has been developed over the last four decades to study electron-solid interactions and is now an established tool for interpretation of SEM images and X-ray microanalysis results. Specifically, the Monte Carlo method can simulate the angular, lateral and depth distributions of secondary, backscattered and transmitted electrons, energy dissipation and generation of characteristic X-rays. These are used to determine the spatial resolution for each signal for a particular operating condition and sample composition. Examples of early pioneering work in this field

include the publications by Shimizu & Murata [1971], Shimizu et al. [1972], Murata [1974], Adesida et al. [1980] and Heinrich & Newbury [1991]. Recent applications include studies of the resolution in semiconductor multilayers [Merli et al, 1995] and the position of phase boundaries in composite materials [Cousens & Joy, 1997].

In a Monte Carlo simulation of the electron-solid interactions, the electron trajectory is followed in a stepwise manner from its entry point until it loses all of its energy and is absorbed, or until the electron is backscattered. At each point, the probability of the electron undergoing scattering, the scattering angle, distance between scattering events and the rate of energy loss is calculated from appropriate physical models. The location of the electron within the sample and its kinetic energy is constantly updated with time, together with the generation of secondary electrons and characteristic X-rays.

Since the electron-solid interaction is essentially a stochastic process, random numbers and weighting factors are used to replicate the statistical distribution of scattering events, hence the name ‘Monte Carlo’. Therefore, the accuracy of the simulation depends entirely on the models and assumptions used, but knowledge of these has been built over the years of improvements to the approximations adopted to describe the elastic and inelastic scatterings. The accuracy and limits of applicability of Monte Carlo simulations has been established by comparison with experimental values, for example, in the work by Shimizu et al. [1975] and Newbury & Myklebust [1984].

Fig. 5.2 shows examples of Monte Carlo simulation of electron-solid interactions in a calcium hydroxide target when hit by an electron beam at 20keV accelerating voltage. Backscattered and transmitted electrons are represented by the black and grey lines respectively. The number of backscattered electrons, divided by the total number of simulated electrons, gives the backscatter coefficient for the studied phase. Figs. 5.2 (A-D) are from four independent simulations of 25 electron trajectories each, showing that the result is highly variable when only a small number of electrons are simulated due to the stochastic process of the Monte Carlo technique. However, when a significantly large and representative number of electrons are observed, the result will approach that of the actual statistical distribution for a specific sample property and electron beam condition.

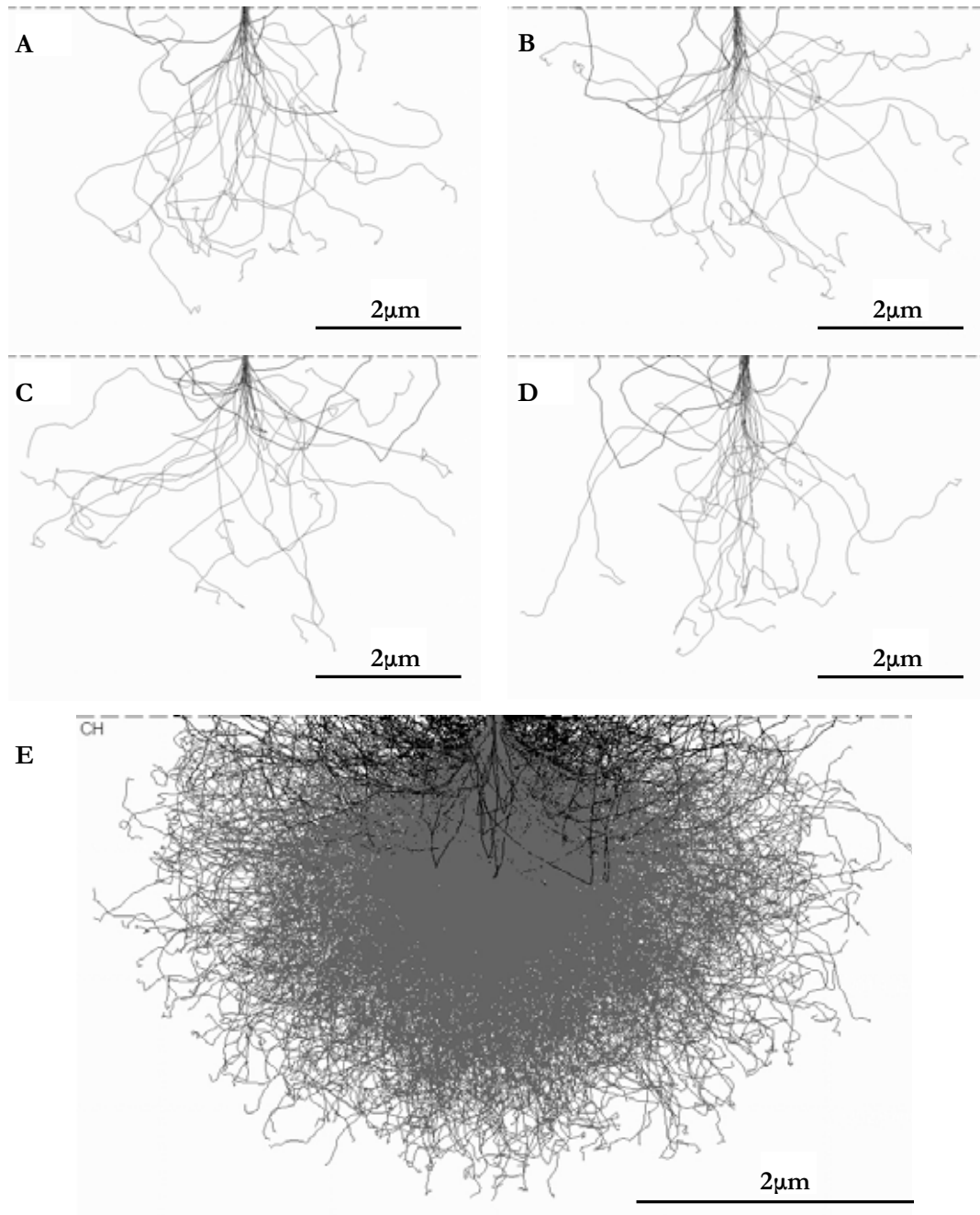
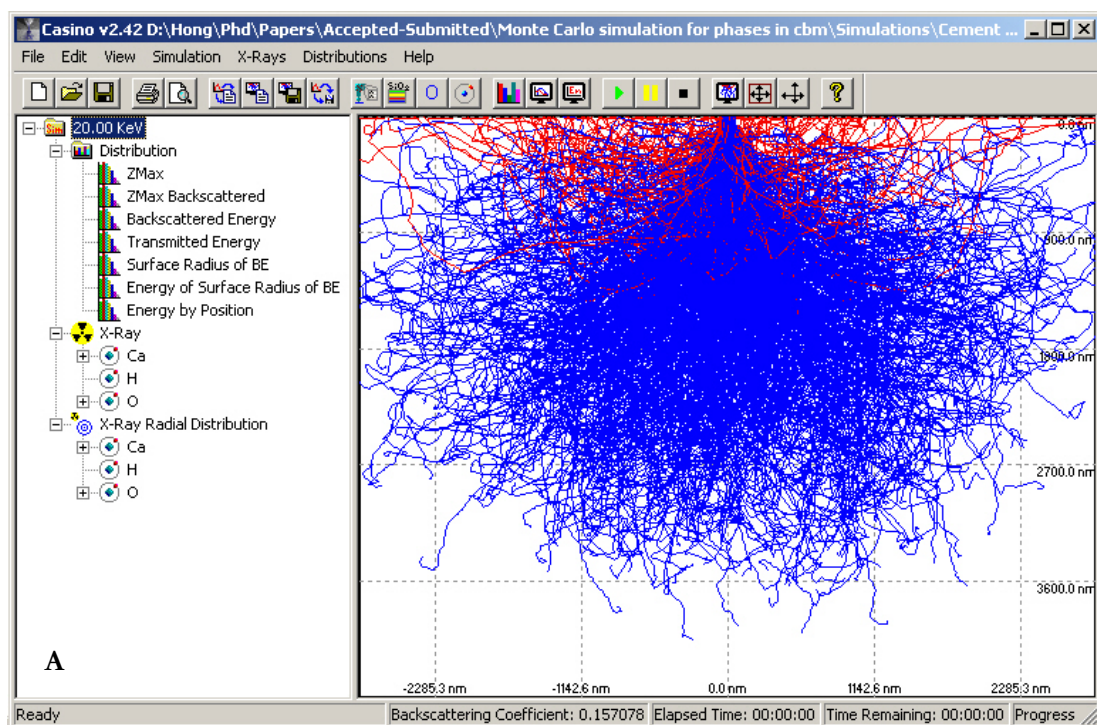


Figure 5.2 Monte Carlo simulations of electron-solid interactions in calcium hydroxide at 20keV. Figs (A-D) are independent simulations of 25 electron trajectories to illustrate the stochastic process of the technique. Fig (E) is a simulation of 2×10^3 electron trajectories. Elastic scattering occurs where the electron changes direction. The electron trajectory is followed until it loses all of its energy (grey lines) or is backscattered (black lines). For each trajectory, the spatial location, energy distribution and generated X-rays are tracked.

5.4 Experimental

The simulation was performed using CASINO (Version 2.42), which is the acronym for monte CARlo SIMulation of electroN trajectory in sOlid. This programme is specifically designed for low energy beam interaction in bulk or thin samples, and can be used to generate backscattered electrons and characteristic X-rays either as a point analysis or as a line-scan for accelerating voltages between 0.1 and 30keV. The first version of the Monte Carlo programme CASINO was developed by the research team lead by Professor Raynald Gauvin at Université de Sherbrooke, Québec, Canada, in 1996. The current version, which has a new Windows™ based interface, was programmed under the supervision of Professor Dominique Drouin in 2000. A detailed description of the programme and its development is given by Hovington et al. [1997a, 1997b & 1997c]. Fig. 5.3 shows several screenshots of the current version of CASINO.

The major phases in cement-based materials are listed in Table 5.1. To create a simulation for a particular phase, the chemical composition, density, weight fraction and atomic fraction of each element is first defined (Fig. 5.3 B). Then, the microscope settings: accelerating voltage (5-30keV), angle of the incident beam (0°, i.e. normal to the sample surface), probe diameter and take-off angle of the X-ray detector (40°) are defined (Fig.5.3 C). The probe diameter is calculated from the brightness and threshold equation, and corrected for lens aberrations for a conventional tungsten-filament electron source, according to the method described by Goldstein et al. [2003]. The steps are summarised in Appendix I and the resultant probe diameters are given in Table 5.2. In the calculations, it is assumed that the microscope is set up to image an atomic number contrast level $C (= (\eta_2 - \eta_1) / \eta_2 \times 100)$ of 2.5% with a detector collection efficiency of 0.1 and scan time of 100s for a 1024 x 768 image; thus a probe current greater than 0.5nA must be applied. According to the Rose visibility criterion ($\Delta S > 5N$), at this imaging condition, the epoxy-filled voids, hydrated cement paste (Aft, Afm, C-S-H), calcium hydroxide and ferrite can be differentiated from their brightness intensity, which is generally observed in routine BSE imaging. It is noted that the uncertainties in the assumptions made in calculating brightness and lens aberrations can lead to an error of several hundred percent in the final effective probe diameter. However, in the results section (Section 5.5.2), it is shown that this does not make a significant difference to the simulated results for most practical situations.



Layer Chemical Composition

Name:

Composition:

Density:

Element	Z	Weight Fraction	Atomic Fraction
✓ Ca	20	0.540930	0.200000
✓ O	8	0.431864	0.400000
✓ H	1	0.027206	0.400000

B

☒ User Defined Density

☐ User Defined Distributions

Microscope and Simulation Properties

☐ Simulate Multiple Energies

Start: End: Step: KeV

Number of electrons to simulate:

Tilt of Specimen (degree):

Beam radius (nm):

☐ Scan the beam to create an image

From: To: Steps: nm

☒ Conserve Data For Each Simulated Points

C

Figure 5.3 Screenshots of CASINO (Version 2.42)

D

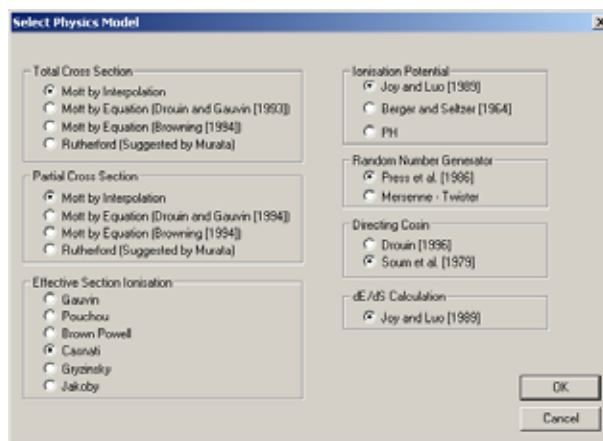


Figure 5.3 Screenshots of CASINO (continued)

Phase	Molecular Wt.	Atomic No.	Mean Atomic No.	Density (g/cm ³)	Backscatter coefficient, η	Contrast, %
Epoxy (Araldite), C ₁₀ H ₁₈ O ₄	202.250	110	6.184	1.14	0.066	-
Brucite, Mg(OH) ₂	58.326	30	9.423	2.39	0.109	39.1
Thaumasite, CaSiO ₃ .CaSO ₄ .CaCO ₃ .15H ₂ O	622.616	326	10.622	1.89	0.120	9.7
Ettringite, 3CaO.Al ₂ O ₃ .3CaSO ₄ .32H ₂ O	1254.648	658	10.769	1.70	0.122	1.5
Dolomite, CaMg(CO ₃) ₂	184.408	92	10.875	2.84	0.124	1.4
Quartz, SiO ₂	60.066	30	10.806	2.62	0.125	1.3
Monosulphate, 3CaO.Al ₂ O ₃ .CaSO ₄ .12H ₂ O	622.320	322	11.665	1.99	0.132	5.3
Calcium silicate hydrate, C _{1.7} -S-H ₄	227.460	118	12.086	2.12	0.137	3.5
Gypsum, CaSO ₄ .2H ₂ O	172.170	88	12.119	2.32	0.138	0.6
Calcite, CaCO ₃	100.088	50	12.563	2.71	0.142	2.9
Portlandite, Ca(OH) ₂	74.076	38	14.302	2.24	0.162	12.1
Tricalcium aluminate, 3CaO.Al ₂ O ₃	270.198	134	14.339	3.21	0.164	1.3
Dicalcium silicate, 2CaO.SiO ₂	172.250	86	14.562	3.28	0.166	1.4
Tricalcium silicate, 3CaO.SiO ₂	228.330	114	15.057	3.03	0.172	3.1
Ferrite, 4CaO.Al ₂ O ₃ .Fe ₂ O ₃	485.980	238	16.651	3.73	0.186	7.8

Table 5.1 Major phases in cement-based materials arranged according to increasing backscatter coefficient. Atomic contrast is calculated from the backscatter coefficients of successive phases.

Finally, the physical model, number of simulated electrons and the minimum energy to which the trajectory is followed, are selected (Fig. 5.3 D). For this study, the Mott model for elastic scattering and the modified Bethe equation [Joy & Luo, 1989] to model deceleration and energy loss, were used. A large number of electron trajectories must be calculated in order to statistically replicate the physical processes involved. For each simulation, 4×10^5 electron trajectories are calculated. This value was derived from the probe current and pixel dwell time. As a rule of thumb, the estimate of relative error is $1/\sqrt{n}$, where n is the number of electrons estimated. For a simulation of 4×10^5 electrons, the relative error is about 0.2%. The trajectory of each electron is followed until its energy falls below 0.5keV, or until the electron has returned to the sample surface. In the simulation, it is assumed that each phase is stoichiometric, dense, topography-free and homogeneous in composition over the entire interaction volume.

E (keV)	β (A/m ² .sr)	d _G (nm)	d _c (nm)	d _s (nm)	d _d (nm)	d _p (nm)
5	2.7×10^8	177	20	1.3	2.1	178
10	5.4×10^8	125	10	1.3	1.5	126
15	8.2×10^8	102	7	1.3	1.2	102
20	1.1×10^9	88	5	1.3	1.1	89
25	1.4×10^9	79	4	1.3	1.0	79
30	1.6×10^9	72	3	1.3	0.9	72

Table 5.2 Calculated values of brightness (β), Gaussian probe diameter (d_G), chromatic aberration (d_c), spherical aberration (d_s), aperture diffraction (d_d) and effective probe diameter (d_p) at several accelerating voltages (E) [See Appendix I].

5.5 Results

5.5.1 Verification of the Monte Carlo code

The accuracy of the Monte Carlo code was tested by comparing the simulated backscatter coefficients (i.e. the ratio of backscattered electrons to the total simulated trajectories) with experimentally measured values or with calculated values. Fig. 5.4 shows the results for all elements between Li and Ca in the periodic table, and for the main phases in cement-

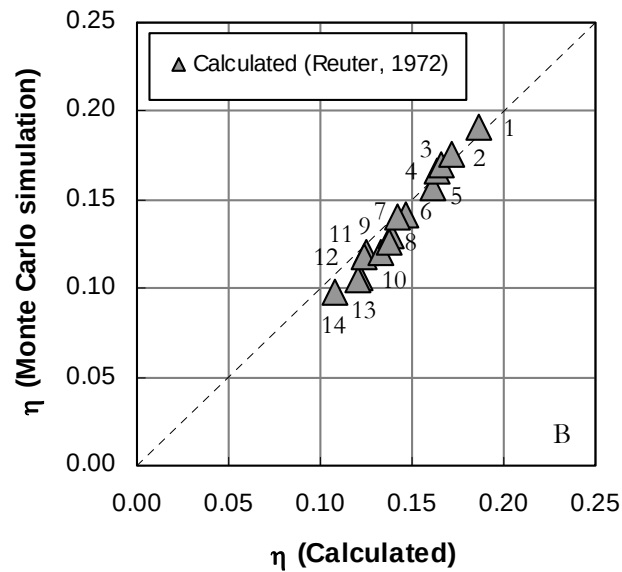
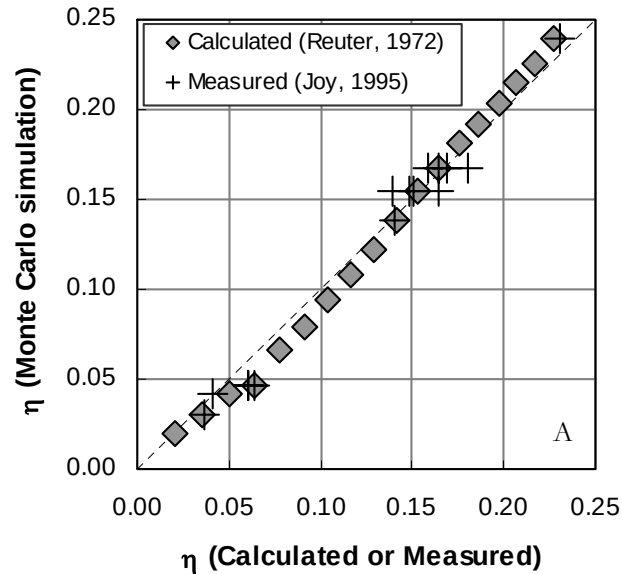
based materials (Table 5.1). The experimental values were obtained from a list compiled by Joy [1995b] of known experimentally measured secondary and backscattered electron coefficients, and electron stopping power data for elements and compounds. The calculated backscatter coefficients were from the empirical equation proposed by Reuter [1972], which was obtained by curve fitting to Heinrich's [1966] experimental data at 20keV:

$$\eta = -0.0254 + 0.016Z - 1.86 \times 10^{-4} Z^2 + 8.3 \times 10^{-7} Z^3 \quad \text{Eq. 5.4}$$

Where η is the backscatter coefficient and Z is the atomic number. For a compound, the mean backscatter coefficient is calculated using Caistaing's rule [1960], which is the summation of each constituent element's backscatter coefficient, factored by the atomic weight fraction c_i :

$$\bar{\eta} = \sum_{i=1}^n c_i \eta_i \quad \text{Eq. 5.5}$$

It can be observed from Fig. 5.4 that the simulated backscatter coefficients were generally in good agreement with the experimental and calculated values for elements ($Z = 3-20$) and for the main phases in cement-based materials ($\bar{Z} = 6-17$). For each phase, five repeat simulations were made to calculate the average backscatter coefficient, and the coefficients of variation for all values were smaller than 1%. This shows that there is no statistically significant difference between different simulations for a given set of input parameters because a very large number of electrons were simulated each time. Therefore, for this number of electrons, repeat simulation is not essential.



Notation: 1 = C_4AF ; 2 = C_3S ; 3 = C_2S ; 4 = C_3A ; 5 = $Ca(OH)_2$; 6 = $CaCO_3$; 7 = $CaSO_4 \cdot 2H_2O$; 8 = $C_{1.7}S-H_4$; 9 = Afm ; 10 = SiO_2 ; 11 = $CaMg(CO_3)_2$; 12 = Aft ; 13 = $CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$; 14 = $Mg(OH)_2$

Figure 5.4 Testing the accuracy of the Monte Carlo simulation by comparing the simulated and experimentally measured [Joy, 1995b] or calculated [Reuter, 1972] BSE coefficients for A) all elements between Li and Ca in the periodic table; and B) main phases in cement-based materials (see Table 5.1).

5.5.2 Effect of accelerating voltage and probe diameter

Figs. 5.5 and 5.6 show the influence of accelerating voltage and probe diameter on the maximum penetration depth of all electrons, which is the maximum depth of each trajectory from the sample surface, and the surface radius of backscattered electrons, in a calcium hydroxide target. The results show that the interaction volume and the surface radius of backscattered electrons is a strong function of the electron beam energy, and this is well known [Goldstein et al., 2003].

The results plotted in Fig. 5.6 also show that an order of magnitude change in the calculated probe diameter (Table 5.2) does not have a significant effect on the penetration depth and backscattered electron escape surface radius. This is because, at 10-20keV accelerating voltages, the interaction volume for cement-based materials is significantly larger than the probe diameter, and therefore the contribution from the probe diameter is small. However, at low accelerating voltages, the probe diameter becomes critical to the backscattered electron surface radius when its dimension approaches that of the escape surface radius.

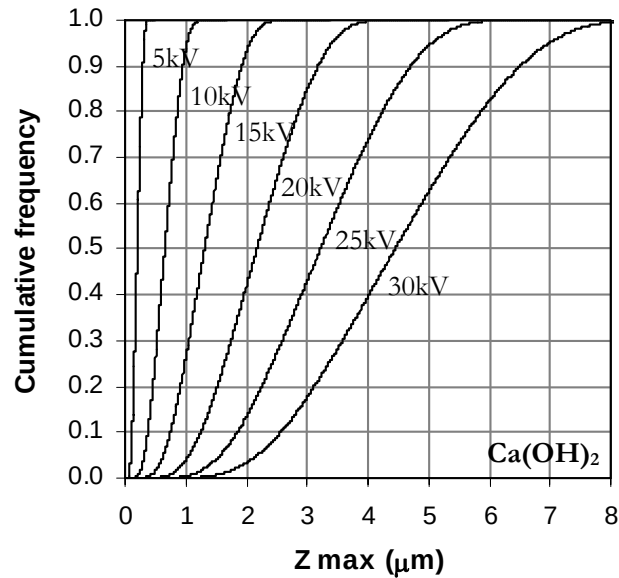


Figure 5.5 Effect of accelerating voltage on the maximum penetration depth of electron trajectories in calcium hydroxide.

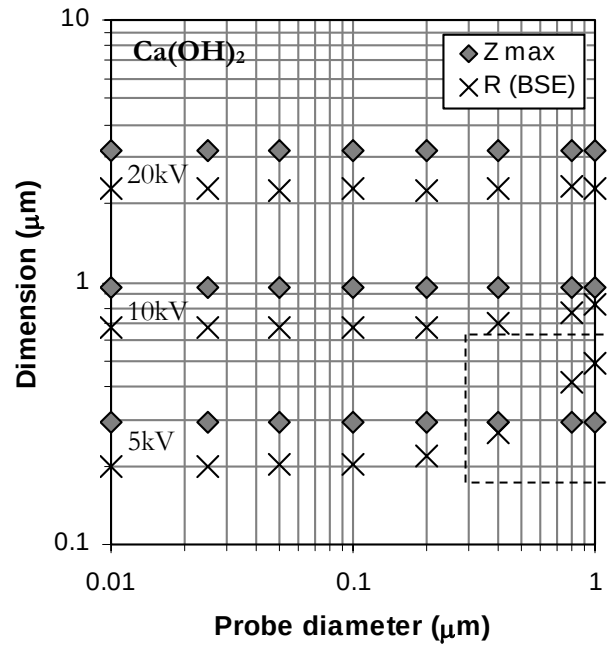


Figure 5.6 Effect of probe diameter on the 90th percentile maximum penetration depth ($Z_{\max}$) of all electrons and surface radius (R_{BSE}) of backscattered electrons for calcium hydroxide at accelerating voltages of 5, 10 and 20keV.

5.5.3 Depth of the interaction volume

Fig. 5.7 shows the cumulative distribution of the penetration depth of all electron trajectories at 10keV and 20keV for ferrite (C_4AF), tricalcium silicate (C_3S), calcite (CaCO_3), calcium hydroxide (CH), calcium silicate hydrate (C-S-H), monosulphate (Afm) and ettringite (Aft). The maximum electron penetration depth ranges from 0.75 to 1.5μm at 10keV and from 2.5 to 5.0μm at 20keV accelerating voltage. At constant beam energy, the depth of the interaction volume generally increases with a decrease in mean atomic number and density. The shape of the interaction volume for all phases follows closely to that shown in Fig. 5.2 for CH, and appears to be more spherical than pear-shaped.

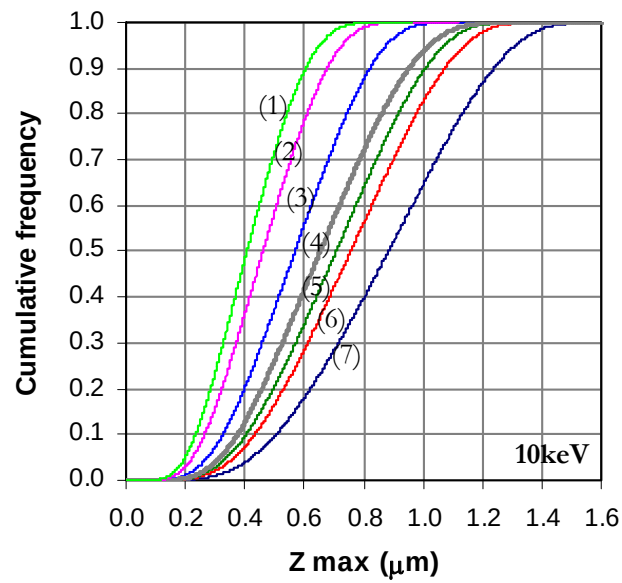
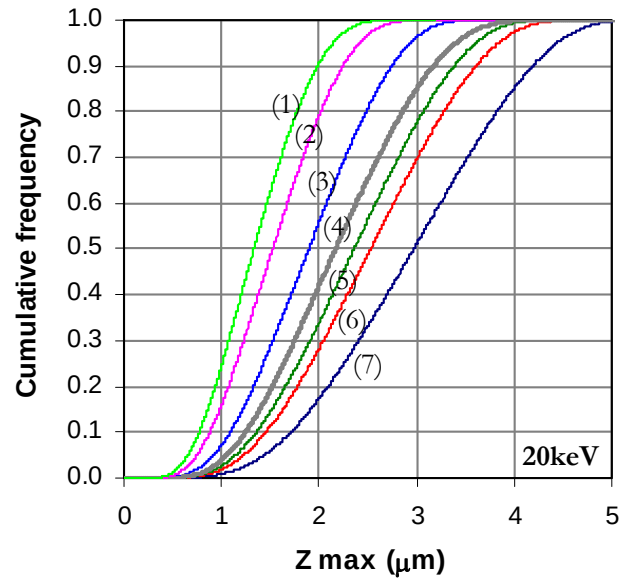


Figure 5.7 Cumulative distribution of penetration depth of electrons at 20keV and 10keV accelerating voltage for selected phases: 1) C_4AF ; 2) C_3S ; 3) $CaCO_3$; 4) CH ; 5) $C-S-H$; 6) Afm ; and 7) Aft .

5.5.4 Sampling volume of backscattered electrons

Fig. 5.8 shows the distribution of penetration depth and escape surface radius of backscattered electrons for ferrite, calcium hydroxide and ettringite at 10keV and 20keV. These phases were selected because they cover the range of mean atomic number in cement-based materials. The sampling depth of backscattered electrons at 90th percentile ranges from 0.23 to 0.46 μm at 10keV and from 0.76 to 1.6 μm at 20keV. This is approximately 30% of the interaction volume depth. The escape surface radius at 90th percentile ranges from 0.43 to 0.87 μm at 10keV and from 1.4 to 2.9 μm at 20keV. Thus, the lateral dimension of the BSE sampling volume is almost equivalent to the depth of the entire interaction volume.

The simulations show that incident electrons can penetrate the sample and emerge at significant distances from the probe impact point, particularly for high beam energies. A large sampling volume and lateral spreading of the backscattered electrons reduces the sensitivity of BSE imaging to fine surface details. However, it may be argued that not all backscattered electrons that escape the sample surface may generate a response in the detector and contribute to the final image intensity because conventional backscatter detectors are sensitive to high-energy backscattered electrons only. Since electrons that travel deeper into the sample and escape further from the probe impact point are likely to have lost a substantial amount of energy via inelastic scattering, these low-energy backscattered electrons may not have a significant contribution to the final image.

Fig. 5.9 shows the energy distribution of all backscattered electrons for ferrite, calcium hydroxide and ettringite at 10keV and 20keV. According to Goldstein et al. [2003], the energy threshold for a typical solid-state detector is in the range of 2 to 5keV. Taking a conservative estimate of 5keV, we find that the amount of ‘detected’ backscattered electrons is still a substantial fraction of the entire population: approximately 95% at 20keV and 70% at 10keV. Thus, it appears that a large proportion of the backscattered electrons that escape the sample surface will contribute to the final image intensity.

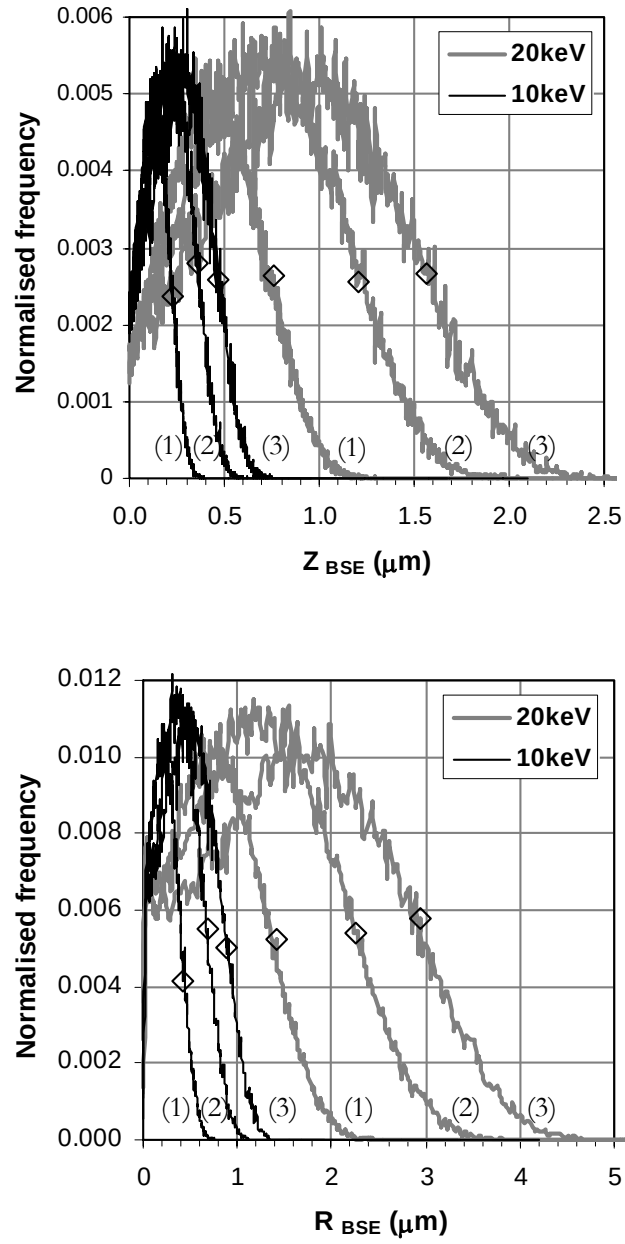


Figure 5.8 Distribution of penetration depth (Z_{BSE}) and escape surface radius (R_{BSE}) of backscattered electrons at 20keV and 10keV accelerating voltage for selected phases: 1) C₄AF; 2) CH; and 3) Aft. The symbol (◊) marks the 90th cumulative percentile.

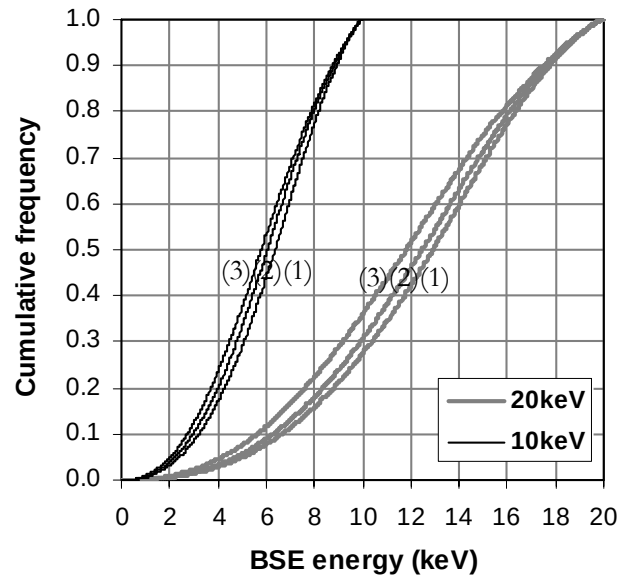


Figure 5.9 Cumulative distribution of backscattered electron energy at 20keV and 10keV accelerating voltage for selected phases: 1) C₄AF; 2) CH; and 3) Aft.

5.5.5 Sampling volume of characteristic X-rays

Ettringite may play an important role in concrete degradation and because X-ray microanalysis is a conventional technique used for its detection, this section will give particular attention to this phase.

Characteristic X-rays may be generated anywhere within the interaction volume, as long as the incident electron energy exceeds the critical excitation energy of the particular element present. For ettringite, the critical excitation energy for CaL α , OK α , AlK α , SK α and CaK α is 0.349keV, 0.532keV, 1.560keV, 2.470keV and 4.308keV respectively [Bearden, 1967]. The smaller the critical excitation energy, the larger the sampling volume of the characteristic X-rays for that particular element since incident electrons will progressively lose energy as they penetrate the sample. However, X-rays generated deep in the sample may not escape as a result of photoelectric absorption. This is the process where the entire energy of the X-ray photon is transmitted to an orbital electron of the sample, which is subsequently ejected.

Fig. 5.10 shows the depth and lateral distribution of the non-absorbed characteristic X-rays in ettringite. As with the case of backscattered electrons, the results show a non-even distribution of X-ray intensity with distance from the probe impact point; the X-ray intensity is highest near the probe impact point and decreases to zero when the electron energy falls below the critical excitation energy. The X-ray sampling volume for each element depends on the electron beam energy and the critical excitation energy, and can be a substantial fraction of the interaction volume. Assuming a hemispherical sampling volume, the amount of material analysed is estimated to be in the order of 1 to 100 μm^3 .

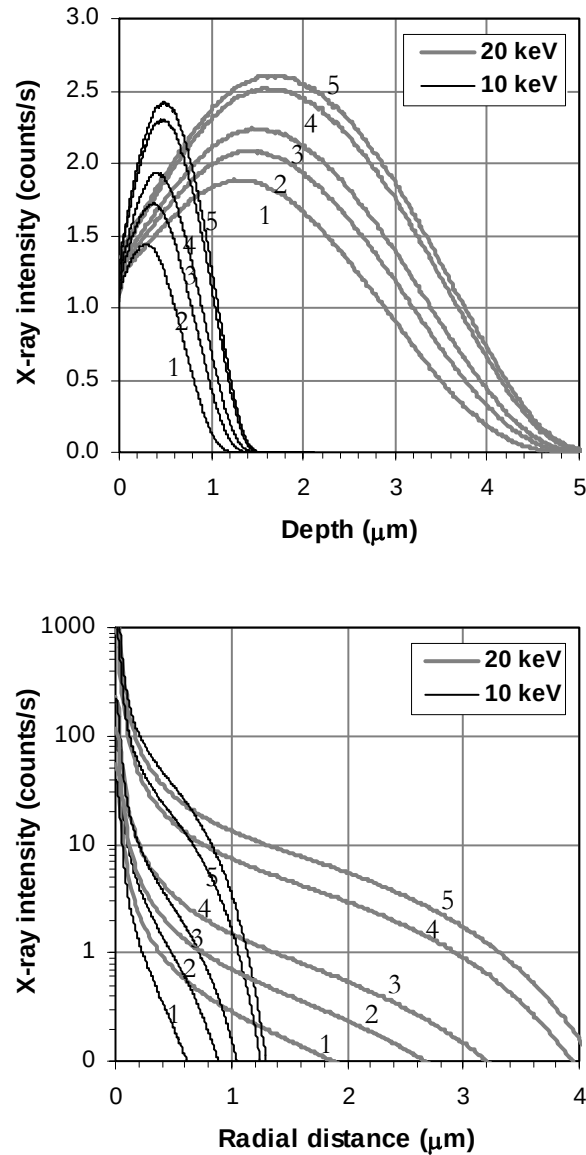


Figure 5.10 Depth and lateral distribution of non-absorbed X-rays in Aft at 20keV and 10keV. Symbols: 1) CaK α ; 2) SK α ; 3) AlK α ; 4) OK α and 5) CaL α .

5.6 Discussion

Since the size of the signal sampling volume is a strong function of the electron beam energy, a low accelerating voltage should be used to obtain high sensitivity to fine surface features. However, at a low accelerating voltage, the signal-to-noise (S/N) ratio drops significantly and this degrades spatial resolution. For cement-based materials imaged using a conventional electron microscope, it is observed that the smallest accelerating voltage that provides a reasonable S/N ratio is around 10keV. To improve the S/N ratio at lower accelerating voltages, the probe current can be increased by using a larger probe size, but there is a limit to this because, as shown in the simulation results, the influence of probe size on the sampling volume will be significant when its dimension approaches that of the sampling volume. A better approach is to increase the probe current by using a higher emission current, and this is now possible with field-emission type electron sources that can maintain high probe brightness and current at a very fine probe size and low accelerating voltage.

The Monte Carlo simulations show that the lateral dimension of the BSE sampling volume is as large as the entire interaction volume depth. This however, does not mean that features smaller than the BSE sampling volume will not be detected because the lateral dimension of the BSE sampling volume does not represent its spatial resolution limit [Merli et al., 1995]. Indeed, features smaller than the BSE sampling volume are usually observed during routine imaging of cement-based materials. This is because the visibility of a particular feature depends on its contrast, i.e. the difference in generated signal between the particular feature and its surrounding areas. The Rose criterion [1948] states that this must exceed the background noise by a factor of five in order for the feature to be visible by an average observer. Therefore, although a large BSE sampling volume reduces contrast, small features can still be observed as long as the signals generated from them satisfy the Rose criterion.

The sampling volume of non-absorbed characteristic X-rays is a substantial fraction of the interaction volume. For ettringite, the simulations showed that the volume of material analysed is estimated to be in the order of 1 to 100 μm^3 at 10 to 20keV. Therefore, to obtain accurate quantitative X-ray microanalysis, one should ensure that the point selected for analysis is homogeneous in chemical composition over this volume of material. As in BSE imaging, a low accelerating voltage is preferable. Selecting higher beam energy may increase the total X-ray counts/s, but at the expense of reduced sensitivity. The suitable beam energy to be used for X-ray microanalysis depends on the characteristic X-rays of interest and the

composition of the sample; typically, 2 to 3 times that of the critical excitation energy is the optimal value [Goldstein, 2003].

5.7 Conclusions

In this chapter, a Monte Carlo technique was applied to simulate the electron-solid interactions in cement-based materials at accelerating voltages used in conventional SEMs (10-20keV), in order to study the shape and size of the interaction volume, the spatial and energy distribution of backscattered electrons and non-absorbed characteristic X-rays. It was first verified that the Monte Carlo code is applicable for cement-based materials by comparing the simulated backscatter coefficients with experimental and calculated values. Good agreement was observed for all major phases in cement-based materials. We showed that the size of the interaction volume and sampling volume of backscattered electrons is a strong function of the beam energy, but independent of the probe size. The probe diameter only becomes critical to the backscattered electron escape surface radius when its dimension approaches that of the escape surface radius at low beam energies (<10keV).

It was observed that the interaction volume in cement-based materials is more hemispherical than pear-shaped. The maximum penetration depth of electron trajectories ranges from 0.75 to 1.5 μm at 10keV and from 2.5 to 5.0 μm at 20keV. The distribution of backscattered electrons and characteristic X-rays within this interaction volume is not uniform, but is concentrated near the probe impact point. The maximum sampling depth of backscattered electrons is approximately 30% of the interaction volume depth and its lateral dimension is almost equivalent to the interaction volume depth. The sampling volume of characteristic X-rays for each element depends on the beam energy and the critical excitation energy, and can be a substantial fraction of the interaction volume. For ettringite, the amount of material analysed in X-ray microanalysis is estimated to be in the order of 1 to 100 μm^3 at 10 to 20keV.

Chapter 6

Monte Carlo simulation of BSE signal variation at pore boundaries

This chapter will apply the Monte Carlo simulation technique that was established in Chapter 5 to study the variation of backscattered electron signal across phase boundaries, in particular pore-solid boundaries in cement-based materials. The focus will be on investigating the effect of sampling subsurface material on the recorded BSE signal and the variation in BSE signal across pore-solid boundaries. The simulations are used to verify the Overflow pore segmentation method that was presented in Chapter 4, as well as to determine the theoretical resolution limit and measurement errors for pore imaging in the backscattered electron mode.

6.1 Introduction

Since its invention and throughout most of the history of its application, the scanning electron microscope has mainly been an instrument used for qualitative observations. Its popularity and success is due to its capability in providing a vast amount of information while, at the same time, being a relatively easy instrument to operate. The interpretation of images collected from the SEM, once properly optimised for brightness and contrast, can be easily done by a novice operator, even for images of a complex multiphase material or for an irregular topography, without having the need to make a systematic consideration of the complex electron-solid interactions that go on during the image formation process.

However, the limitation of such an approach becomes evident when one wishes to extract quantitative information from SEM images, such as using image analysis to determine the true size of micrometer or nanometre-scale objects. As emphasised earlier (Chapter 4), feature segmentation is one of the most important, but error prone, processes in quantitative microscopy. Although the boundary between two phases may be atomically sharp, the signal measured across the boundary may change over a range of hundreds of nanometres. The requirement for accurate measurement becomes more stringent with the emergence of a new class of high-resolution field-emission gun SEM that can reliably place a 1nm diameter focussed probe on the sample, over a beam energy range from 1 to 30keV. The qualitative or

the ‘experience-based’ approach to electron microscopy and image interpretation becomes inadequate as more emphasis is placed on making accurate measurements on finer and finer structures.

To assist in quantitative interpretation of SEM images, the Monte Carlo simulation technique has been developed over the last four decades as a tool to provide the theoretical foundation, which underpins scanning electron microscopy and X-ray microanalysis [Joy, 1995a]. The Monte Carlo technique allows for a stepwise simulation of the elastic and inelastic scattering events as the incident electrons from the electron beam interact with the sample (Section 5.3). Because electron scattering is essentially a stochastic process, random numbers with appropriate weighting factors are used to distribute the scattering events depending on the variables involved in a realistic manner. By continuously monitoring the spatial (x, y, z) position of the incident electron as it penetrates the target, as well as its energy and velocity vector, the Monte Carlo technique can deal with practically any sample type and boundary conditions [Joy, 1995a].

In this chapter, Monte Carlo simulation will be used to generate the recorded BSE signal from a pre-defined sample geometry and chemical composition. The idea is to simulate the electron trajectories under similar conditions to those during real SEM imaging, and thus predict theoretically the signal observed in the SEM. This is done by extending the Monte Carlo simulation from a single point analysis (Chapter 5) to a series of points separated by a known distance, i.e. a line scan, so as to mimic the signal formation process in the SEM. The applications for this include investigating the signal variation across multi-layer composites and phase boundaries, which allows for accurate determination of the true inter-phase position.

6.2 Sampling of subsurface material

As mentioned in Chapter 4, one of the reasons why pixels near an interphase boundary show gradually transitional grey values is that there is a possibility of sampling of subsurface material. This effect, which is a result of the finite size of the signal sampling volume, is well known. However, there is yet to be a comprehensive study on this phenomenon in the field of cement and concrete research.

Sampling of subsurface material is particularly relevant in the case of pores in cement-based materials. The pores are intentionally filled with a low mean atomic number material (epoxy) so that a high contrast is generated between the pore and its surrounding solid

phase, which allows for its visibility. However, this results in a large signal sampling volume for the pore phase and increases the likelihood of sampling subsurface material. Fig. 6.1 shows the cumulative distribution of the BSE penetration depth, BSE escape surface radius and the maximum electron penetration depth at 10keV and 20keV electron beam energy. The maximum BSE penetration depth (Z_{BSE}) and the maximum electron penetration depth (Z_{max}) for araldite epoxy are approximately $1\mu\text{m}$ and $2\mu\text{m}$ respectively at 10keV. These values increase to $3\mu\text{m}$ and $7\mu\text{m}$ respectively at 20keV.

Capillary pores have size ranging from submicron up to about $10\mu\text{m}$ or more, and their orientation in hydrated cement paste is expected to be random and tortuous. The hydration products themselves have a very diffuse morphology and therefore, the imaging plane can section the pore-solid boundary at any angle. When the distance separating the pore surface and the nearest solid (either from a sidewall or base) is in the order of the interaction volume, then the incident electrons that first penetrate the pore phase will also penetrate the underlying material. Thus, the brightness intensity of a pixel located on the pore phase will increase because of additional scattering events occurring in the solid phase. This sampling of subsurface material effect adds on to the uncertainty of the location of the pore-solid boundary.

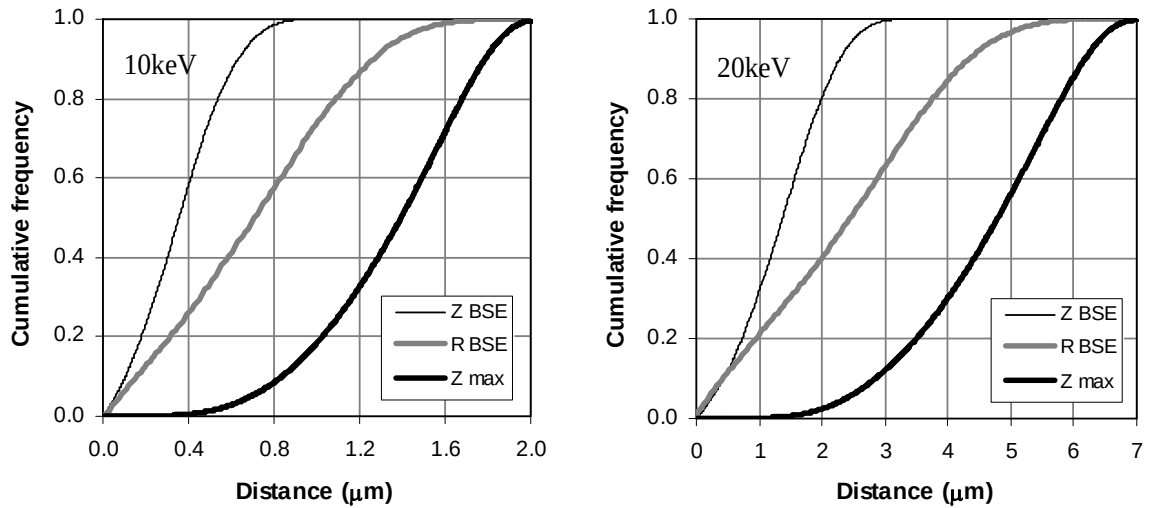


Figure 6.1 Cumulative distribution of BSE penetration depth (Z_{BSE}), BSE escape surface radius (R_{BSE}) and maximum electron penetration depth (Z_{max}), for araldite epoxy at 10keV and 20keV accelerating voltages.

To investigate the magnitude of this effect, we look at a multi-layer composite material comprising of two phases, a top epoxy layer representing the pore phase, and a substrate layer representing hydration products. Since the C-S-H gel is the main cement hydration product, we will select this as the substrate layer. To be more precise, it is the ‘low-density outer hydration products’ formed in the originally water-filled spaces that are of most interest. However, the difficulty with simulating the C-S-H gel is in the uncertainty of its chemical composition, morphology and molecular structure, which is largely still under debate. For simplicity, we will use the general formula: $x\text{CaO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O}$ to represent the C-S-H gel. The CaO/SiO₂ ratio reported in the literature for mature C₃S pastes hydrated at ambient temperature range between 1.4 and 2.0, with the correct value probably close to 1.7 [Odler, 1998]. The C-S-H gel density and the H₂O/SiO₂ ratio depend on the equilibrium drying condition. For C₃S pastes dried at 11% relative humidity, Young & Hansen [1987] suggested a C-S-H composition of 1.7CaO·SiO₂·2.1H₂O and a specific gravity close to 2.2. Hence, these values will be used. We assume that the variation in electron scattering characteristics and the resulting BSE coefficient within the various forms of C-S-H is small and insignificant compared to the variation across the pore-solid boundary.

Fig. 6.2 (A) shows an example of electron trajectory simulation in the two-layer composite with a 1000nm thick epoxy layer above a C-S-H substrate. By varying the thickness of the epoxy layer and simultaneously monitoring the BSE signal, the effect of sampling underlying C-S-H during pore imaging can be inferred. The composite model is shown in Fig. 6.2 (B). We assume that the entire thickness of the composite and the lateral distance between beam sampling points is infinite with respect to the interaction volume. We also assume that the composite is free of surface topography.

Fig. 6.3 plots the change in BSE signal with epoxy thickness up to a depth of 2μm and 4μm for beam energies of 10keV and 20keV respectively. The microscope set-up conditions (angle of the incident beam, probe diameter, number of electrons simulated) are essentially the same as in the previous chapter (Section 5.4). The results show a rapid increase in BSE signal when the epoxy thickness or the ‘pore depth’ is less than a critical value, around 0.9μm and 3.0μm for 10keV and 20keV respectively. Note that this value is slightly smaller than the maximum BSE penetration depth in the case of a pure epoxy. This shows that sampling of subsurface material can have a significant effect on the brightness of pore pixels, and as expected, the severity of this increases with beam energy. The grey value of pixels lying on pores shallower than 0.9μm for 10keV (or shallower than 3μm for 20keV) will increase accordingly to the decrease in depth of the nearest underlying solid material.

We can also investigate the change in BSE signal for C-S-H when there is a pore located below the imaging plane, by reversing the order of the two-layer composite in Fig. 6.2 (B). In this case, the thickness of the top C-S-H layer is varied and the change in BSE signal is monitored. Results are plotted in Fig. 6.4. The results show that underlying pores near the surface can also cause a decrease in the pixel intensity of the C-S-H phase; the critical depth is around $0.5\mu\text{m}$ and $1.6\mu\text{m}$ for 10keV and 20keV respectively. Note that this is less severe compared to the previous case because the BSE sampling volume for a pure C-S-H is smaller than that of a pure epoxy.

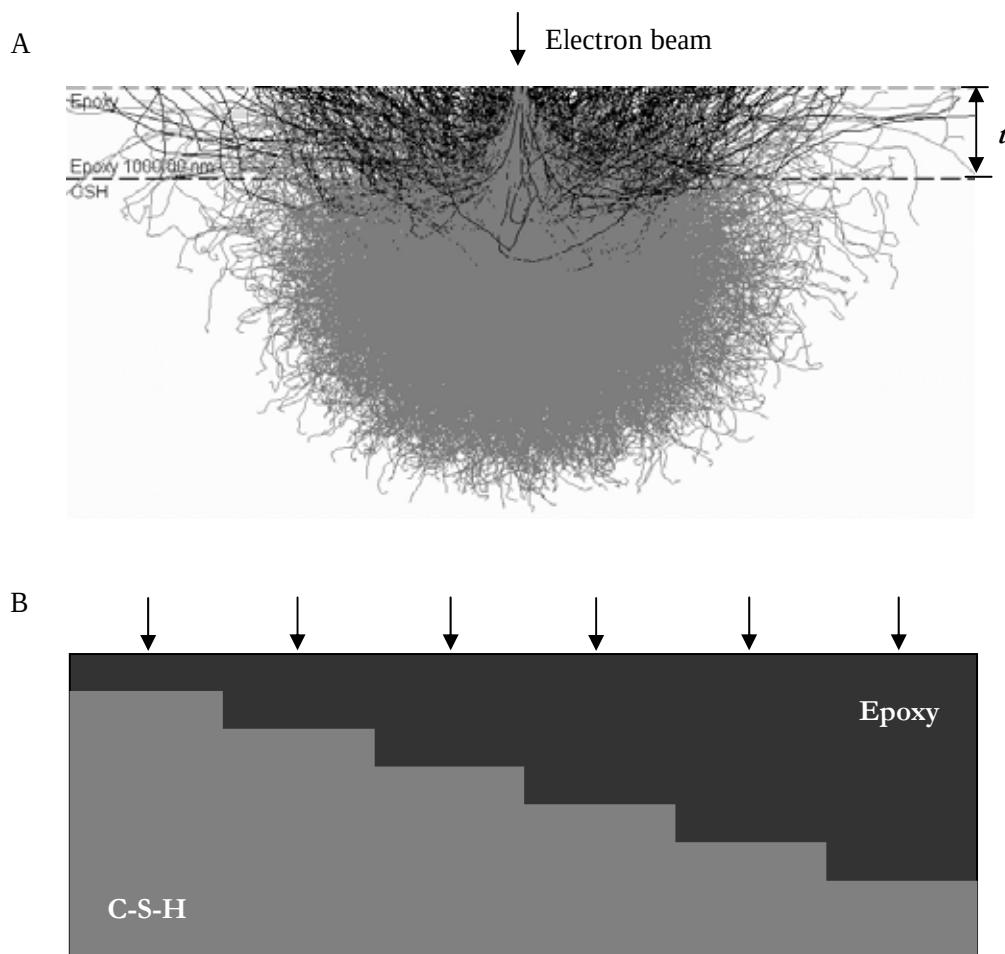


Figure 6.2 Effect of sampling subsurface material on the generated BSE signal: A) Monte Carlo simulation on a two-layer composite comprising of araldite epoxy (i.e. pore) as top layer and C-S-H as substrate; B) Cross-section of the two-layer composite model where the thickness of the top epoxy layer is varied.

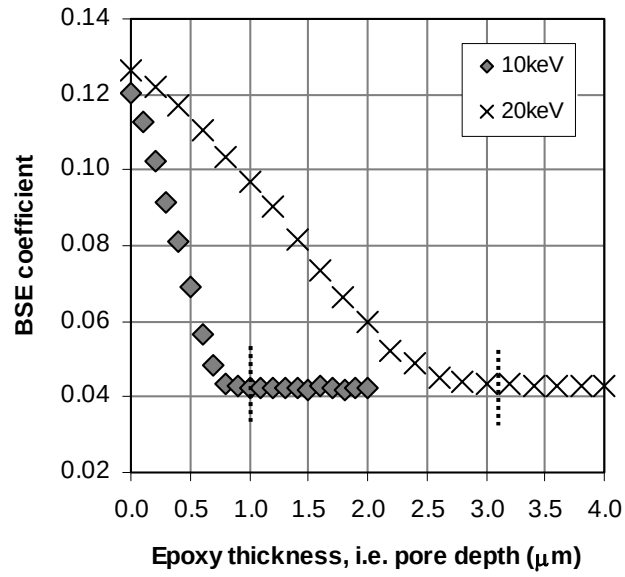


Figure 6.3 Change in the observed BSE signal at 10keV and 20keV as the epoxy thickness (i.e. pore depth) is varied. The vertical dotted line marks the maximum BSE penetration depth for pure epoxy.

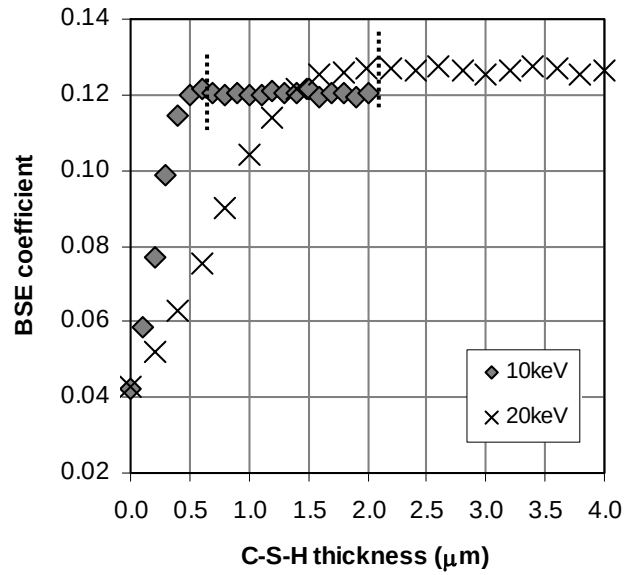


Figure 6.4 Effect of sampling subsurface pores on the generated BSE signal for C-S-H at 10keV and 20keV. The vertical dotted line marks the maximum BSE penetration depth for pure C-S-H.

The simulations presented in Fig. 6.3 and Fig. 6.4 show that sampling of subsurface material can drastically change the expected pixel intensity for pores or C-S-H. The severity of this effect scales to the size of the BSE sampling volume; hence, is more significant for pores, where the critical depth is almost twice that of for C-S-H. Undoubtedly, this effect will increase the ambiguity concerning the true position of the pore-solid boundary and limits the smallest pore size that can be imaged reliably.

6.3 BSE signal variation across pore-solid boundaries

The electron scattering process is extremely complex at phase boundaries as the electron beam approaches the interfaces to within distances of the order of the interaction volume. This is especially true if the two phases have relatively large differences in the mean atomic number and density, as in a pore-solid boundary in cement-based materials, because the volume of material from which the various signals emerge will be significantly different in each side of the interface. Scattered electrons can move from one phase to another and would experience different scattering behaviour because of differences in the electron range, scattering distribution and mean free path of the two materials.

Fig. 6.5 shows the shape of the interaction volume and BSE sampling volume as the incident electron beam is scanned across a CH-pore boundary. Note how the incident electrons begin to sample more than one material as the beam approaches the boundary. As such, the shape of the interaction volume becomes more distorted from the expected shape as it crosses the boundary. The effect of this on the recorded BSE signal is a gradual transition over a distance in each material of the order of half the lateral resolution in that material. As emphasised in Section 4.3, the true position of the boundary between the two phases is not at the mid-point of the transition, but is shifted towards the level associated with the higher atomic number [Cousen & Joy, 1997], i.e. closer to the solid phase. The amount of shift obviously depends on the mean atomic number of both materials and the scattering characteristics in them, as well as the beam energy. Therefore, it appears feasible to be able to predict the true position of the boundary using the variation in the signal level.

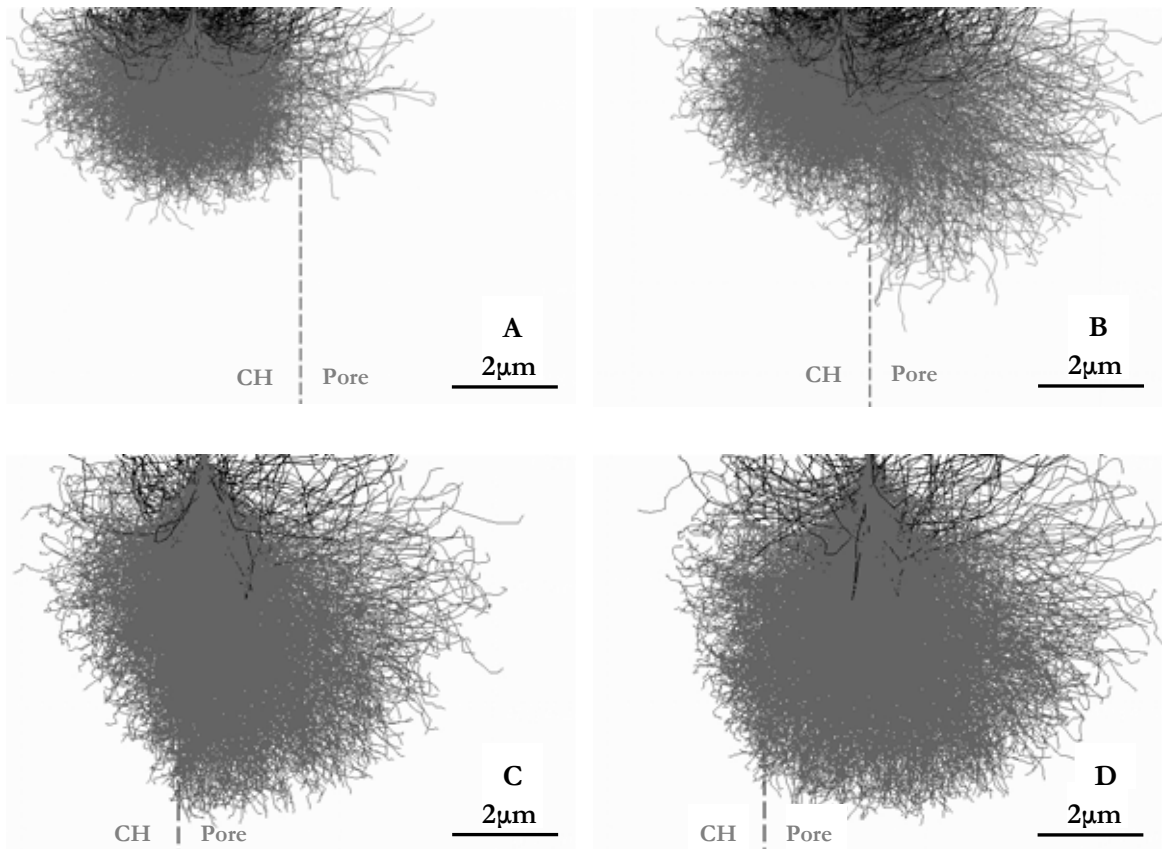


Figure 6.5 Change in the shape and size of the electron interaction volume as a 10keV electron beam is scanned across a CH-pore boundary. The simulations were done at: A) $-2\mu\text{m}$; B) $-0.5\mu\text{m}$; C) $+0.5\mu\text{m}$; and D) $+2\mu\text{m}$ from the boundary.

Fig. 6.6 shows the change in BSE signal as the electron beam is scanned across various boundaries between a pore and a solid phase where the solid can be ettringite (Aft), calcium silicate hydrate (C-S-H), calcium hydroxide (CH) or ferrite (C_4AF). Again, these are selected to span the entire range of the mean atomic numbers for phases in cement-based materials. The simulations are performed at beam energy 10keV and 20keV. For each curve, a total of 160 points spread across the pore-solid interface were simulated; that is $\pm 2\mu\text{m}$ from the boundary at 25nm beam spacing for 10keV, and $\pm 4\mu\text{m}$ from the boundary at 50nm beam spacing for 20keV. The distance from the first point to the boundary was chosen to cover the BSE escape surface radius of epoxy at the respective beam energy. We assume that the surface is flat, the pore-solid boundary is abrupt and normal to the surface, the depth of each phase is significantly larger than the electron range and that there is no compositional variation in either phase

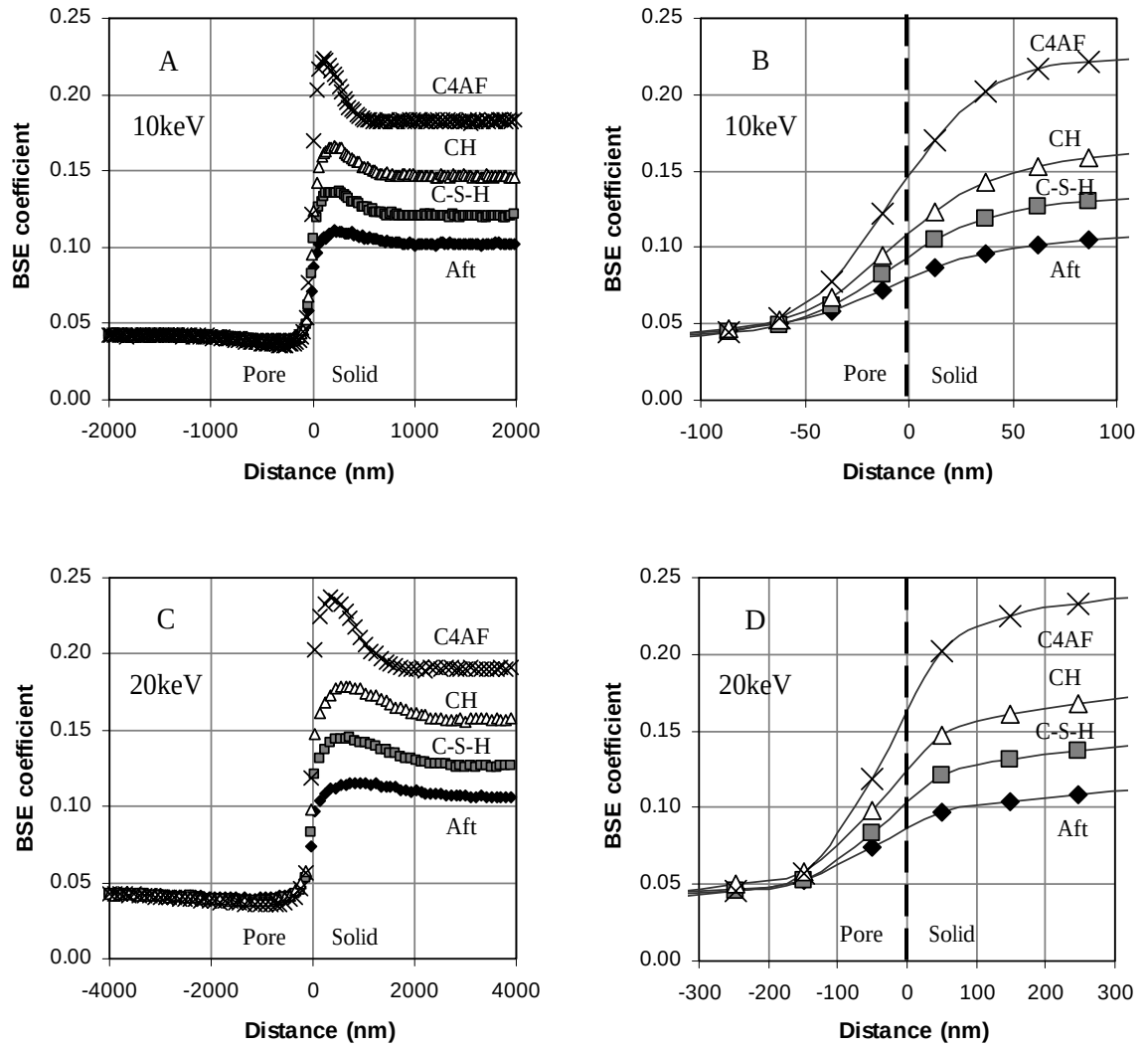


Figure 6.6 Change in BSE signal across pore-solid boundaries where the solid phase can be Aft, C-S-H, CH or C₄AF. The simulations are performed at 10keV (A, B) and 20keV (C, D).

The generated profiles shown in Fig. 6.6 are plotted at a two different scales to provide clarity to the signal transition near the boundary. The plots exhibit a number of features, particularly the signal increase close to the boundary on the solid side and the signal decrease on the pore side of the boundary. This is known as the 'edge-effect' and is due to the strong elastic scattering on the solid side (high atomic number) that results in a significant scattering into the pore side (low atomic number), which consequently has a greater probability of es-

caping to the surface. There is a slight dependency of the BSE coefficient on beam energy; a marginally higher BSE signal is observed for higher electron energy. This slight beam energy dependence of the BSE signal is well known, however the exact relationship is complex. Experimental data show a small change, generally less than 10% [Goldstein et al., 2003] in the BSE coefficient for beam energy in the range of 5 to 50keV. However, the energy dependence for specific elements behaves in a complex manner, increasing, decreasing or remaining nearly constant and depending on the particular element [Heinrich, 1966].

From the obtained data, we can predict the theoretical BSE coefficient value at the pore-solid boundary by interpolation. As can be seen in Fig. 6.6 (B) and (D), this value depends on the solid phase and increases with its mean atomic number. However, as emphasised earlier, we are most concerned with the C-S-H phase because capillary pores would more likely be surrounded by it than other phases would. At 10keV, the interpolated boundary BSE coefficient is 0.0937 and represents about 66% of the transition from epoxy (~ 0.0425) to C-S-H (~ 0.121). At 20keV, the boundary value is 0.102 and represents about 71% of the transition from epoxy (~ 0.0425) to C-S-H (~ 0.127).

We compare the interpolated boundary BSE coefficient with the threshold grey value as predicted by the Overflow method for the pore shown in Fig. 4.2. Note that this image was captured at 20keV. The predicted greyscale threshold value from the inflection point is 89 (Fig. 4.5), which represents about 76% of the transition from the grey value for epoxy (~ 22) to C-S-H. (~ 110). Fig. 6.7 shows another example of a pore that was cropped from a larger BSE image of a 28-day concrete at w/c 0.4, captured at 10keV. The predicted greyscale threshold value is 76, which represents about 75% of the transition from the grey value for epoxy (~ 5) to C-S-H (~ 100).

The comparison suggests that the Overflow method has slightly over-predicted the threshold value by about 7 to 14% when compared to the simulated value. The true threshold grey level should probably lie just before the inflection point in the cumulative brightness histogram. However, the over prediction could be due to the fact that some pores border on phases with higher atomic number, such as CH, and sampling of subsurface material in shallow pores. Both conditions tend to increase the brightness intensity of boundary pore pixels, and were not taken into account in the simulation. Hence, the Overflow method is probably erring on the ‘safe side’. Nevertheless, the discrepancies between the methods are marginal and this shows the general validity of the Overflow pore segmentation method.

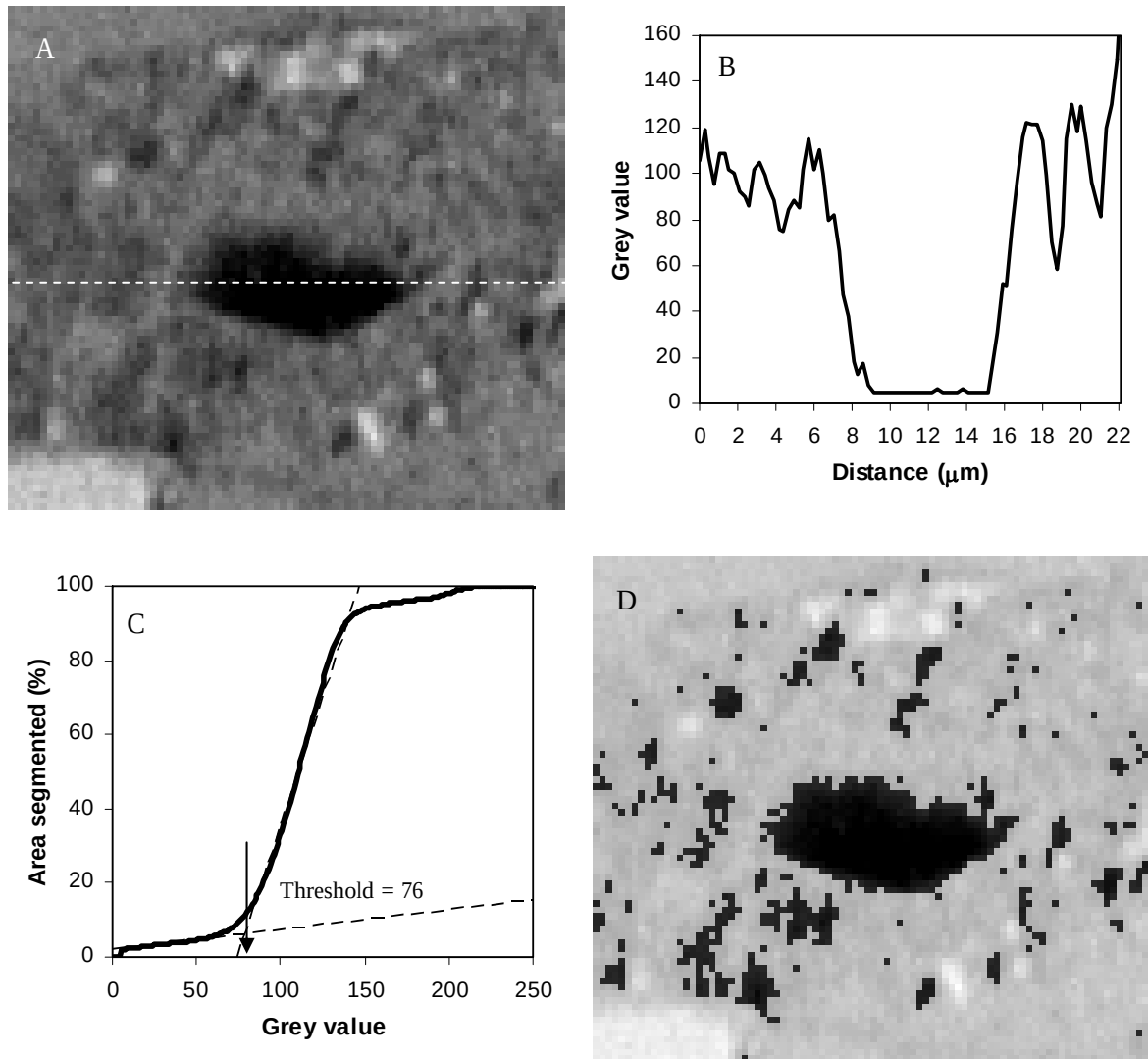


Figure 6.7 A) Image of a pore cropped from a larger 500x BSE image of C 0.4 – 28d, captured at 10keV; B) variation in grey value along the white horizontal dotted line; C) the threshold value for the pore is estimated from the inflection point of the cumulative brightness histogram; D) segmented pores.

6.4 Verification of the Overflow pore segmentation technique

As an additional test of the Overflow pore segmentation method, we ran a series of Monte Carlo simulated line scans on a model porous material to mimic the scanning action in a SEM. The BSE coefficient for every simulated 'pixel' was recorded and linearly transposed to a fixed grey scale range. Subsequently, a cumulative brightness histogram was plotted for the model and this was compared to the cumulative brightness histograms for pores obtained from real BSE images shown previously.

For the purpose of this study, we again consider an idealised material in which the surface is flat, the pore-solid boundary is abrupt and normal to the surface, the depth of each phase is significantly larger than the electron range and that there is no compositional variation across the phase between boundaries. The model consists of an epoxy-filled pore that follows a perfect circular geometry, surrounded by a C-S-H matrix. This is shown in Fig. 6.8 (A). The pore has a diameter of $10\mu\text{m}$ and is placed at the centre of a $20 \times 20\mu\text{m}$ C-S-H matrix, thus the theoretical pore volume fraction of this material is 19.6%.

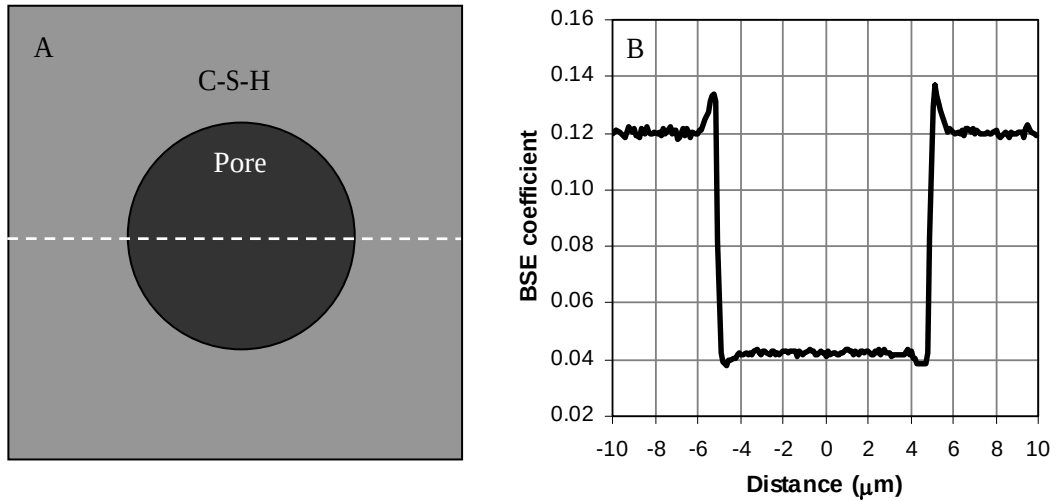


Figure 6.8 A) A hypothetical $10\mu\text{m}$ diameter epoxy-filled circular pore placed at the centre of a $20 \times 20\mu\text{m}$ C-S-H matrix; and B) a generated BSE line scan along the white horizontal dotted line through the pore centre.

For the simulation, one-hundred horizontal line scans at 0.2 μm apart were computed across the model at 10keV beam energy. Two-hundred individual points were simulated for each line scan, giving an effective pixel spacing of 0.1 μm . The line scan distance and pixel spacing value were chosen because they approximate the pixel spacing of a real BSE image taken at 500x magnification. Given that the formula for a perfect circle is $x^2 + y^2 = r^2$, where x and y are the coordinates with respect to the origin, which is located in the centre of the pore in this case, and r is the pore radius, the length of each horizontal line scan that transverse the pore can be computed as equal to $2 * \sqrt{25 - y^2}$. Fig. 6.8 (B) shows an example of a simulated BSE line scan through the pore origin.

In total, 2×10^4 points were simulated, giving a reliable amount of data for subsequent analysis. The signal produced in a solid-state backscattered electron detector is proportional to the backscatter coefficient, η and if neglecting any energy response characteristics of the detector, can be written as [Goldstein et al, 2003]:

$$S = \varepsilon_{BSE} * \eta \quad \text{Eq. 6.1}$$

Where ε_{BSE} is the detector collection efficiency for backscattered electrons, which depends on the geometry of the detector (angular size) as well as the energy response of the detector. ε_{BSE} is approximately constant for two phases with elements of similar atomic number. If this is true for the case of epoxy and C-S-H, then the detector signal and hence, the resulting pixel grey level will be a linear response to the BSE coefficient. For phases with significantly different atomic numbers and BSE energy distribution, however, ε_{BSE} will vary, generally increasing as a function of mean atomic number [Goldstein et al., 2003].

The smallest recorded BSE coefficient was found to be about 0.035 while the maximum value was close to 0.14. These values were used to calibrate the BSE coefficients to a grey scale ranging from zero to 100, that is a grey value of zero represents BSE coefficient 0.035 and a grey value of 100 represents a BSE coefficient of 0.14. Intermediate BSE coefficient values were then linearly scaled accordingly to this grey level range, and the results were used to plot the cumulative brightness histogram shown in Fig. 6.9.

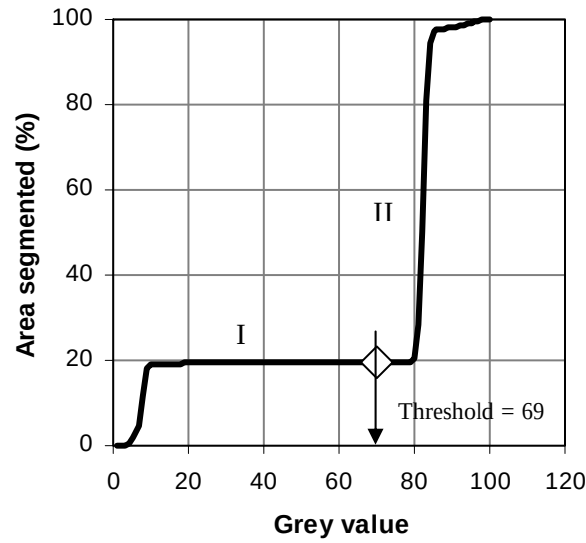


Figure 6.9 Cumulative brightness histogram for the pore model in Fig. 6.8 (A), obtained from Monte Carlo simulation. The symbol (◊) marks the threshold grey value (= 69) that gives the correct pore volume fraction of 19.6%.

The simulated cumulative brightness histogram displays a similar sigmoidal behaviour as in the cumulative brightness histograms for pores from real BSE images (see Fig. 4.5 and Fig. 6.7). The greyscale value that correctly segments the pore phase by giving a pore volume fraction that is closest to the theoretical value is 69. This grey value matches a BSE coefficient of 0.107, which represents about 70% of the transition from the grey value for epoxy to C-S-H at the boundary. As suspected, the correct pore threshold value is located just slightly before the inflection point in the cumulative brightness histogram.

Since the depth of the pore and C-S-H phase in our model is infinite with respect to the electron range and the pore-solid boundary intercepts vertically to the surface, the simulated pixel grey values will not be significantly affected by sampling of subsurface material. Pores bordering on phases with a higher atomic number than C-S-H were also not taken into consideration in the model. As shown previously, the pore pixel intensity will be increased while the solid phase pixel intensity will be decreased due to these effects in real BSE images. This essentially will increase the slope prior to the inflection (I) and decreases the slope after the inflection point (II) in the cumulative brightness histogram shown in Fig. 6.9. Therefore, the inflection point in real BSE image will not be as sharp and well defined compared to the model. Other factors such as surface topology and composition variation will also cause grey level variation in real images, but were not simulated in the model.

6.5 Resolution of backscattered electron microscopy for pores

In quantitative microscopy, it is of interest to know the dimension of the smallest feature that can be reliably imaged and measured. The resolution limit not only informs us of the capability of a particular instrument, but also the potential error and the accuracy of our measurement. Understanding how resolution is affected by various parameters allows us to select the best imaging condition that optimises resolution. In this aspect, Monte Carlo simulation can be used to establish the spatial resolution of a particular imaging signal as a function of the operation conditions and/or sample composition, where these are not always experimentally measurable.

The spatial resolution of SEM images is generally considered to be determined by the following factors: 1) the electron probe diameter, which is a function of the brightness of the electron source and lens aberrations; 2) the size of the signal sampling volume, which depends on the beam energy, density and chemical composition of the material; 3) the contrast produced by the sample and the detector system; and 4) the signal-to-noise ratio. Since images are digitised to picture elements of a finite size, the pixel spacing value can also have an effect on resolution. Certain publications tend to quote the image pixel spacing value as equivalent to the image resolution, although this is not always the case. For images captured at low magnification, the spatial resolution is likely to be limited by the pixel dimension, but for images captured at high magnification, the spatial resolution will be much less, when the pixel dimension approaches that of the beam diameter or the signal sampling volume. The working resolution of the SEM can be no better than the pixel size, but generally is less than the pixel size due to various factors such as probe diameter and sampling volume effects.

According to Goldstein et al. [2003], for a given choice of magnification, images are considered to be in sharpest focus if the measured signal from any given location when the electron beam is directed at it comes only from that particular picture element. When the pixel dimension becomes smaller than the beam diameter or the signal sampling volume, the area sampled will begin to overlap more than one picture element and this will be perceived as 'blurring' at phase boundaries. This is also known as the hollow or blank magnification effect, that is, beyond a certain magnification, no additional gain in information is obtained due to overlapping sampling areas of adjacent pixels. As such, for optimum image quality, the image pixel dimension should be set to be compatible with the probe dimension or the signal sampling volume.

The pixel dimension rapidly decreases with increase in magnification, therefore, at high magnification, overlapping of signal from adjacent pixels will eventually occur. From the calculations of brightness and probe current presented in Section 5.4, we showed that in order to achieve adequate signal to image cement-based materials at 10keV, a probe diameter of the order of 0.1 μm is required. At these conditions, we found that the maximum sampling depth of backscattered electrons at 90th percentile ranges from 0.23 μm (C₄AF) to 0.64 μm (epoxy) and the maximum diameter of the BSE sampling volume at 90th percentile ranges from 0.86 μm (C₄AF) to 2.5 μm (epoxy). Surprisingly, if we compare these values to the pixel spacings at various magnification levels reported in Table 3.3, we observe that even at a very low magnification of 100x, the BSE signals from adjacent pixels have begun to overlap.

The fact that features smaller than the interaction volume or the BSE sampling volume are usually observed during routine imaging shows that the dimension of the interaction volume or the BSE sampling volume does not represent, in itself, a limit to spatial resolution. This is because the visibility of a feature depends on the difference in the signal detected from that particular feature when the electron beam is positioned on it and its neighbouring region, i.e. contrast. Therefore, features smaller than the signal sampling volume can still be detected, as long as the obtained signal contrast satisfies the visibility criteria.

We can estimate the spatial resolution of BSE microscopy for imaging pores in cement-based materials using Monte Carlo simulation by following a similar approach proposed by Merli et al. [1995]. Consider a multi-layer composite consisting of alternating C-S-H and epoxy layers representing pores in cement-based materials (Fig. 6.10). The epoxy layers are placed at a sufficient distance apart so that the electron beam placed at any point does not sample more than one epoxy layer. The thickness of the epoxy layers are set to range from 10nm to 1 μm . The width and depth of the entire composite is larger than the interaction volume and again, we assume that the surface is flat, the phases are stoichiometric and the interfaces are abrupt and normal to the surface.

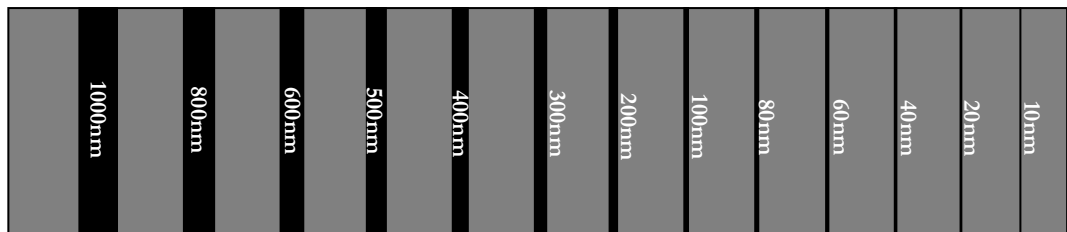


Figure 6.10 Model of a multi-layer composite comprising of alternating C-S-H and epoxy layers representing capillary pores of various dimensions from 10nm to 1 μm .

Fig. 6.11 and Fig. 6.12 plot the BSE coefficients measured across the multi-layer composite model at 10keV and 20keV respectively. The distance between beam sampling points, i.e. the pixel spacing, was set at $0.1\mu\text{m}$. The figures display several interesting characteristics. The edge effect (the signal increase close to the boundary on the C-S-H side) decreases with epoxy thickness and becomes insignificant when the epoxy is less than 100nm thick. It is also observed that the BSE coefficient measured from the centre of each epoxy layer increases as the epoxy layer becomes thinner, and approaches the value for C-S-H. This is due to the increasing contribution of adjacent C-S-H layers to the BSE signal measured on thin epoxy layers. This effect is slightly more significant in the case of 20keV due to a larger BSE sampling volume. A similar trend is observed when the simulation is repeated at a much smaller pixel spacing of $0.01\mu\text{m}$ as shown in Fig. 6.13.

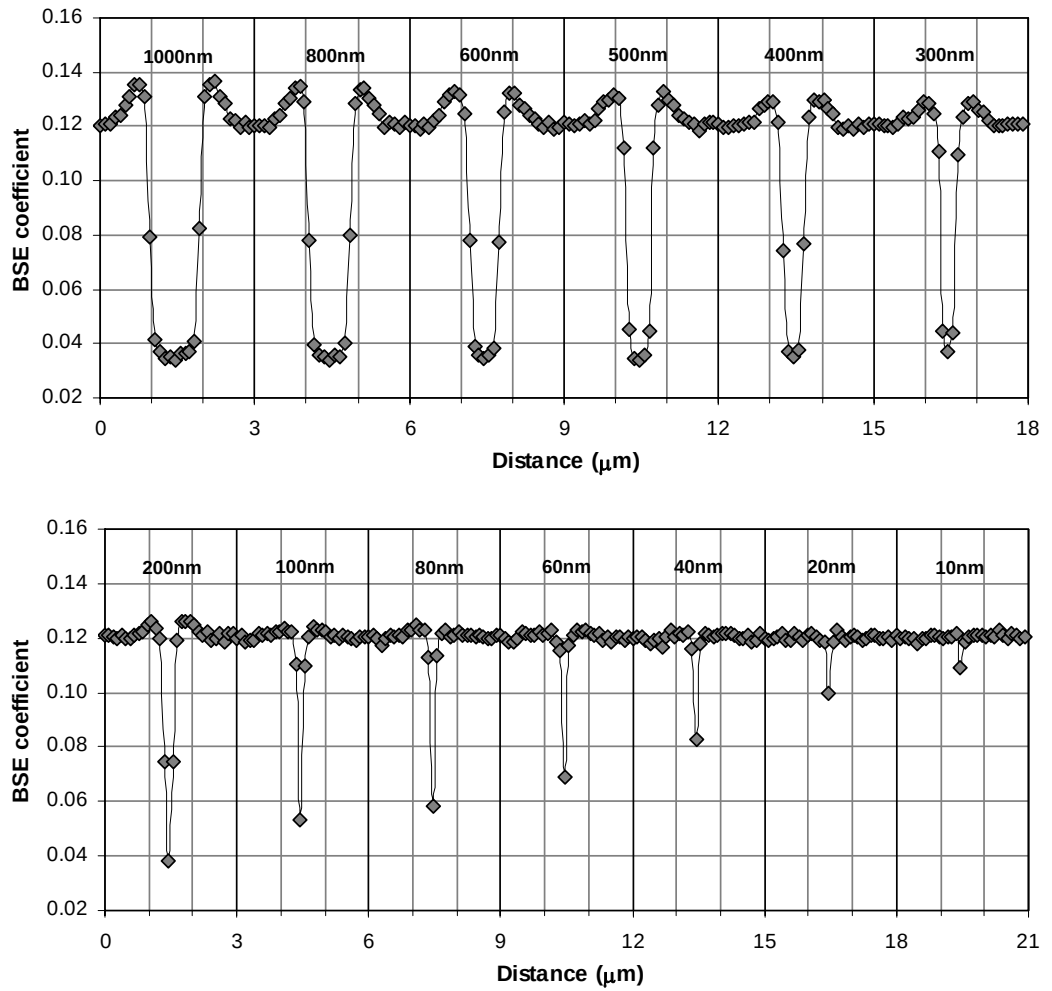


Figure 6.11 Change in BSE coefficient across epoxy layers of various thicknesses at 10keV and $0.1\mu\text{m}$ pixel spacing. Note that the figure only plots data from $\pm 1.5\mu\text{m}$ from the centre of each epoxy layer.

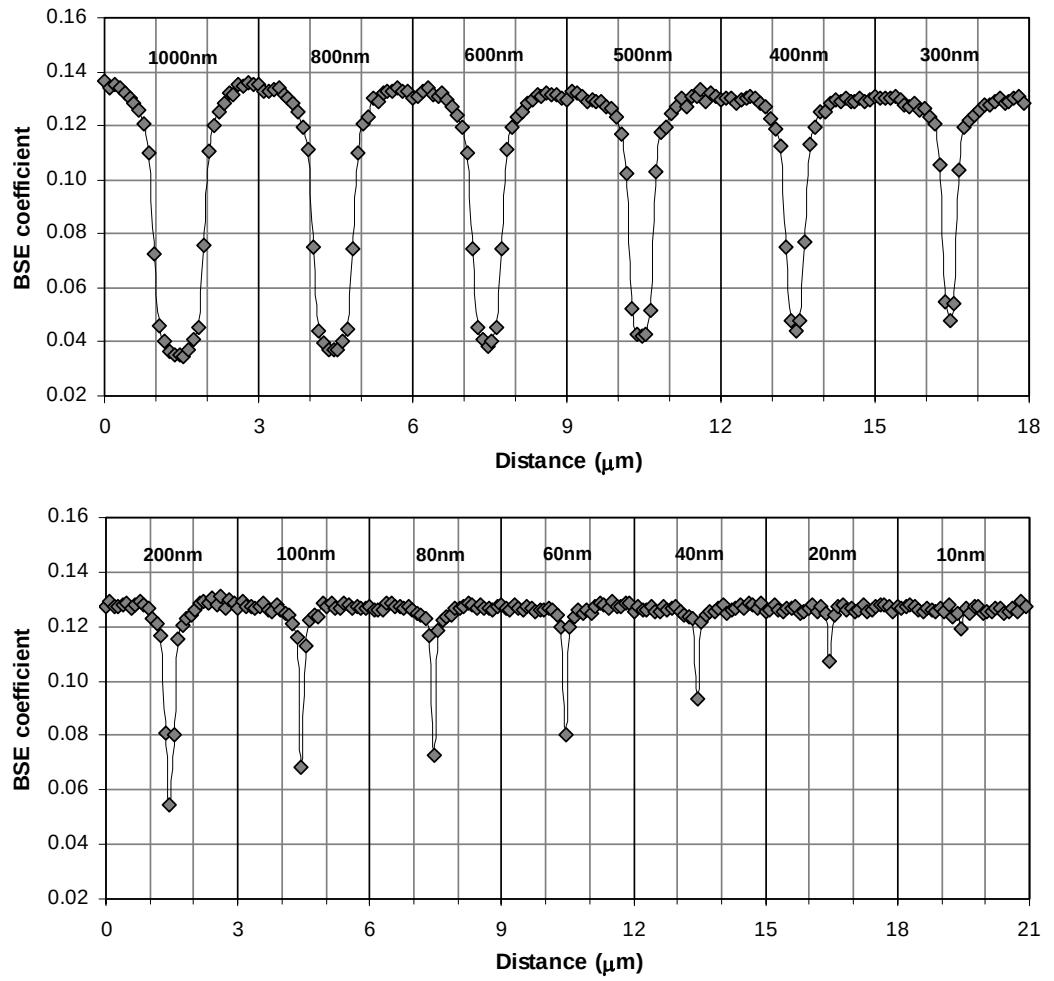


Figure 6.12 Change in BSE coefficient across epoxy layers of various thicknesses at 20keV and 0.1μm pixel spacing. Note that the figure only plots data from $\pm 1.5\mu\text{m}$ from the centre of each epoxy layer.

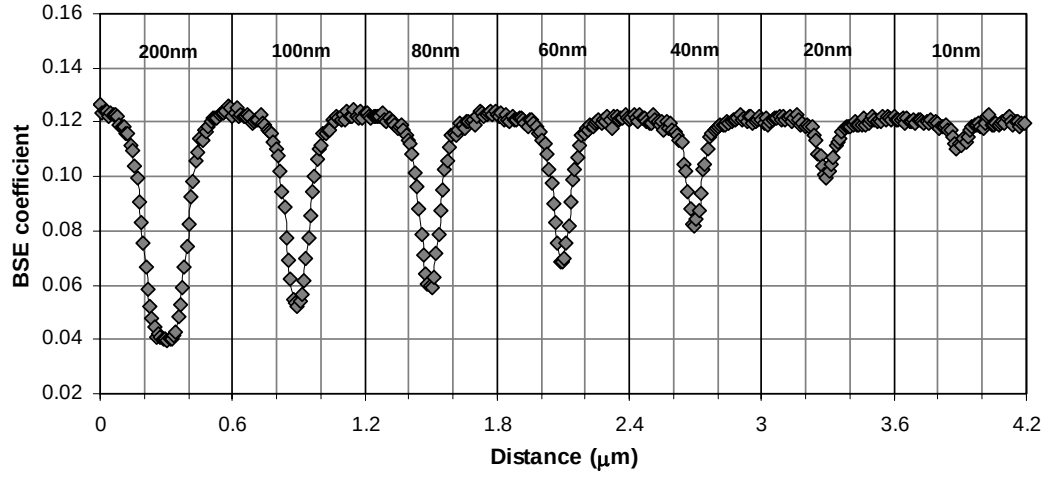


Figure 6.13 Change in BSE coefficient across epoxy layers of various thicknesses at 10keV and 0.01 μm pixel spacing. Note that the figure only plots data from $\pm 0.3\mu\text{m}$ from the centre of each epoxy layer.

Because the BSE signal for the epoxy layer progressively increases as the layer becomes thinner, there would be a limit when the difference in signal between epoxy and adjacent C-S-H layers is too small to be discernable, and this would represent its spatial resolution. Whether or not this visibility limit is exceeded for an epoxy layer of a certain thickness can be estimated by calculating the contrast with respect to the background C-S-H using the following equation:

$$C = \frac{S_1 - S_2}{S_1} \approx \frac{\eta_1 - \eta_2}{\eta_1}, \quad \eta_1 > \eta_2 \quad \text{Eq. 6.2}$$

Where S_1 and S_2 represent the BSE signal detected at the C-S-H and epoxy layer respectively. Assuming that the BSE detector collection efficiency is the same for C-S-H and epoxy, the collected signal is approximately proportional to the backscatter coefficient, η (Eq. 6.1). Thus, according to this definition, contrast is always positive and is restricted to a range of 0 to 1. A contrast value of zero indicates that the detected signal is the same for both points, i.e. both points are sampling an identical phase. Contrast is equal to unity in the case, for example, in which an object is suspended over a hole from which no signal emerges so that $S_2 = 0$ [Goldstein et al., 2003].

Fig. 6.14 shows the BSE contrast for epoxy layers at various thicknesses with respect to adjacent C-S-H layers computed at 10 and 20keV. Note that the additional data for thickness greater than 1 μm came from simulation results presented in Section 6.4. Thus, in total, the epoxy layers have dimensions covering three orders of magnitude from 10nm to 10 μm , which should be sufficient to represent the size of epoxy-filled capillary pores in cement-based materials. The contrast was calculated using Eq. 6.2, where η_1 and η_2 are the BSE coefficients for C-S-H and epoxy respectively, obtained from the centre of each layer.

The figure shows that the signal contrast for epoxy layers greater than 2 μm thick is relatively constant at about 65%. The signal contrast increases slightly and peaks at about 0.8 μm , then drops significantly with decrease in epoxy thickness, as the epoxy layer approaches the dimension of the electron probe. The contrast peak at 0.8 μm is likely to be artificially induced by the drop in BSE signal due to edge effects, when the boundary on both sides of the epoxy layer approaches its centre (Section 6.3). It is somewhat surprising to observe that the contrast at 20keV is only marginally lower than the contrast at 10keV. In addition, assuming that a minimum visible contrast for an average observer is about 5-10% [Goldstein et al, 2003], the simulation suggests that an epoxy layer as thin as 10nm can generate sufficient contrast from the surrounding C-S-H matrix to enable its detection. This appears to be true despite the fact that its dimension is substantially smaller than the signal sampling volume and electron probe diameter.

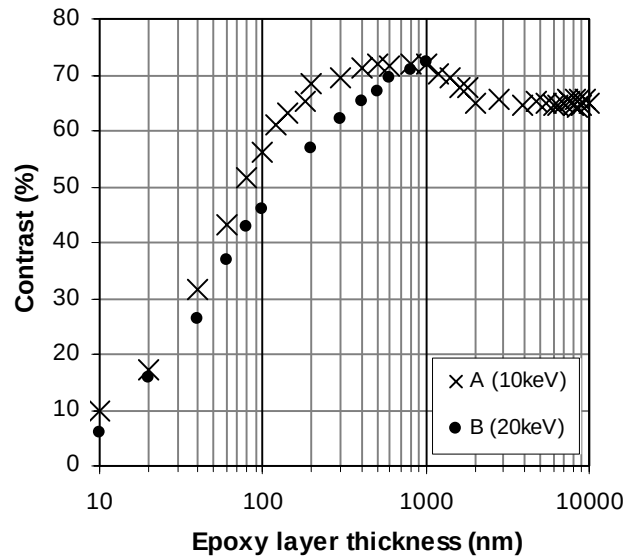


Figure 6.14 BSE contrast for epoxy layers of various thicknesses with respect to neighbouring C-S-H layers at 10keV and 20keV.

According to Merli et al. [1995], the spatial distribution of the backscattered electrons does not govern the spatial resolution because all backscattered electrons contribute positively to the image formation process, regardless of their trajectories and sample exit points. This is due to an obvious physical fact that the detectors do not differentiate backscattered electrons according to their trajectories in the sample, but just count their number. Therefore, even though the size of the signal sampling volume will affect contrast, it does not represent in itself a limit to the resolution.

In practice, however, the spatial resolution obtained from real images would be somewhat smaller than that presented in Fig. 6.14. This is because an important factor that is not considered in the Monte Carlo simulation is the effect of noise. Feature contrast does not only depend on atomic number contrast generated from the electron-solid interactions, but also the geometry of the sample and phase boundaries, surface topography, the position, size and response of the detector, as well as a host of other sources of noise from the environment and the signal digitisation process. Thus, the resolution limit inferred from Fig. 6.14 represents a theoretical maximum resolution that is only achievable in an ideal situation where the various sources of disturbance do not exist.

The question that is most relevant to this study remains, that is: what is the size of the smallest pore that can be reliably imaged and measured in a BSE image captured using the present instrumentation and set up? We have learnt from Section 6.2 that the pore pixel intensity increases substantially because of sampling of subsurface material. This was shown in Fig. 6.3, which plots the gain in BSE coefficient for epoxy as the ‘pore’ depth is decreased. The pore segmentation threshold determined from the Overflow method in Fig. 6.9 is equivalent to a BSE coefficient of 0.107; hence, by applying this threshold to Fig. 6.3 we find that pores shallower than $0.2\mu\text{m}$ at 10keV, or $0.8\mu\text{m}$ at 20keV, will not be segmented (despite the fact that they may be visible). Using the same argument, a solid phase where there is an underlying pore close to the surface can also be incorrectly segmented as a pore phase.

We also know that the lateral resolution for imaging multi-epoxy layers in a C-S-H matrix can be as small as the probe diameter. However, in performing quantitative work using image analysis, large errors in the measurement can be expected when the feature size approaches the image resolution. The magnitude of this error would depend on how small the feature is with respect to the image resolution, the accuracy of the segmentation method as well as the effect of spatial digitisation on the measurement.

Fig. 6.15 compares the actual thickness with the measured thickness of epoxy layers, after having been segmented using the Overflow method. Three cases were studied; case A

and B are for 10keV and 20keV respectively at a pixel spacing of $0.1\mu\text{m}$, while case C is for 10keV, but at a much smaller pixel spacing of $0.01\mu\text{m}$. The figure shows that a good agreement between measured and actual values is achieved for thicknesses greater than $1\mu\text{m}$, where the percentage error is small and insignificant. However, for values smaller than $1\mu\text{m}$, the error increases and becomes significant ($>50\%$) when the thickness of the epoxy layer is less than the probe size ($\sim 0.1\mu\text{m}$). The large errors persisted even when the pixel spacing was reduced to $0.01\mu\text{m}$, suggesting that the errors are not due to spatial digitisation.

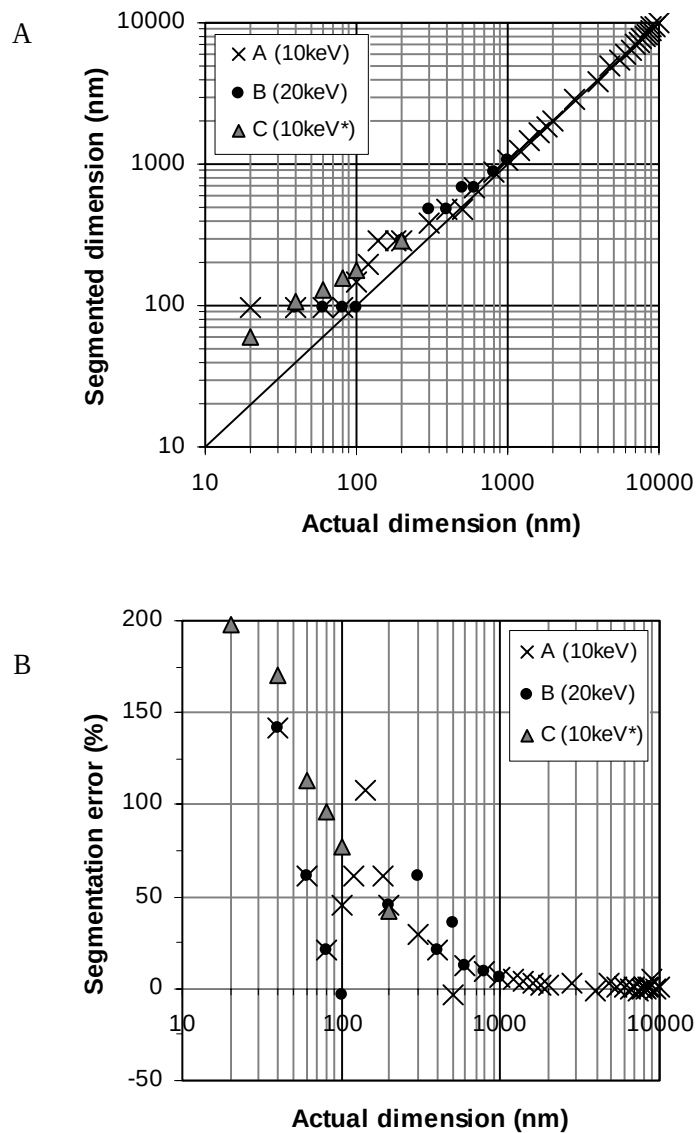


Figure 6.15 A) Comparison between the Overflow segmented thickness and the actual thickness of the epoxy layers for values ranging from 10nm to $10\mu\text{m}$; and B) segmentation error plotted against epoxy thickness.

6.6 Discussion

It must be stressed that the work presented here in determining the true position of phase boundaries is not simply of academic or theoretical interest. The accuracy of the boundary position or the segmentation procedure will affect the accuracy of subsequent measurements of the feature of interest. This is especially important for small particles that are inevitably represented by few pixels, such as in the case of sub-micron pores in cement-based materials. The choice of grey level to threshold the pore phase will have a dramatic effect on the measured volume fraction and specific surface, and can compound the errors that are already inherent from the finite image resolution.

Monte Carlo simulations show that for an ideal pore-C-S-H boundary normal to the surface, the position of the true boundary lies at about 70% of the signal transition at the boundary. This is slightly overestimated by the Overflow segmentation method, but the error is expected to be on the safe side. This is because the accuracy of the Monte Carlo simulation is confined to ideal boundaries that are normal to the sample surface. Effects of sampling subsurface material and pores bordering on phases with a higher atomic number than C-S-H, which would increase the threshold value, were also not taken into consideration in the model. Nevertheless, we stress that a perfect segmentation method for a random multiphase material does not exist; there will always be errors in image analysis especially when the feature size is small, and the magnitude of such errors needs to be taken into consideration in quantitative work.

Monte Carlo simulation on a multilayer composite consisting of alternating epoxy and C-S-H layers shows that the spatial distribution of the backscattered electron does not govern the spatial resolution of the resulting image. All backscattered electron positively contribute to the image formation, independently of their exit points. The spatial resolution for BSE imaging an ideal epoxy layer can be smaller than the electron probe size although this would be reduced in practice when imaging pores in cement-based materials due to various noise effects and sampling of subsurface material.

Clearly, there is a need for an improved resolution, so that the entire range of capillary pores (about 0.01 to 10 μm) can be imaged. This can be achieved by using a brighter electron source, such as in a field emission scanning electron microscope, which is able to produce a high-density probe current with a size in the order of several nanometres, but at very low beam energy.

6.7 Conclusions

Monte Carlo simulation was used to investigate the variation of backscattered electron signal across pore-solid boundaries in cement-based materials. The study verified that the inflection point in the cumulative brightness histogram is a good estimate for the upper threshold value for pores, as proposed by the Overflow method. Sampling of subsurface material can drastically change the pixel intensity of the pore or solid phase. This effect limits the detection of pores that are shallower than about $0.2\mu\text{m}$ at 10keV and $0.8\mu\text{m}$ at 20keV . This effect also causes solid phases to be incorrectly segmented when there is an underlying pore close to the surface. We found that the lateral resolution for imaging an ideal multilayer composite consisting of alternating epoxy and C-S-H layers can be smaller than the electron probe size, but for a real random pore structure, this resolution would be degraded due to various sources of noise. In quantitative image analysis, large errors in the measurement can be expected when the feature size approaches the image resolution. The comparison between actual thickness and measured thickness of epoxy layers, after having been segmented using the Overflow method shows good agreement for thicknesses greater than $1\mu\text{m}$. However, for values smaller than $1\mu\text{m}$, the error increases and becomes significant when the thickness of the epoxy layer is less than the probe size.

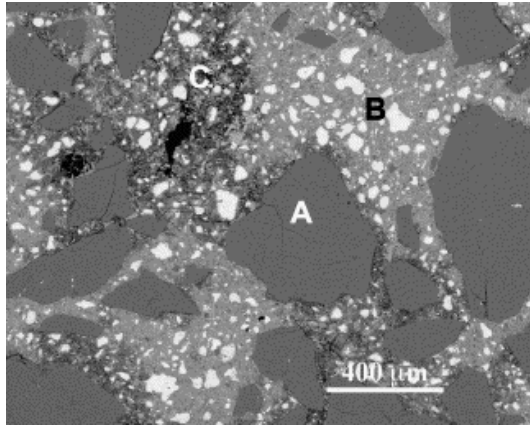
Chapter 7

Patch microstructure in cement-based materials: Fact or artefact?

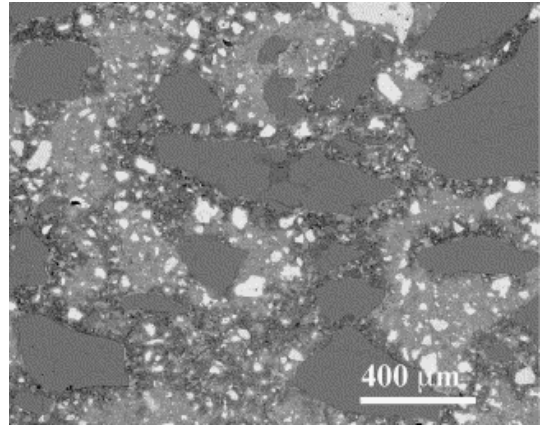
The appearance of patch microstructure, i.e. broad dense and porous regions separated by sharp and distinct boundaries and occurring randomly in bulk and interfacial transition zones has been reported previously in various site- and laboratory-mixed concretes and mortars. Patch microstructure challenges the conventional ITZ/bulk paste model and has major implications for the current understanding of microstructure and molecular/ionic transport processes in cement-based materials. In this chapter, evidence is presented to show that patch microstructure is an artefact of sample preparation and does not reflect the true nature of the hydrated cement paste. The appearance of dense patches comes from paste areas that have been ground and polished beyond the epoxy intrusion depth. In a backscattered electron image, small capillary pores not filled with epoxy are not visible because the signal is generated from the base or side walls of the pores. A modified method for epoxy impregnation, which can achieve a much deeper epoxy penetration than conventional vacuum impregnation, is presented.

7.1 Introduction

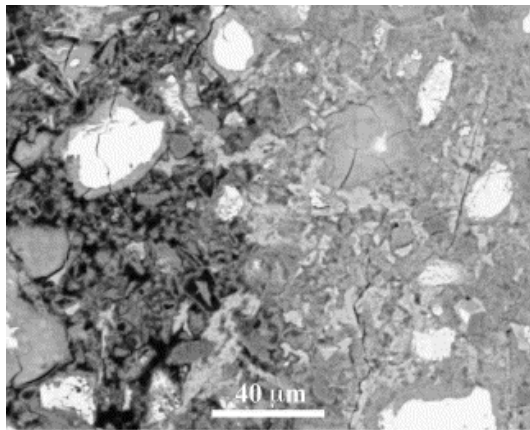
Patch microstructure was first reported in the journal *Cement and Concrete Research* in an experimental investigation using backscattered electron microscopy in the context of the phenomenon of percolation due to overlapping of interfacial transition zones (ITZs) in mortars [Diamond, 2003]. Further reports on patch microstructure by the same author have since appeared elsewhere [Diamond, 2004a; Diamond 2004b; Diamond, 2005]. The original paper [Diamond, 2003] claimed to invalidate the conclusion of Winslow et al. [1994] that the mercury intrusion porosimetry results that showed increased intruded pore space at pressures below the threshold pressure in mortars with sand contents of at least 48% can be attributed to percolation of overlapping porous ITZs. Some examples of BSE images of patch microstructure, obtained from Diamond [2003], are reproduced in Fig. 7.1 and Fig. 7.2.



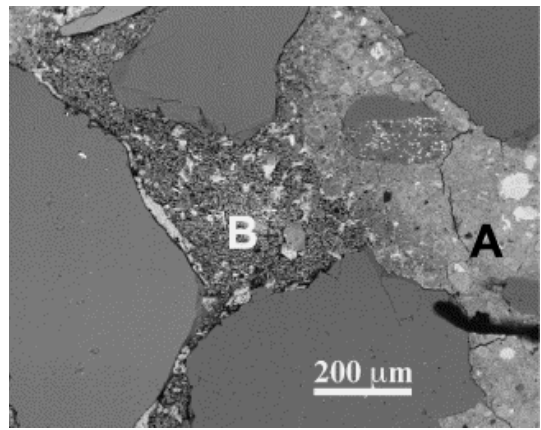
a) 28-day w/c 0.4 mortar with 44.8% sand vol. at low magnification (A = sand, B = dense patch, C = porous patch).



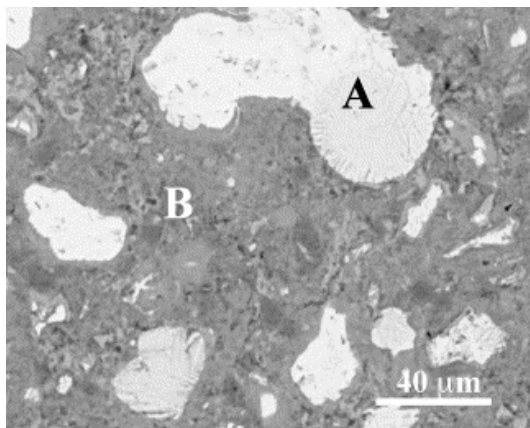
b) 28-day w/c 0.4 mortar with 48.6% sand vol. at low magnification.



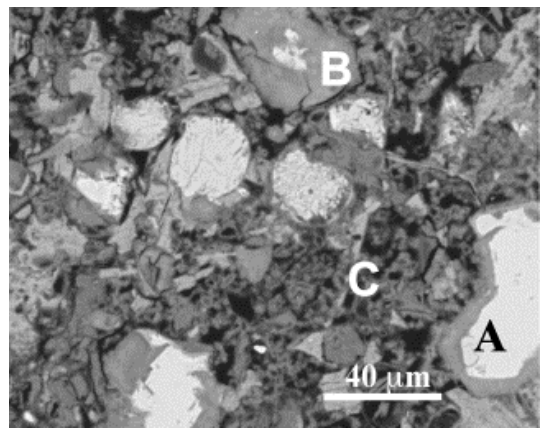
c) Sharp boundary observed between porous and dense patch.



d) Sharp boundary observed in an 8-year old mortar (55.5% sand vol., w/c 0.4).

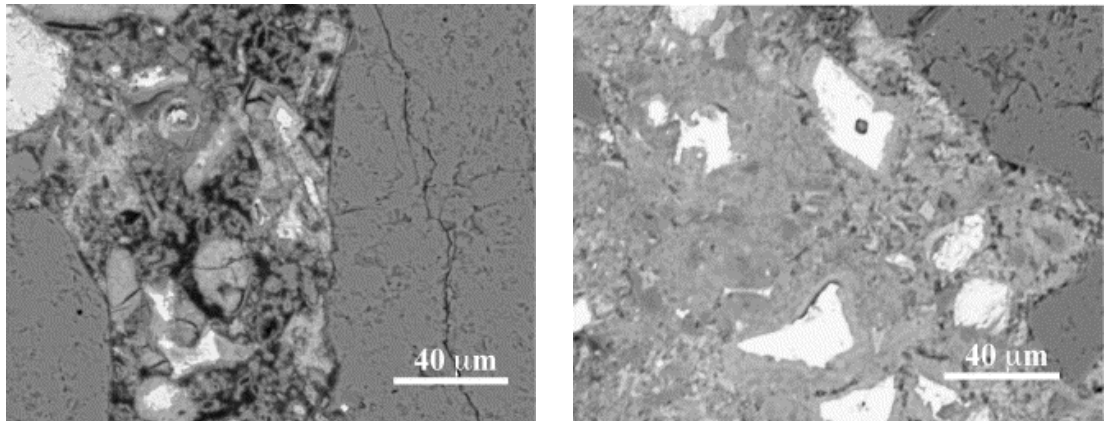


e) An area of bright, dense patch at high magnification (A = unreacted cement grain, B = isolated small pores).



f) An area of dark, porous patch at high magnification (A = unreacted cement grain, B = inner hydration product, C = outer hydration product).

Figure 7.1 BSE images of patch microstructure obtained from Diamond [2003].



a) Patch of dark, porous cement paste between two closely spaced sand grains.

b) Area of sand grain in contact with bright, dense cement paste

Figure 7.2 Patch microstructure is inconsistent with conventional ITZ/bulk paste model, e.g. the hard core/soft shell model [from Diamond, 2003].

Diamond [2003] made the following observations:

- The hardened cement paste in mortars (w/c ratio 0.4, 28 days old, sand volume fraction $>48\%$) consists of 'patches of brighter, dense, almost nonporous regions and dark, highly porous patches; the patches indifferently occupying both classical 'ITZ' and classical 'bulk' locations'.
- Dense and porous patches 'do not blend together, but form sharp boundaries'.
- The porous regions occur in broad patches through the bulk paste. Many sand particles are 'surrounded or partly surrounded by the dense, almost non-porous hardened cement paste'. This is inconsistent with the conventional ITZ model.
- The proportion of porous patches increases with sand content and at high (48.6 %) sand contents the porous patches are 'visibly interconnected on the plane of observation'.

From the above observations, Diamond [2003] concluded that if percolation occurs in high sand content mortars, the percolative effect is a result of the interconnection of highly porous patches and not from the overlapping of ITZs [Bentz & Garboczi, 1999]. In another paper, Diamond [2004a] found similar porous and dense patches in site- and laboratory-mixed concretes of 0.45 w/c ratio. More recently, Diamond [2005] showed that this distinctive patchy microstructure is not a result of inadequate mixing. The dense and porous patches persisted despite prolonged mixing of up to 30 minutes.

We have made similar observations (unpublished) of patch microstructure, in our routine work using backscattered electron imaging. An example is shown in Fig. 7.3, which is a BSE image of a mortar (w/c 0.6, sand 50% vol., 28 days sealed cured) that has been vacuum impregnated with epoxy, then ground and polished using conventional methods. As can be seen in the figure, the cement paste appears to consist of two distinct types of hardened cement paste. One appears dark and porous while the other appears relatively bright, dense and almost non-porous. The dense/porous patches often extend to several hundreds of microns in width, occur indiscriminately in both ITZ and bulk paste regions and do not seem to be influenced by the size, orientation and spatial distribution of the aggregate particles. Some aggregate particles are completely surrounded by porous paste while others are in contact with both the porous and dense pastes.

The most remarkable feature is the boundary between the dense and porous patches, which is unusually distinct and sharp. In Fig. 7.3 (B), the paste on the left appears very porous with interconnected capillary pores and hollow-shells. In contrast, the paste on the right appears almost non-porous with several unreacted cement grains visible, surrounded by very dense hydration products. A continuous microcrack can be seen on the bottom left of the image (indicated with arrows), extending between the dense and porous patches. It should be noted that the patch microstructure shown here is very similar to those reported previously (see, for example, Fig. 7.1 and Fig. 7.2). In this chapter, we will provide evidence that such patch microstructure, in particular where a sharp boundary is present, is an artefact of specimen preparation and does not reflect the true nature of the cement paste.

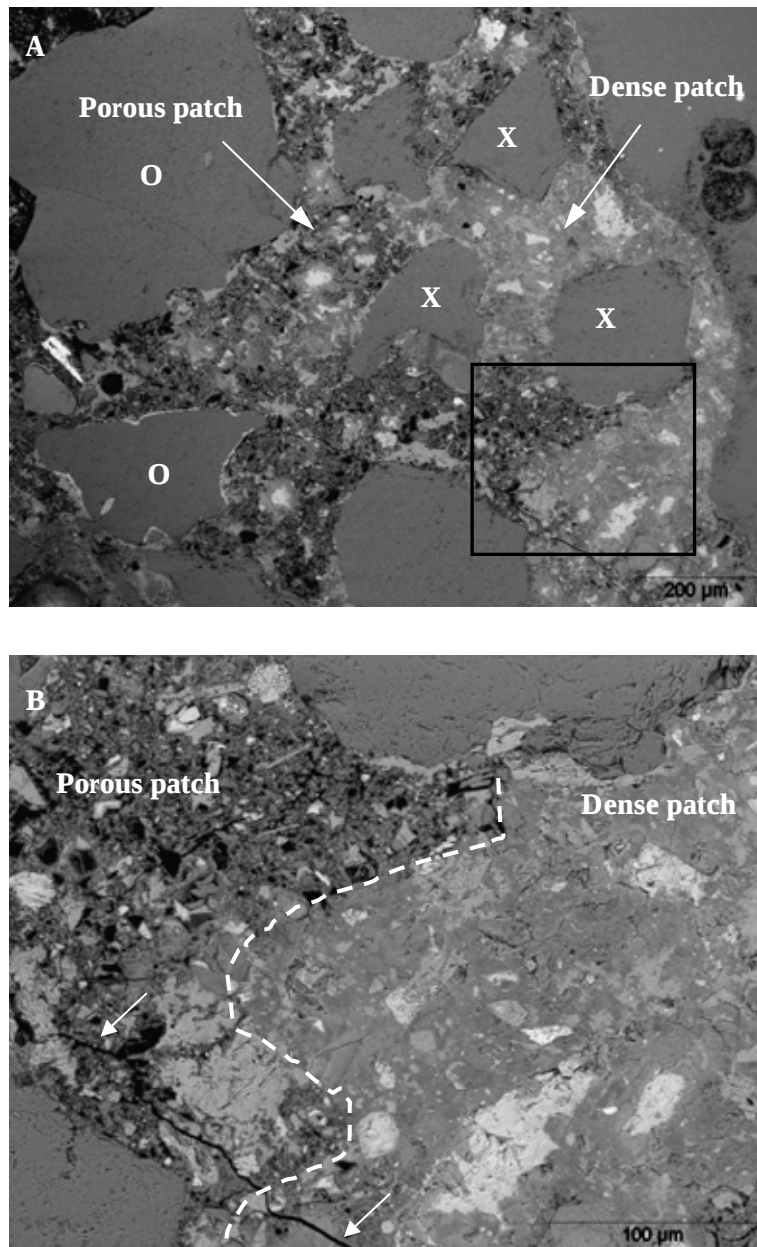


Figure 7.3 A) Patch microstructure observed in an OPC mortar (w/c 0.6, sand 50% vol., 28-day cured) where dark porous cement paste appears to be intermixed with bright, almost non-porous paste. Particles marked 'O' represent sand particles that are fully surrounded by porous cement paste while particles marked 'X' are in contact with both porous and dense patches. Field of view is 1333 x 1000μm; B) Magnified portion of (A) showing the boundary between the porous and dense patch is sharp and distinct. Field of view is 381 x 286μm.

7.2 Epoxy impregnation

For microstructural examination of porous media using backscattered electron microscopy, it is essential for the pores to be first saturated with epoxy resin, which upon hardening, supports the delicate pore structure and enables it to withstand subsequent grinding and polishing with minimal induced damage. The epoxy also serves a second, but equally important, purpose; due to its low average atomic number, the epoxy provides atomic contrast to allow pores to be visible and be differentiated from solid phases during BSE imaging. When the microscope electron beam is directed on to a pore that is not resin-filled, the incident electrons will continue to travel below the observation plane until they hit a solid material, which is either the base or side wall of the pore. The incident electrons will interact with the solid phase and after a series of scattering events, may re-emerge as backscattered electrons, escape the empty pore and be collected by the detector. This is schematically illustrated in Fig. 7.4. In the resulting BSE image, the corresponding 'pore' pixel will then appear bright, depending on the average atomic number of the solid phase that surrounds the pore. Unfortunately, this phenomenon is often overlooked.

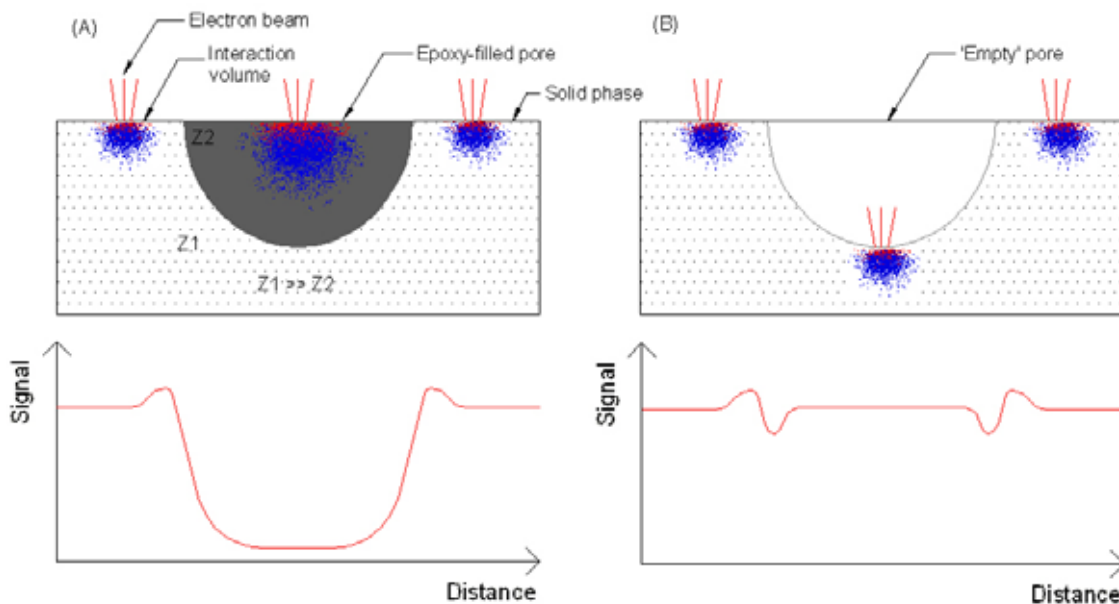


Figure 7.4 The importance of epoxy for providing atomic contrast in pore imaging. Schematic showing the effect of epoxy on the detected BSE signal, when an electron beam is scanned across an epoxy-filled pore (A) and an 'empty' pore (B).

The general procedure for conventional epoxy impregnation is shown in Fig. 7.5 and is briefly described here. The sample is first dried either by oven drying, vacuum drying, freeze-drying after immersion in liquid nitrogen, or by solvent replacement which takes a longer time. Removal of water from the pore channels is essential because it interferes with the penetration and polymerisation of the epoxy. The dried-sample is then fitted into a casting mould and evacuated in a vacuum chamber. The epoxy, preferably de-aired, is fed into the mould whilst still under vacuum until the sample is completely submerged. The epoxy and sample are allowed to out-gas, and after some time, the vacuum is slowly released to allow air in, which theoretically pushes the epoxy into the pores. In reality, the intrusion depth achieved by this method is very small, because the pores in most cement-based materials are very fine, and this is well known [Kjellsen et al., 2003; St. John et al., 1998]. For example, Kjellsen et al. [2003] showed that the epoxy penetration depth for a 0.4 w/c ratio paste was only around 120µm and this decreased with decreasing w/c ratio and with the presence of silica fume.

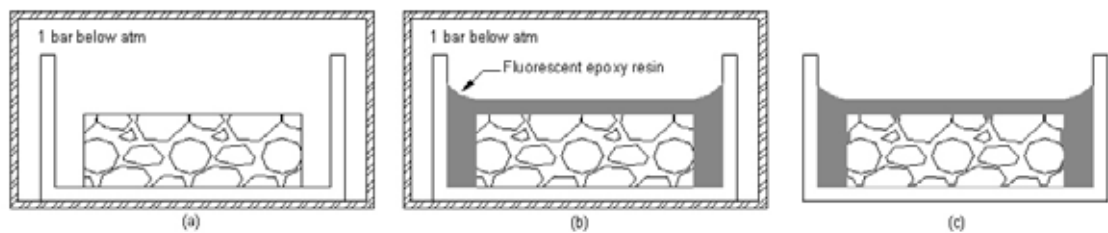


Figure 7.5 Epoxy impregnation using conventional procedure: a) the sample is first de-aired; b) then epoxy is introduced under vacuum; c) and finally the vacuum is released.

Obviously, grinding and polishing should not go beyond the epoxy intrusion depth, but this is extremely difficult with such a shallow epoxy penetration. Also, in the first stage of dry grinding, silicon carbide papers of a very coarse grit size, typically 100-150 grit (90-160µm grain diameter) [Stutzman & Clifton, 1999; Kjellsen et al., 2003] are used to remove excess resin from the sample surface, and thus, this stage has to be controlled with extreme care. The difficulty is compounded by the uneven thickness of the surplus resin, uneven rate of material removal during grinding (the sample edge is usually ground faster than its centre) and surface roughness from previous cutting operations that must be removed in order to achieve a plane section. If the coarse grinding stage is not done sufficiently, to reveal the epoxy-filled surface, then many large and irregularly shaped pockets of black resin-filled voids

will be seen in the BSE images, giving a false impression of a very porous, poorly consolidated sample. In addition, it is very difficult to tell if the sample surface remains saturated with epoxy after the polishing stages unless a coloured dye is added into the epoxy.

We have developed a slight modification to the resin impregnation procedure to achieve deeper epoxy penetration. The steps are illustrated in Fig. 7.6. First, the dried sample is cast in a clear epoxy resin with the observation plane at the bottom. When the resin has achieved sufficient hardness, the sample is dry ground to remove the excess clear resin and to expose a fresh, planar surface. Then, compressed air is used to dislodge any grinding material or dirt from the surface. Next, the sample is placed under vacuum for four hours; this is important to ensure that the pores are completely de-aired. Without breaking the vacuum, a low viscosity fluorescent resin (araldite) that has been previously de-aired and diluted with 5% wt. toluene (to reduce viscosity further) is poured onto the sample, covering the entire surface. The vacuum is released and subsequently, an additional 2.5 bars above atmospheric pressure is applied on the sample via a gas (O_2) bottle, and maintained for about 30 minutes. Pressuring the sample at this level is routinely used in liquid permeability testing and is not known to cause damage.

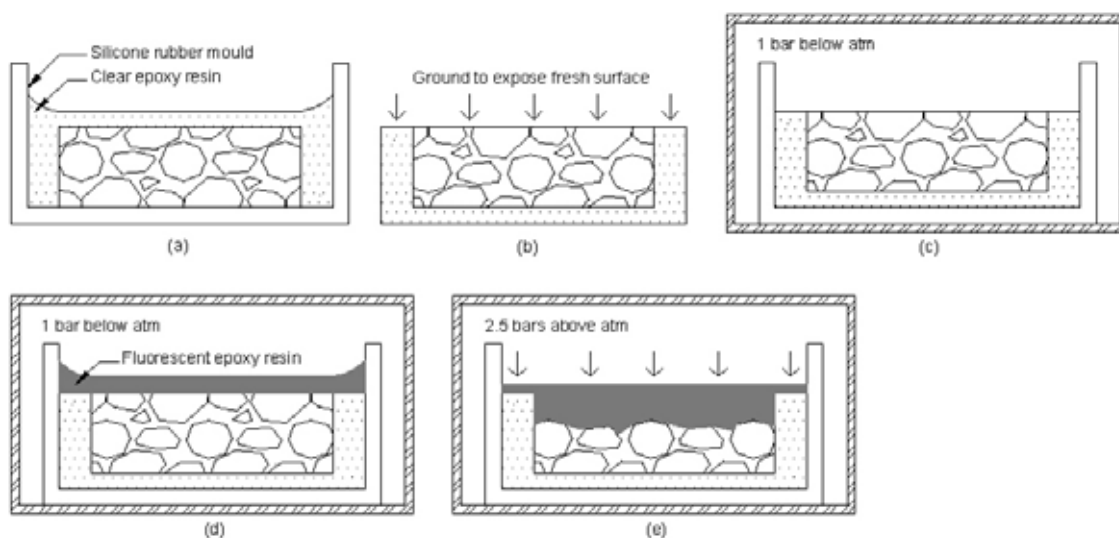


Figure 7.6 Schematic of the new epoxy impregnation method: a) The dried sample is first cast in clear epoxy resin; b) when the resin has hardened, the bottom face is dry-ground to expose a fresh and plane surface for observation; c) the sample is placed under vacuum for several hours to evacuate the pores; d) a de-aired fluorescent epoxy resin is added while the sample is still under vacuum; e) and finally the vacuum is released and a 2.5 bars gas pressure is applied for 30 minutes.

Fig. 7.7 shows parallel mortar samples that were impregnated using the conventional vacuum technique (A & B) and the new method (C & D). The difference in penetration depth is clear. Whilst the epoxy penetration front is less than 1mm into the vacuum impregnated samples, a full (7mm) depth of penetration was achieved for the 0.6 w/c ratio mortar specimen and approximately 3mm penetration was achieved for the 0.4 w/c ratio mortar when the new method was used. However, we note that although the new method achieves a deeper penetration depth, it does not necessarily imply that all capillary pores have been filled with epoxy to that depth. Nevertheless, a greater epoxy penetration depth gives more tolerance during the grinding stages and ensures that the observation plane remains filled with epoxy after polishing.

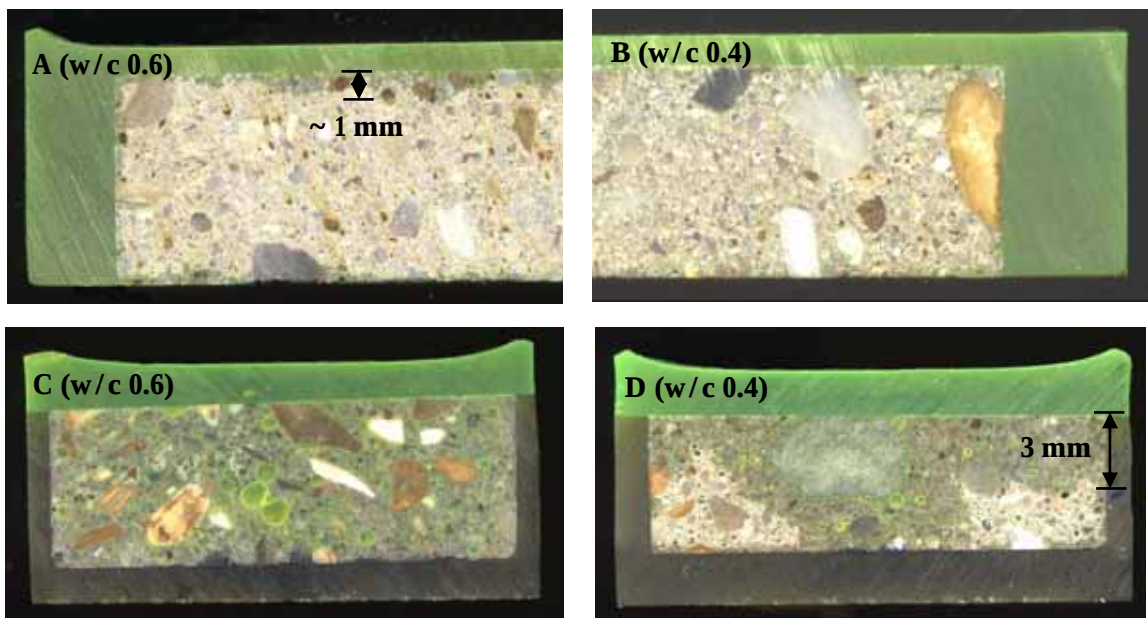


Figure 7.7 Cross sections of mortar samples showing the depth of resin penetration using the conventional vacuum impregnation method (A, B) and the new technique (C, D). The epoxy penetration front is less than 1mm on samples that were impregnated using the conventional method. Full depth penetration is evident for the w/c 0.6 mortar (C) and a penetration of around 3mm for the w/c 0.4 mortar (D). The deeper epoxy penetration provides confidence that the observation plane remains saturated with epoxy after the grinding and polishing stages.

7.3 Experimental

Two mortars of w/c ratio 0.4 and 0.6 were prepared using ordinary Portland cement and medium graded siliceous sand at 50% volume fraction. A conventional pan mixer was used. The sand and cement were dry-mixed for 2 minutes and then water was added as the mixer continued to rotate. The total wet mixing time was 3 minutes. The mortars were cast in steel cylindrical moulds (100Ø x 250 mm) and compacted in three uniform layers using a vibrating table. After 24 hours, the samples were demoulded, sealed in cling film and cured at 20°C for 28 days. At the end of the curing period, an 8mm thick disc was cut from each cylinder at approximately 125mm from the bottom cast face, from which a block specimen (40 x 20 x 8mm) was extracted. Cutting was performed using a precision diamond saw and a nonaqueous lubricant. The blocks were freeze-dried using liquid nitrogen and vacuum-impregnated with a low viscosity epoxy following the conventional procedure described in the previous section. The block samples were then dry-ground using silicon carbide papers of successively finer grit size (120, 220, 500, 1000 and 1200) and finally polished using cloths embedded with diamond abrasives (9, 6, 3, 1 and ¼ micron) with a non-aqueous lubricant (Section 3.2.1). Each grinding and polishing step was done at 70rpm and 7N applied force. Polishing time was kept short (~5 minutes) to minimise relief. The sample was cleaned ultrasonically in acetone after each polishing stage.

A JEOL 5410LV scanning electron microscope equipped with a backscatter electron detector was used for imaging. The microscope was operated at low vacuum (9Pa), hence carbon coating was not necessary, 10kV accelerating voltage and 10mm free working distance. The images were digitised to 1024 x 768 pixels. Each image was captured with constant brightness and contrast settings for reproducibility. The brightness and contrast were adjusted so that the greyscale histogram of the image was stretched to cover the entire greyscale spectrum, but was not over-saturated at the low or high ends of the spectrum. However, it was observed that the lens current tended to fluctuate even after a long warm-up time and hence, the brightness and contrast settings were checked and readjusted periodically. The brightness and contrast were calibrated with an aluminium-epoxy microanalytical standard prior to the capture of each image (Section 3.2.4).

Areas that showed patchy microstructure were imaged at several magnifications. The co-ordinates of these locations were stored so that they could be revisited later. In total, ten locations were chosen per sample. The samples were then re-impregnated with epoxy using

the proposed technique, but without the initial grinding stage (Fig 7.6 b). After that, the samples were ground and polished according to the same procedure as described above. The locations that initially showed patchy appearance were revisited in the electron microscope to establish if the dense/porous patches persisted.

7.4 Observations

In all the locations that we re-examined, it was found that the dense patches disappeared after the samples were re-impregnated and re-polished. Fig. 7.8 shows BSE images of the same area as the one in Fig. 7.3 after having been re-impregnated and re-polished. By measuring the change in diameter of the air void (indicated by an arrow in Fig. 7.8 A), and by assuming that it follows a spherical shape, it is estimated that the thickness of material that had been removed during the second grinding/polishing stage was around 50 μ m. It is clear from Fig. 7.8 that the apparently dense patches that were visible in Fig. 7.3 have now disappeared. The originally dense patches are now filled with many capillary pores and hollow-shell pores. The same microcrack can be seen in Figs 7.3 (B) and 7.8 (B), suggesting that the crack runs deep into the sample and was more easily penetrated by epoxy than the fine capillary pores. This probably explains why the crack was visible in the dense patch of Fig. 7.3 (B).

Fig. 7.9 (A) is a low magnification image that shows dense and porous patches that occupy both ITZ and bulk paste regions indiscriminately. The porous patches appear to form an interconnected link, suggesting that molecular/ionic transport may occur via these percolated porous patches. When the sample was re-impregnated with epoxy and re-polished, it was observed that the dense paste had disappeared and the interconnection of porous patches in the previous image is no longer visible. Nevertheless, there remain some areas that have a higher local concentration of large unreacted cement grains (circled in Fig. 7.9 B), but these micro inhomogeneities are not the broad dense patches in the context of 'patch microstructure' because: 1) no sharp boundaries exist, and 2) the size is much smaller.

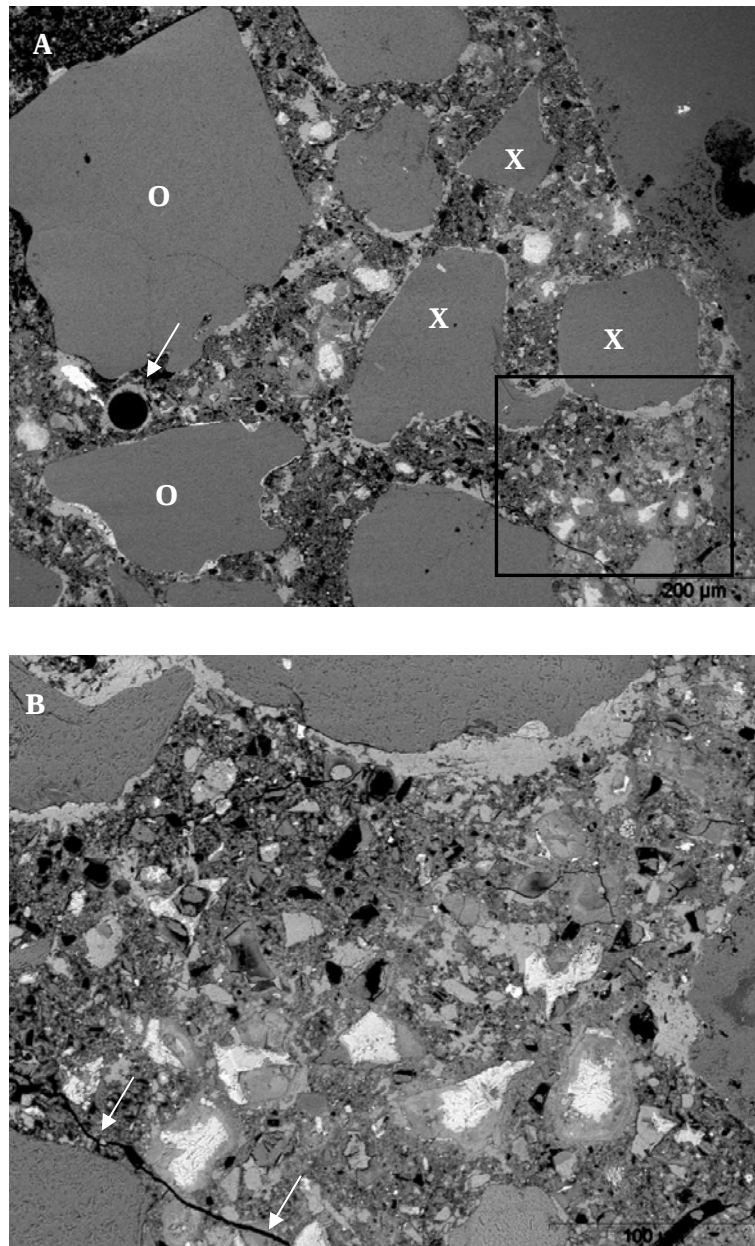


Figure 7.8 Area matching BSE images of those shown in Fig. 7.3, after re-impregnation and re-polishing. The originally dense patches are now filled with capillary pores and hollow-shell pores that were previously unseen. By monitoring the change in diameter of the spherical air void (indicated with an arrow in (A)), the amount of material that has been removed from the re-grinding and re-polishing is estimated to be around 50μm. The microcrack (indicated with arrows in (B)) is also visible in Fig. 7.3 (B).

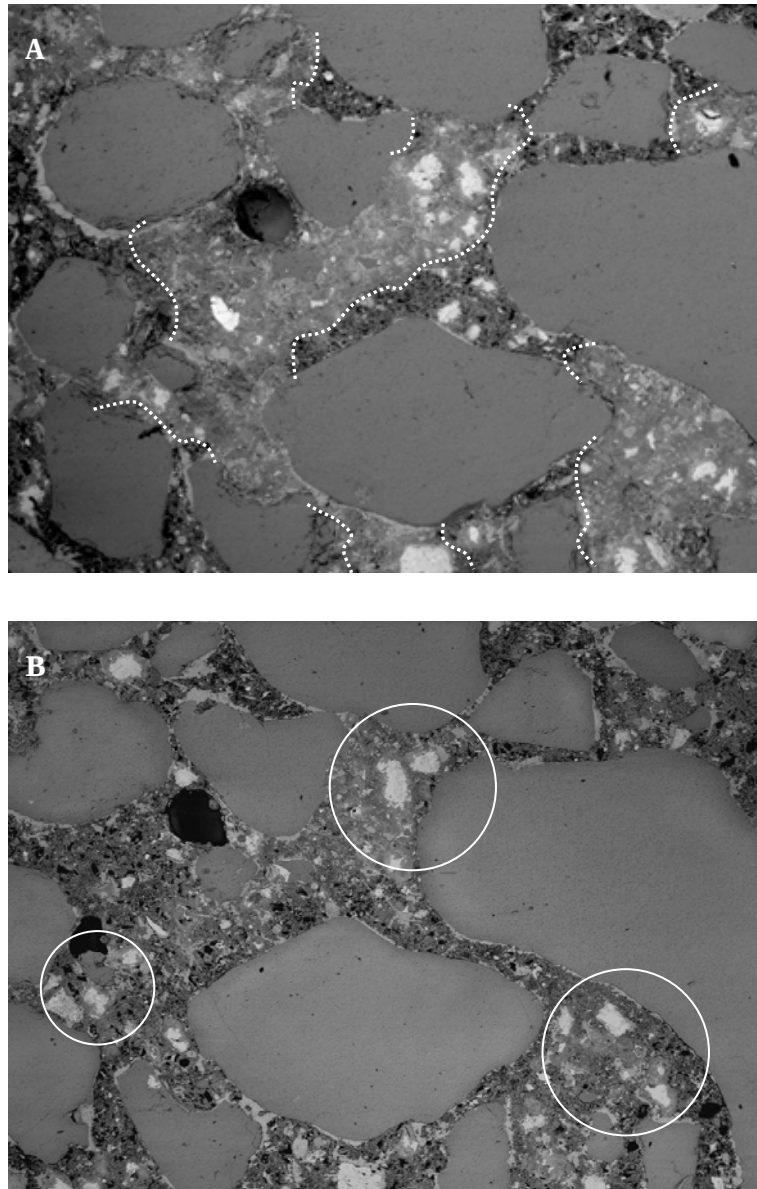


Figure 7.9 Area matching images of before (A) and after (B) epoxy re-impregnation. In (A), the porous patches appear to form a continuous path, suggesting that molecular/ionic transport may occur via these interconnected porous patches. In (B), the dense patches have ‘disappeared’ upon epoxy impregnation. Some areas (circled) contain a higher local concentration of large, unreacted cement grains, but these are not ‘patch microstructure’ (w/c ratio 0.6, field of view: 1333 x 1000 μ m).

Fig. 7.10 (A) shows a large sand particle in the top right corner that is in contact with both dense and porous patches, giving a false impression concerning the nature of the interfacial transition zone. In the same image, an empty air void (arrowed) is located in the dense patch. The edge of the void appears darker than the centre because near the edge, some of the emitted backscattered electrons from the bottom will hit the sidewalls and re-penetrate the sample. These re-entry electrons are of much lower energy than incident electrons and are unlikely to escape again as backscattered electrons. However, this pore edge darkening effect will be less obvious in smaller voids such as capillary pores and hollow-shells. Therefore, 'empty' capillary pores and hollow-shells (not filled with epoxy) will have a similar intensity to the surrounding solid phase, and appear like a dense mass of hydration products and unreacted cement grains. In Fig 7.10 (B), when the sample is properly saturated with resin, the paste appears to be more homogeneous and the same air void shown in Fig. 7.10 (A) is now completely black.

Fig. 7.11 (A) shows a sand particle at the top right corner that is apparently surrounded by a very porous ITZ. Quantitative image analysis, i.e. strip analysis, performed on this particle would most certainly lead to a false conclusion. In Fig. 7.11 (B), after the sample is re-impregnated, the paste is more homogeneous with no clear indication of a porous ITZ. Fig. 7.12 and Fig. 7.13 show higher magnification images of areas that originally had a sharp and almost linear boundary between the porous and the dense patches. After epoxy re-impregnation, the sharp boundary disappears and more pore features are visible in the 'dense patch'. In Fig. 7.13 (B), the paste region between the two closely spaced sand particles appears to be more porous than the paste region farther away from the aggregate surface, perhaps suggesting the ITZ phenomenon.

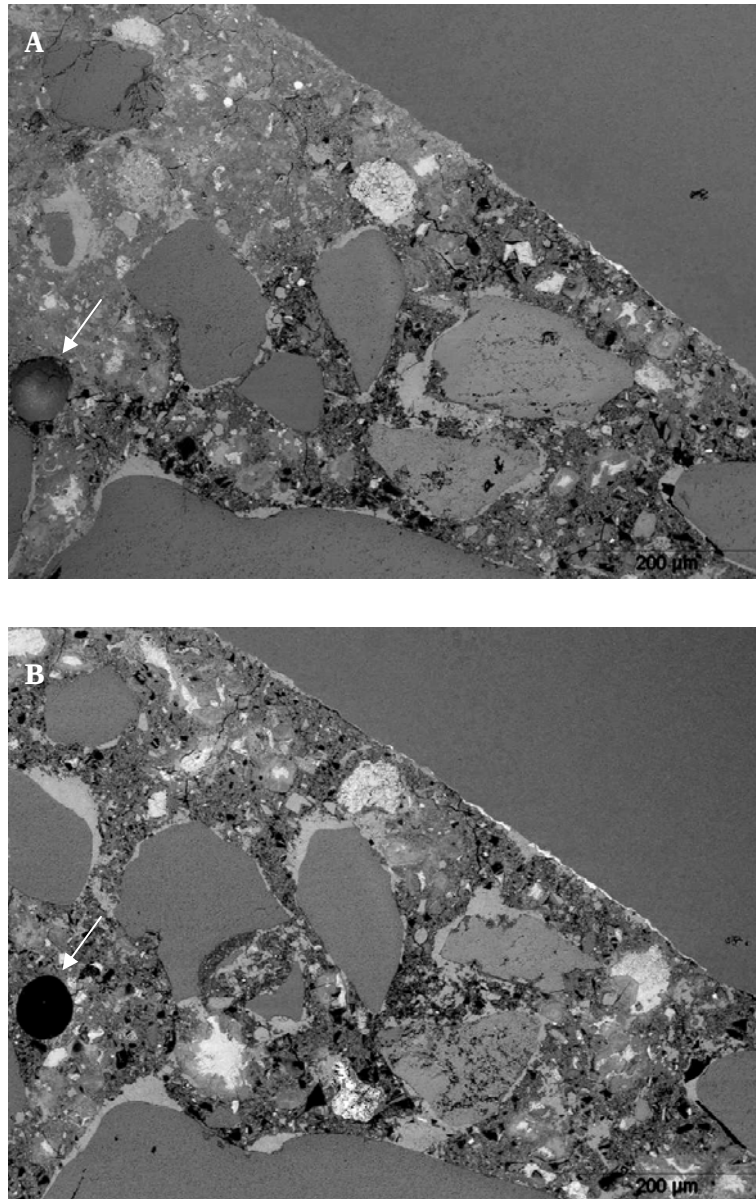


Figure 7.10 Area matching images of before (A) and after (B) epoxy re-impregnation. In (A), the large sand particle at the top right corner was originally in contact with both dense and porous patches. An empty air void can also be seen (arrowed) in the dense patch (w/c ratio 0.4, field of view: 889 x 667μm).

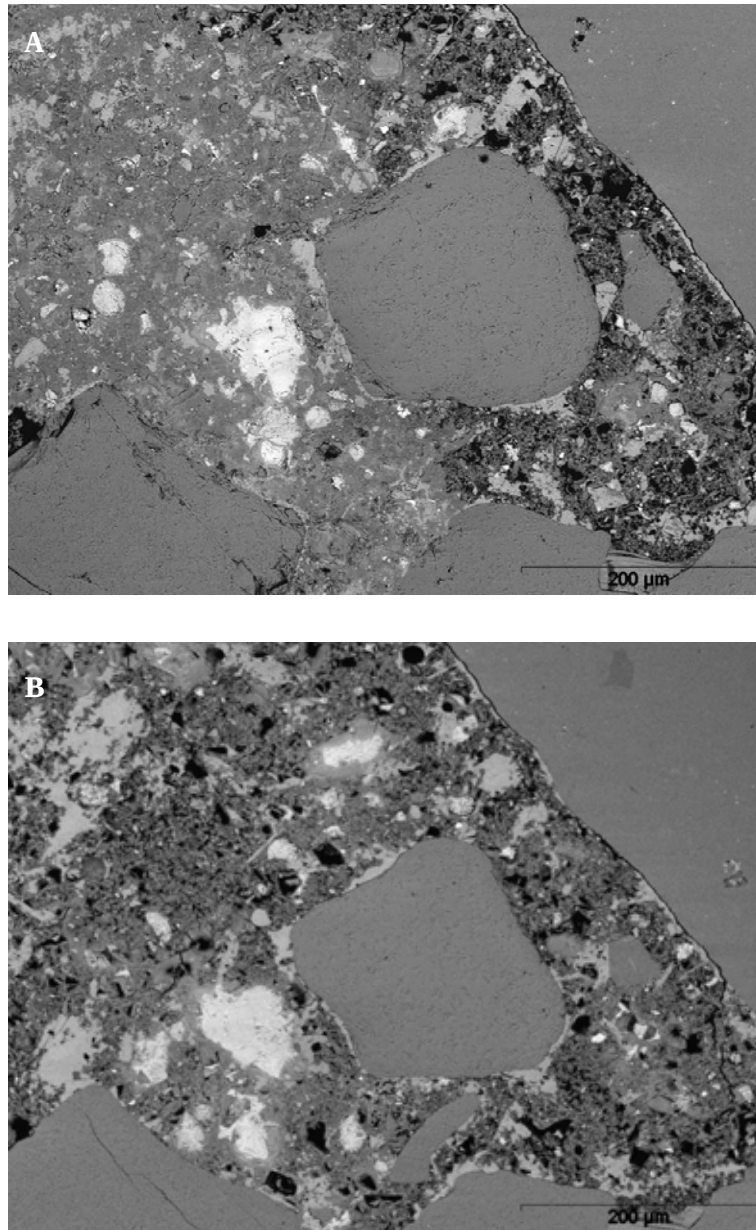


Figure 7.11 Area matching images of before (A) and after (B) epoxy re-impregnation. Image (a) gives a false impression that the sand particle at the top right corner is surrounded by an ITZ that is much more porous than the adjacent bulk paste (w/c ratio 0.6, field of view: 667 x 500μm).

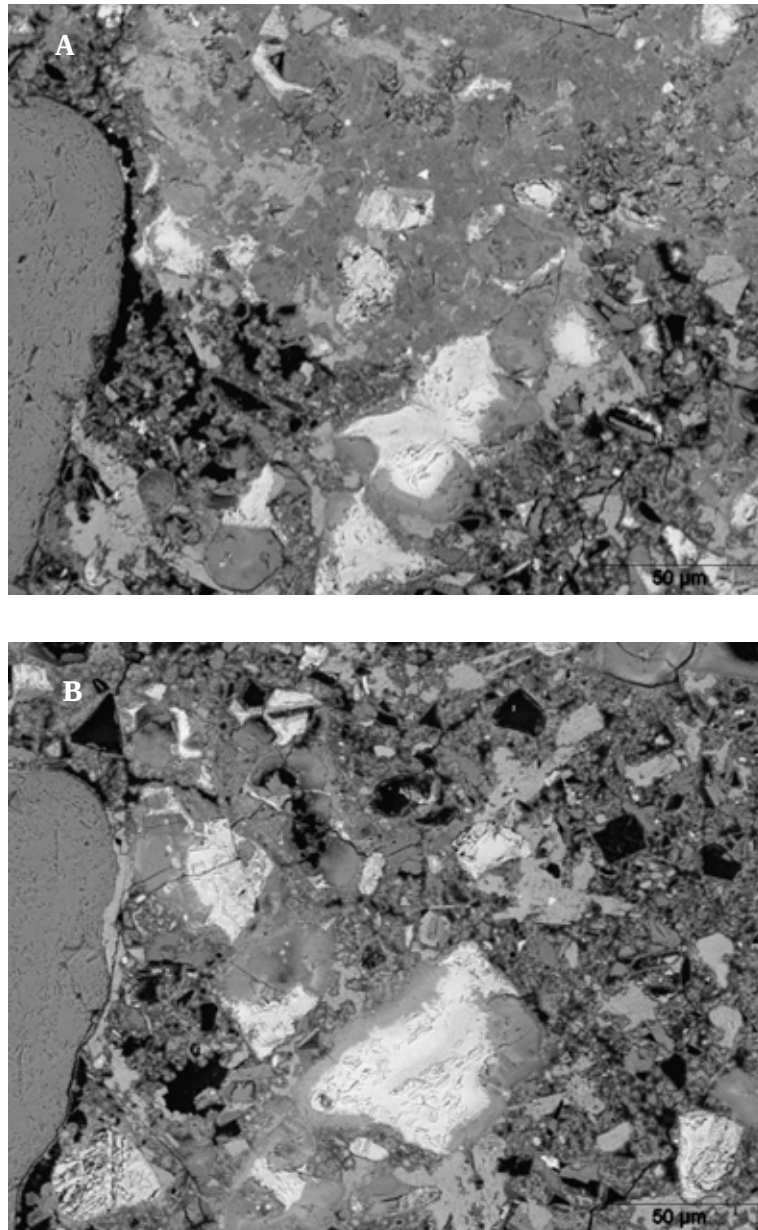


Figure 7.12 Higher magnification image of a sharp boundary between a dense and a porous patch (A) which disappears after re-impregnation (B) (w/c ratio 0.6, field of view: 267 x 200µm).

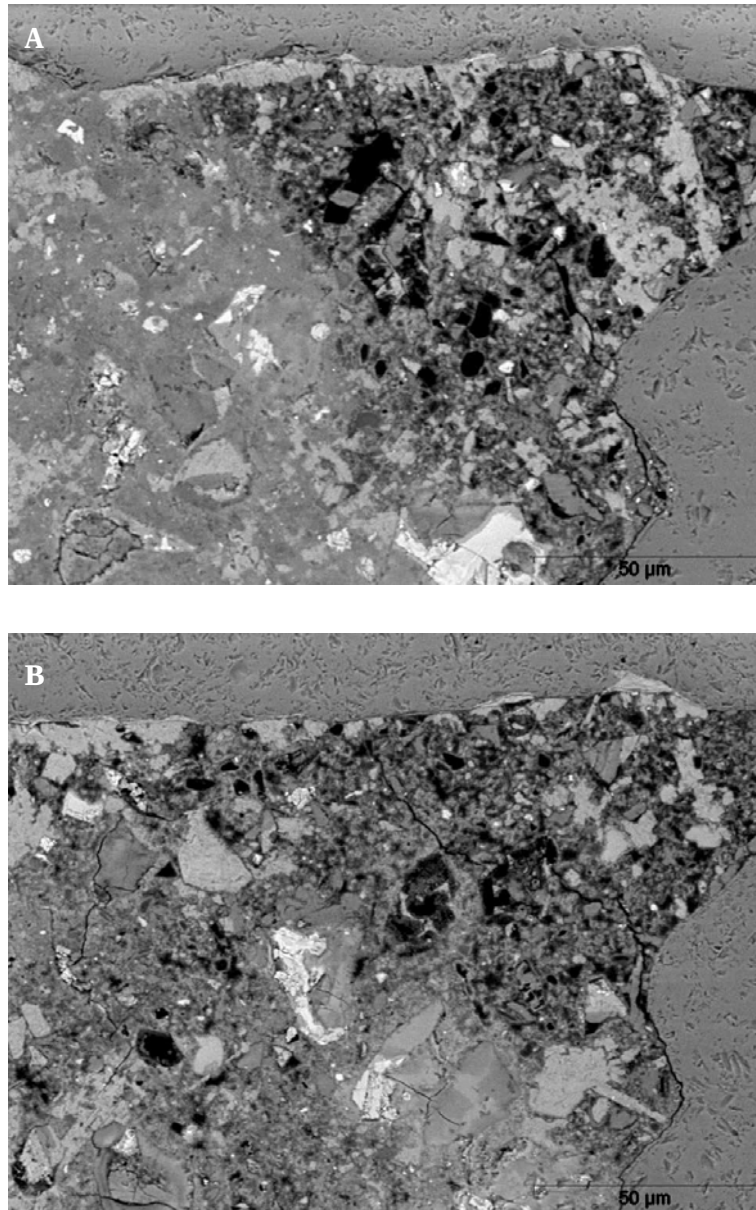


Figure 7.13 Higher magnification image of a sharp boundary between a dense and a porous patch (A) which disappears after re-impregnation (B). The paste region between the two closely spaced sand particles appears more porous than the bulk paste, suggesting the ITZ effect (w/c ratio 0.4, field of view: 178 x 133μm).

7.5 Discussion

It might be argued that the unique specimen preparation procedure applied in this study has somehow altered the nature of the pore structure. The small amount of toluene, which was added to the epoxy to lower its viscosity, is not known to have any dissolving action on cement hydration products. Samples were not ground prior to the second epoxy impregnation. Thus if the dense patches are real features, the epoxy should not be able to penetrate into the sample during the second impregnation. The higher pressure may force the epoxy into the dense patches, but if this were the case, then the originally dense patches should re-appear as pastes with much finer capillary pores compared to the originally porous patches.

Re-grinding and re-polishing the sample inevitably removes some material and therefore the second image is not of exactly the same area as the first. However, the layers that were removed were only very thin, because the samples were already plane. Many features such as sand particles, cracks and large cement grains that were in the first image could still be seen in the second image. It might also be argued that re-grinding discarded the dense patches, exposing an underlying porous patch in the second image. If this were true, then the reverse would also be expected, i.e. a porous patch being replaced by a dense patch, yet such occurrences were not observed in any of the samples that were examined.

The capillary pores and hollow-shells observed appear to be typical of those normally seen in a BSE image and do not appear to be artefacts. In fact, the re-polished samples were found to have significantly fewer microcracks and less preparation damage compared to the initial sample with dense/porous patches. All the locations that were initially marked showing patchy microstructure have produced a similar change upon re-impregnation. A random search on the re-impregnated samples failed to locate any more of the dense patches. Therefore, we are convinced that the second set of images shown here is representative of the true microstructure and is not the result of a series of coincidences.

As stated earlier, it is essential that the sample be thoroughly dried prior to epoxy impregnation because any remaining moisture will interfere with the intrusion and polymerisation of the epoxy. However, removing the pore-solution from cement-based materials may cause shrinkage related damage or an irreversible alteration to the microstructure and so researchers have treated this with care. Over the years, a range of techniques to dry samples prior to epoxy impregnation for BSE imaging have been used and proposed. Examples in-

clude freeze drying, that is immersion in liquid nitrogen followed by vacuum drying [Scrivener & Gardner, 1988; Scrivener et al, 1988; Kjellsen et al., 2003], freeze-drying followed by oven drying at 105°C [Kjellsen, 1996; Kjellsen et al. 1998], solvent exchange using methanol followed by vacuum drying over silica gel [Scrivener et al, 1987], ethanol exchange followed by replacement with an ethanol miscible epoxy [Struble & Stutzman, 1989], acetone exchange followed by vacuum drying and oven drying [Wang & Diamond, 1995; Diamond et al., 1998], or straightforward oven drying at 105°C [Zhao & Darwin, 1992; Darwin et al., 1995], at 80°C [Chen et al., 2002], at 65°C [Stutzman & Clifton, 1999], at 50°C [Elsharief et al., 2003] or at 30-35°C [Jakobsen et al, 1998].

Clearly, the final moisture state of the sample will depend on the type of drying technique used, the duration of treatment, as well as the initial moisture state of the sample. On one hand, severe drying at high temperatures, for example at 105°C, will guarantee complete removal of all evaporable water, but is damaging. On the other hand, milder drying methods will be less damaging, but will cause difficulties to epoxy impregnation and as a result, higher risks of sample preparation artefacts. In addition, since moisture trapped in smaller pores is harder to extract, the degree of drying will have an influence on the smallest possible pore intruded with epoxy and this is an important aspect that must be considered for quantitative image analysis of pore structure. At present, there appears not to be a consensus on the most appropriate drying technique for quantitative BSE imaging, presumably because, the chosen technique depends on available instrumentation, time and effort involved, the objective of the study and whether or not drying shrinkage cracking is an issue. To the best of our knowledge, there is yet to be a systematic study on the effect of drying and epoxy impregnation method on the depth of intrusion, and more importantly, on the smallest possible intruded pore. Such studies in the future will surely be of value.

The lack of epoxy in the polished sample will reduce the resolution of the obtained BSE image. It will not only affect the ability to differentiate between pore-solid phases, but also between solid-solid phases, for example, between the inner and outer C-S-H hydration products. In fact, Diamond [2003] made this observation in his original paper when comparing the differences in morphology of cement paste observed in the dense and porous patch region at high magnification. Diamond [2003] noted that in the porous patches, most unhydrated cement grains are 'encased in a layer of easily visible inner C-S-H hydration product' (Fig. 7.1 f) and that these inner hydration products are 'easily separable from surrounding porous outer product C-S-H'. The distinction between inner and outer product is easily made in the porous patch, but not in the dense patch (Fig 7.1 e).

If the patchy appearance reported in previous publications and reproduced in this paper is indeed an artefact of specimen preparation, it then raises the question of the validity of quantitative image analysis results that have been published on the ITZ phenomena by the same author [Diamond & Huang, 1998, 2001]. These investigations found that the detectable porosity of cement paste in the ITZ differs on average, only slightly from the cement paste in the bulk regions and that the spatial distribution of detectable pores was highly irregular. It was observed that porous patches and relatively dense patches intermingled irregularly in both bulk and ITZ regions, which led the authors [Diamond & Huang, 1998, 2001] to doubt the conventional picture of the ITZ. Unfortunately, not much information was provided on the sample preparation procedure, except that in Diamond [2003], it was mentioned that the sample preparation was carried out at the laboratories of R.J. Lee Group, which involved 'gentle drying', impregnation of very low viscosity epoxy resin under vacuum, followed by the 'usual' grinding, polishing and carbon coating procedures. This information alone, however, is insufficient to gauge if the samples have been ground beyond the epoxy penetration depth.

This study has also raised other issues. Since capillary pores are only visible when they are resin-filled, it makes one wonder whether the appearance of dense paste in mature or high-performance concretes is really due to lack of capillary pores, or due to the fact that the pores are too fine to be impregnated by the epoxy resin. Related to this is the issue of whether the smallest detectable pore in a BSE image is controlled by the resolving power of the imaging system, or, limited by the ability of the epoxy resin to penetrate fine capillary pores. These questions are important because they affect the interpretation of BSE images of cement-based materials.

7.6 Conclusions

Scanning electron microscopy in the backscattered electron mode, within its limits, can be an invaluable tool for cement and concrete research. The key lies in having the right sample preparation technique and a good understanding of the principles of electron microscopy, signal generation and image formation, to avoid misunderstanding and misinterpretation of the BSE images.

For examination of cement-based materials by BSE imaging, it is critical to ensure that the observation plane is saturated with an epoxy resin. The resin stabilises the microstructure and minimises damage during grinding and polishing, and provides contrast be-

tween the pore and solid phase. However, conventional epoxy impregnation under vacuum can only achieve a very shallow penetration depth. Thus, extreme care must be followed so that the sample is not ground beyond the epoxy penetration depth.

In this chapter, a modified epoxy impregnation method is proposed. This method can achieve a deeper epoxy penetration, in the order of several millimetres, compared to hundreds of microns in the conventional technique. The deeper epoxy penetration gives more allowance for grinding and polishing, assuring that the finished surface remains saturated with epoxy.

BSE imaging on mortars that were prepared using conventional vacuum impregnation showed that hydrated cement paste consists of large patches of dense almost non-porous and porous regions that occur irregularly in the ITZ and bulk regions. The boundary between patches is very distinct and sharp. When the same samples were re-impregnated using the proposed method and re-polished, it was observed that all the dense patches disappeared, replaced by a paste that showed many capillary pores and hollow-shells previously not seen. It is concluded that the patchy microstructure is an artefact of sample preparation; the dense patch is a false impression caused by pastes that have been ground beyond the epoxy intrusion depth.

This study has shown that an incorrect sample preparation technique can give a very misleading picture of cement paste microstructure and can have a major influence on qualitative assessment or quantitative measurements via image analysis of BSE images. Unfortunately, the true extent of this problem is yet to be known. Concrete and cement-based materials are naturally heterogeneous materials, with the heterogeneity occurring across different scales, but previously reported occurrence of broad patches of dense and porous regions is almost certainly an artefact of sample preparation and is not a true feature. Thus, the conclusion that the overlapping of these porous patches could lead to percolative effects should be viewed with caution. However, it is emphasised that the results presented in this chapter do not, in anyway, validate or provide additional support for the conventional ITZ model or the NIST hard core/soft shell model.

Chapter 8

ITZ: Characterising its microstructural gradients using Euclidean Distance Mapping and its role in molecular transport

This chapter presents a new image analysis procedure using Euclidean Distance Mapping to compute microstructural gradients at interfaces in composite materials. This method is capable of producing phase distribution plots at single pixel strip width very quickly and efficiently. Compared to conventional dilation-subtraction strip analysis, the new method is faster and is not constrained by feature geometry and boundary conditions. This allows for a truly random and unbiased sampling. The new method was applied to investigate microstructural gradients at the interfacial transition zone (ITZ). The results show strong gradients in average anhydrous cement and detectable porosity at the ITZ, but this is highly variable from location to location. The ITZ characteristics depend on the amount of calcium hydroxide deposited on aggregate particles and the new method was able to detect the effect of these calcium hydroxide deposits on the porosity gradient, which has not been reported before. Molecular transport testing on mortars showed a consistent decrease in oxygen diffusivity, oxygen permeability and water absorption, as the aggregate content (ITZ fraction) increases, indicating that the effects of decreasing paste volume (and total porosity) and increase in transport path tortuosity outweigh any effects of increased transport in the porous ITZ. The observed spatial variability of the ITZ porosity gradient and its dependence on calcium hydroxide deposits, may resolve the inconsistencies between experimental observation and computational models, which invariably assume a uniform thick porous ITZ layer surrounding aggregate particles, regarding the role of ITZ in molecular/ionic transport.

8.1 Introduction

Interfaces influence the bulk properties and overall performance of composite materials. In hardened concrete, interfaces exist between cement paste and steel reinforcement, fibres and between the various phases within the cement paste itself. An important interface is the paste region adjacent to aggregate particles, known as the interfacial transition zone

(ITZ), which is often regarded as the ‘weakest link’ that controls mechanical strength and is suspected to be detrimental to most aspects of the durability of concrete.

Researchers have used image analysis on backscattered electron images to investigate and quantify microstructural gradients across the ITZ. This procedure, pioneered by Scrivener and co-workers [Scrivener & Gardner, 1988; Scrivener et al., 1988a & 1988b], measures the distribution of phases, typically pores, anhydrous cement and calcium hydroxide, from the aggregate boundary. This is done by computing the area fractions of each phase in a series of narrow and equidistant strips, starting from the interface and extending outward to the ‘bulk’ paste. The relative fraction of each phase is averaged over a large number of images taken from different aggregate particles and the results plotted against distance from the aggregate surface.

Fig. 8.1 shows the typical routine for quantitative phase analysis via a series of equidistant strips from the interface. The phase of interest, pores in this example, is segmented from the BSE image by greyscale thresholding (Fig. 8.1 b). A binary aggregate mask (Fig. 8.1 c) is also generated, usually by manually tracing the aggregate boundary. This is then dilated (Fig. 8.1 d) for a number of iterations depending on the pixel spacing and width of the strip to be created. The original aggregate mask is subtracted from the dilated image to give the first strip (Fig. 8.1 e) and a logical operation AND between the strip and pore mask is performed to give the fraction of pores located in that strip (Fig. 8.1 f). To generate the subsequent strip and phase fraction, the aggregate mask is dilated again (Fig. 8.1 g) and the whole process is repeated.

The dilation-subtraction strip method requires significant processing time and computer memory due to the iterative nature and large number of images involved. For each strip, three images have to be created: the dilated boundary mask, the strip and the phase fraction contained within the strip. Additional steps are the area measurements of the strip and pores contained within it. A typical ITZ analysis of 50 frames at a 2.5 μm strip width up to a distance of 50 μm from the aggregate will require 20 strips per interface, hence involving 60 images per frame and 3000 images for the complete analysis. If a different strip width is needed, then the whole process would have to be repeated. Investigation using a greater number of frames in smaller bands enables a detailed analysis, but narrower strips would be impractical for the dilation-subtraction method. Another disadvantage of the strip method is that special care has to be taken so that the strips are not generated beyond mid-distance to the next aggregate. To implement this into an automated image analysis algorithm is difficult because a randomly selected area in a typical concrete may contain aggregates separated at a

distance of several microns to hundreds of microns. The strips may be generated manually, but this is extremely laborious and impractical. Thus, the operator is resigned to only selectively analyse paste areas where the distances between aggregate particles are large, but these results are not representative because of biased sampling.

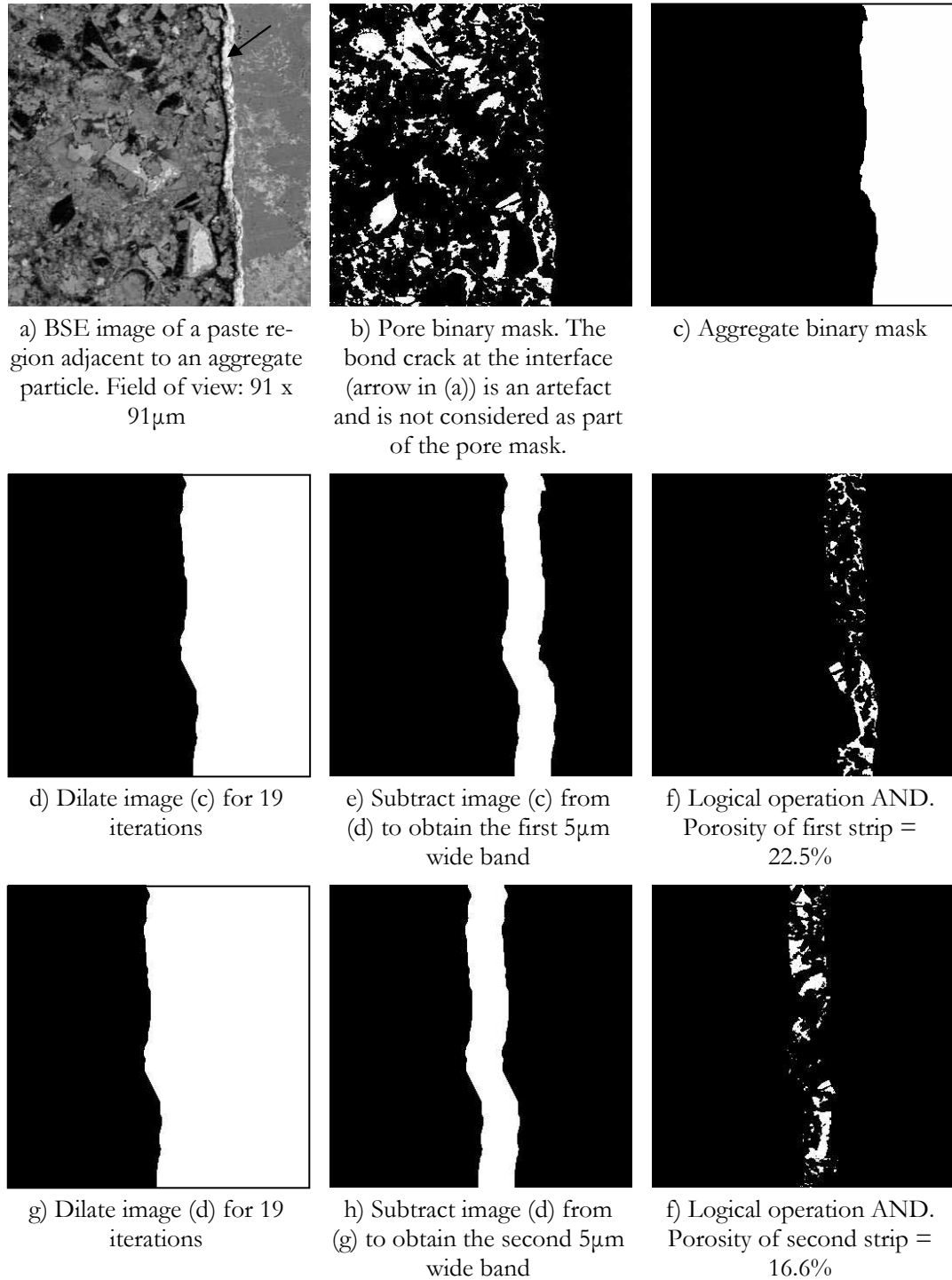


Figure 8.1 Conventional dilation-subtraction strip method for phase analysis.

In this chapter, an alternative approach to interfacial analysis using Euclidean Distance Mapping (EDM) is proposed. The new method is more efficient as it does not require a repetitive strip producing stage. The method only involves two additional images per location in order to obtain a gradient plot at a single pixel resolution, i.e. at one pixel wide strips. It is also more flexible than the conventional strip method because the information obtained from the EDM is sufficient to generate distribution plots at any strip width without requiring additional images. The new method is also applicable to any paste geometries and boundary conditions. This chapter presents applications of the new method to investigate microstructural gradients at the ITZ, emphasising that the same technique can be used for any type of interphase boundary.

8.2 Euclidean distance mapping for phase analysis

Euclidean distance mapping (EDM) is a basic operation used in computer vision, pattern recognition and robotics [Danielsson, 1980], where high speed computation is essential. It uses distance transformation to convert a binary image consisting of foreground and background pixels into a grey-scale image where each background pixel has a brightness value equal to its Euclidean (linear) distance to the nearest foreground pixel [Rosenfeld & Pfaltz, 1968; Russ, 2002]. This can be expressed mathematically as follows. Consider a digital image $\mathbf{M} = \{m_{ij}\}$ consisting of an array of $N \times M$ unit square pixels. The element in the i th row and j th column is denoted by (i, j) . A binary image of $\mathbf{M}$ is defined by $\mathbf{B} = \{b_{ij}\}$ where each pixel element $b_{ij} \in \{0, 1\}$, 0 represents black (or background) and 1 represents white (or feature). The Euclidean distance mapping $\mathbf{D} = \{d_{ij}\}$ of the binary image $\mathbf{B} = \{b_{ij}\}$ is defined by:

$$d_{i,j} = \min_{p \geq 1, q \leq N} \left\langle \sqrt{(i-p)^2 + (j-q)^2} \mid b_{pq} = 0 \right\rangle, \text{ for all } i, j \quad \text{Eq. 8.1}$$

Fig. 8.2 shows the effect of an EDM operation when applied to a binary image consisting of a white circle (foreground) in a black background. In the resultant image (Fig. 8.2 B), the white circle remains unaltered but the black background pixels are converted to pixels with incremental grey value from the boundary.

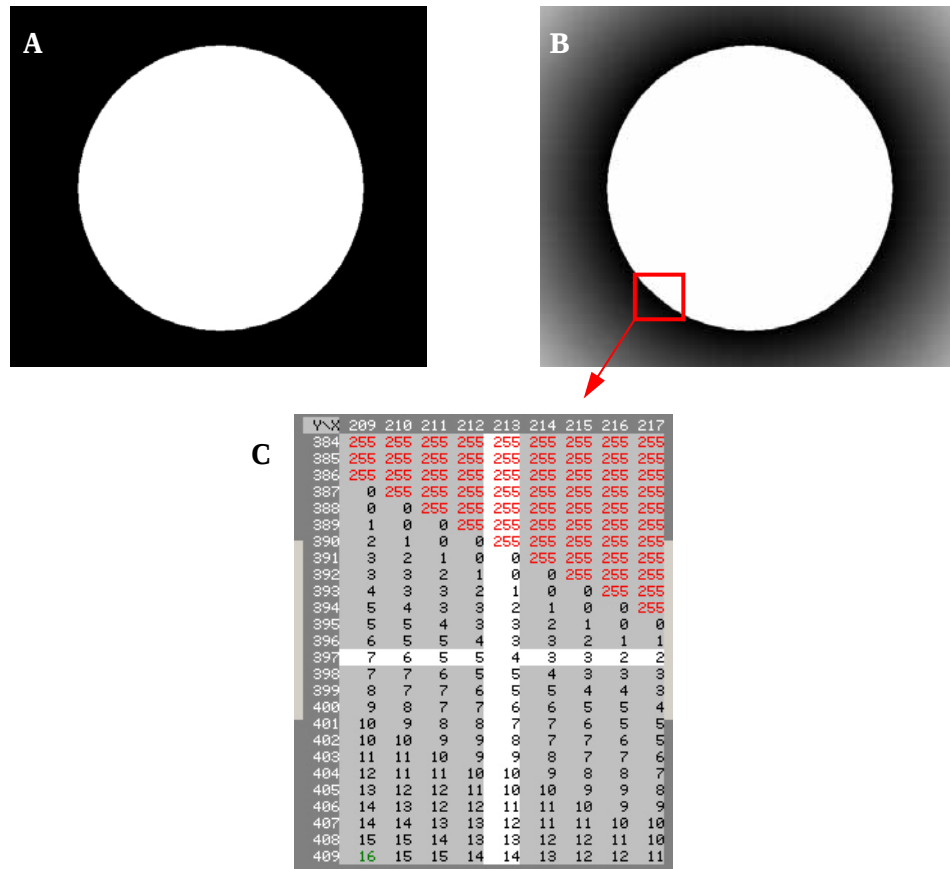


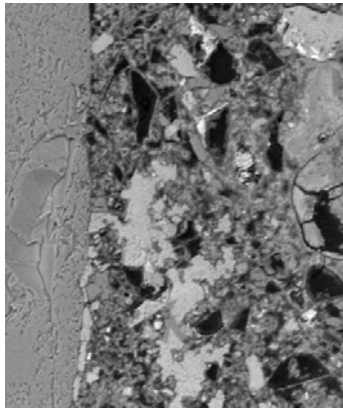
Figure 8.2 Euclidean distance mapping applied to an image of a white circle in black background. The binary image (A) is converted to a greyscale image (B) where each background pixel has a brightness value equal to its Euclidean distance to the nearest foreground pixel. Image (C) is a pixel map of the boxed area, showing incremental grey value (rounded off to the nearest integer) of the pixels from the feature boundary.

Since its introduction by Danielsson [1980], many algorithms have been proposed for generating an efficient, fast and error-free EDM. Examples of applications are segmenting touching and overlapping features (watershed segmentation), computing fractal dimension and skeletonisation [Russ, 2002]. The EDM function is now available in almost all commercial image processing software packages. The EDM is advantageous because it is more isotropic and avoids directional bias that is present in pixel-by pixel morphological operations such as erosion and dilation. The distance map can be constructed quickly and does not require iteration, so the run time does not increase with feature size [Russ, 2002].

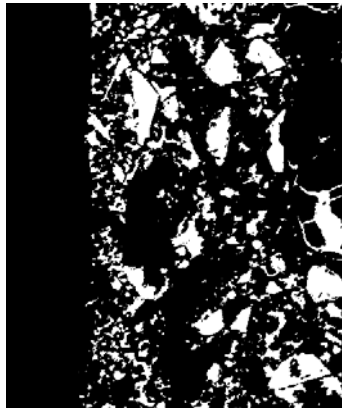
Fig. 8.3 shows how the EDM method is applied for phase analysis at interfaces using a BSE image of the paste region adjacent to an aggregate particle (Fig. 8.3 a) as an example. To determine the porosity gradient from the aggregate boundary, first, the binary mask of the pore (Fig. 8.3 b) and aggregate (Fig. 8.3 c) phase is created. Next, an EDM of the paste (Fig. 8.3 d) is generated from the aggregate binary mask. Then, a multiplicative operation is performed between the paste EDM and the pore mask, giving an EDM of the pore phase only (Fig. 8.3e). Observe that each pore pixel in the original pore binary image is now transformed to a grey value that has a numerical value equal to its linear distance to the nearest aggregate pixel, i.e. a particular pore pixel with grey value of x is located x pixels away from the nearest aggregate boundary.

Next, the brightness histogram of the paste and pore EDM are plotted in Fig. 8.4 (a) and Fig. 8.4 (b) respectively. Normalising the brightness histogram of the pore EDM to the paste EDM, and converting the grey values to actual distances by factoring with the pixel spacing, gives the porosity distribution from the interface at a single pixel step (Fig. 8.4 c). From this data, the porosity distribution can be re-plotted at any strip width, if desired. Fig. 8.4 (d) gives an example where the porosity gradient is re-plotted at $5\mu\text{m}$ intervals.

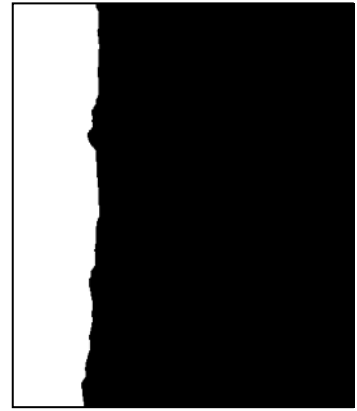
Another advantage of the new method is that it can be easily applied to any geometry and boundary conditions. A BSE image of an OPC concrete is shown in Fig. 8.5 (a). Note the random nature of the paste and the range of separation distances between aggregates. As mentioned earlier, unless the strips are generated manually, the conventional dilation-subtraction strip method can only be applied where the separation distance between adjacent boundaries are at least twice the distance to the farthest strip, typically around $50\mu\text{m}$. Therefore, for the example in Fig. 8.5 (a), only the lower half of the image is suitable for strip analysis. This can create biased sampling and non-representative results, no matter how many images are averaged. Figs. 8.5 (b-d) show that the new method is applicable to any paste geometry easily, thus all areas are included. Note that there is an uncertainty in the distance map for features near the image border because influences from aggregate particles outside the image have not been accounted for. Therefore, in Fig. 8.5 (b) and Fig. 8.5 (c), the distance maps are cropped by an amount equal to the distance of the farthest ‘strip’, in this case $50\mu\text{m}$.



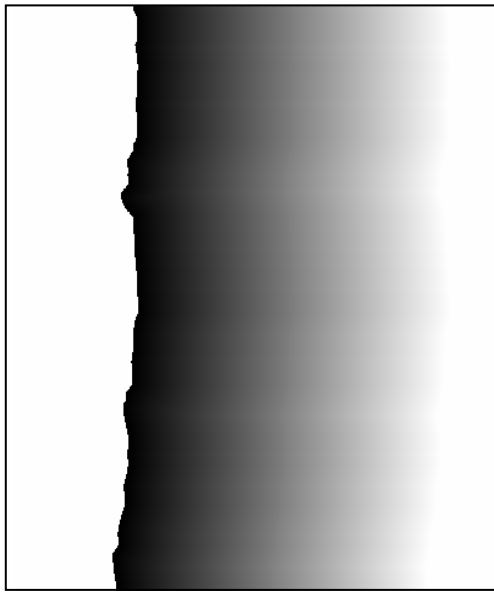
a) BSE image of a paste region adjacent to an aggregate particle. Field of view: 100 x 120 μ m



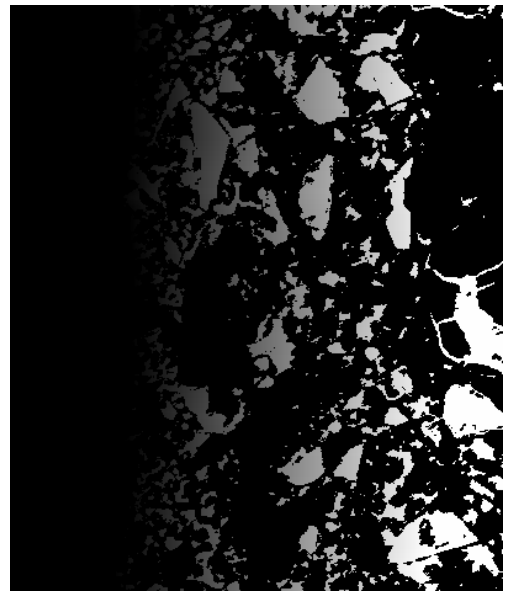
b) Pore binary mask.



c) Aggregate binary mask

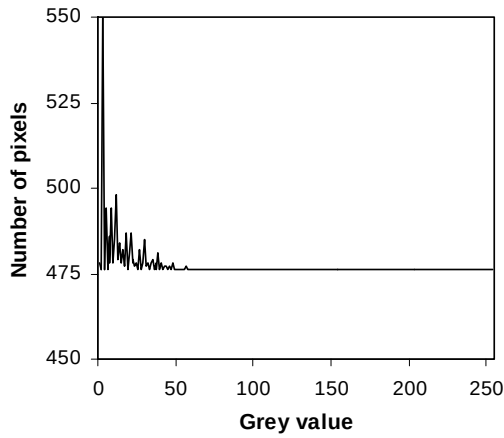


d) EDM of paste from the aggregate boundary. The grey value of each pixel in the paste increases with its nearest distance from the boundary.

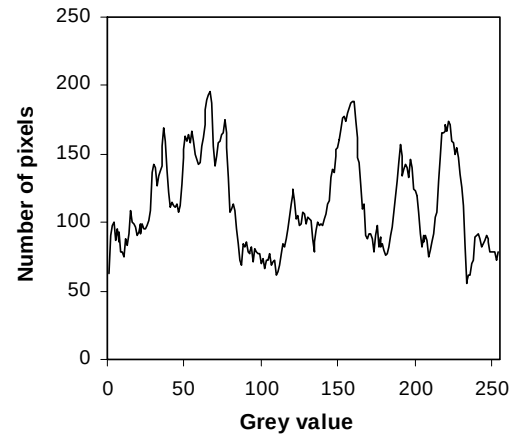


e) Distance map of the pore phase from the aggregate boundary. The brightness of each pore pixel represents its nearest distance to the aggregate.

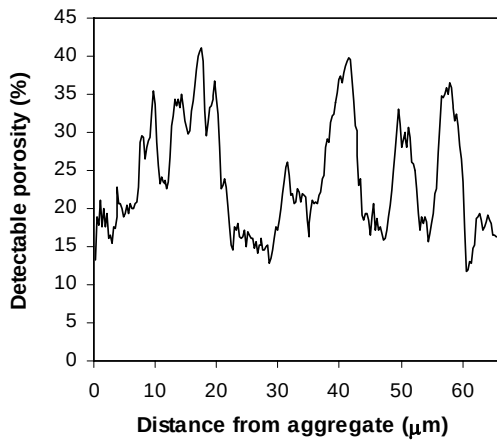
Figure 8.3 Generating a Euclidean Distance Map (EDM) of the pore phase from the aggregate boundary.



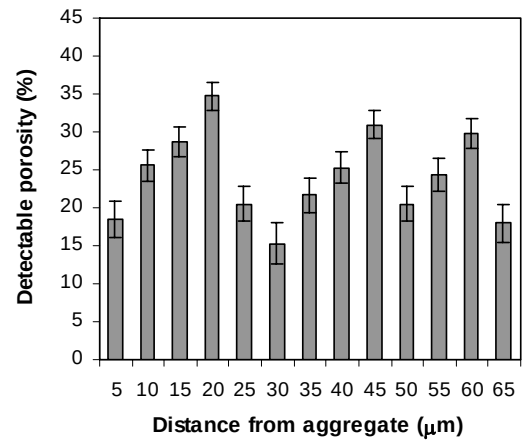
a) Brightness histogram of Fig. 8.3 (d). The grey value 255 (white) representing aggregate is not plotted.



b) Brightness histogram of Fig. 8.3 (e). The grey value 0 (black) representing the solid phase is not plotted.

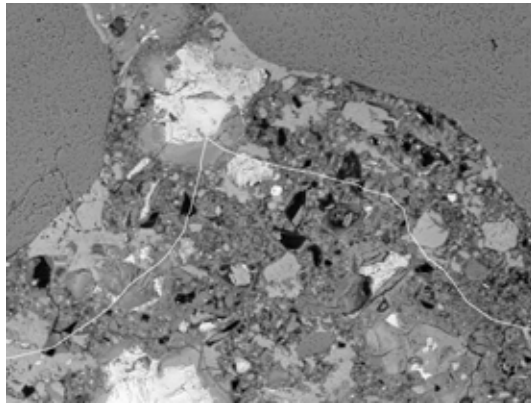


c) Porosity distribution from interface at 1pixel (0.26 μm) strip width.

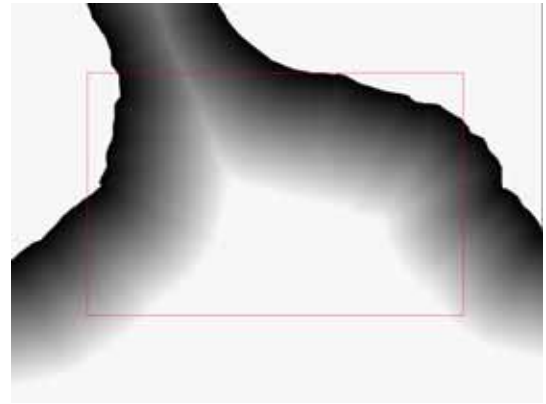


d) Porosity distribution from interface at 5 μm strip width resolution. The y-error bars represent relative standard error ($100 * 1/\sqrt{N}$), where N is the number of pore pixels counted.

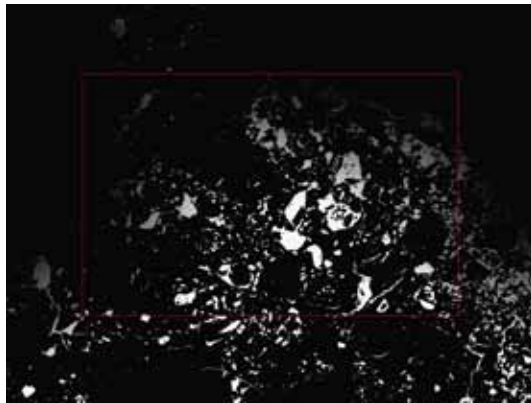
Figure 8.4 Use of EDM for quantitative phase analysis at the aggregate-paste interface



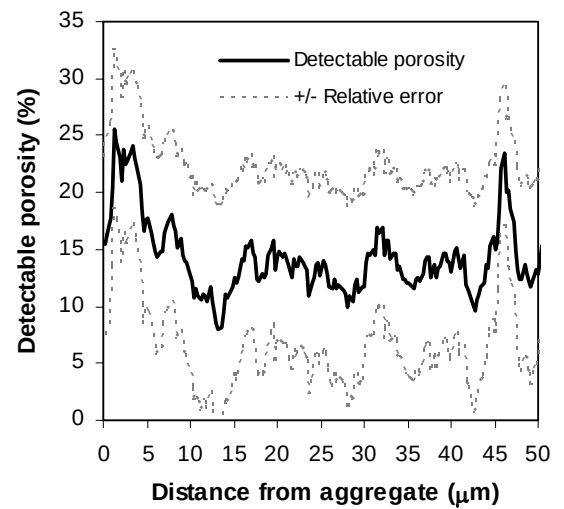
a) Concrete (w/c 0.5). The white border represents the 50µm strip. Field of view: 267 x 200µm



b) EDM of paste from aggregate boundary. The phase analysis is confined to features located 50µm from the edge of the image, i.e. contained in the box.



c) Distance map of pores.



d) Porosity distribution from interface at 1 pixel (0.26µm) strip width.

Figure 8.5 Applying the EDM method on a random section of an OPC concrete. The porosity distribution from the aggregate-paste interface is obtained by normalising the brightness histogram of the pore EDM to the brightness histogram of the paste EDM.

8.3 The Interfacial Transition Zone

In this section, the EDM method will be used to investigate spatial distribution of detectable porosity and anhydrous cement at the ITZ. For this purpose, an OPC concrete at w/c ratio 0.4 and an OPC mortar at w/c ratio 0.6 were prepared and cured for 3 days and 28 days respectively. Thames Valley sand and gravel were used as aggregates. Table 8.1 provides details of the mix composition. A cylindrical sample (100Φ x 250mm) was cast, demoulded after 24 hours and then immediately wrapped in cling film for curing. After curing, an 8mm thick disc was cut approximately 100mm from the bottom cast face, from which a block sample (40 x 20mm) was sectioned. The block sample was freeze-dried, vacuum-impregnated with a low viscosity epoxy, then ground and polished using successively finer grit size down to ¼µm (Section 3.2.1). To ensure a deep epoxy penetration, the vacuum impregnated sample was pressurised at 2.5bar above atmospheric pressure for 30 minutes (Section 7.2). A non-aqueous solution was used as lubricant for cutting and polishing. Acetone was used as cleaning fluid.

Mixture	Cement (kg/m ³)	Sand (kg/m ³)	Gravel (kg/m ³)	Aggregate vol. (%)	w/c ratio	Curing (days)
C 0.4	346	723	1085	75	0.4	3
M 0.6	434	1560	-	60	0.6	28

Table 8.1 Mixture composition for ITZ study

A JEOL 5410LV scanning electron microscope, operated at low vacuum (~9Pa), 10keV accelerating voltage and 10mm free working distance was used for imaging. Thirty images (1024 x 768 pixels, pixel spacing 0.26µm) were captured at 500x magnification. In order to minimise risk of local variation, the sampling procedure should obtain many images taken at different locations, dispersed over a large area and different aggregate particles. Thus, a uniform random sampling procedure was adopted (Section 3.2.6). The microscope stage was programmed to move in a grid, stopping at thirty predefined, equally spaced coordinates spanning the entire sample. If a frame fell entirely on an aggregate particle or entirely on paste, it was replaced by another location within the neighbouring grids, chosen from a random number table.

Each image was captured with constant brightness and contrast settings for reproducibility. The brightness and contrast were calibrated with an aluminium-epoxy microanalytical standard so that the image greyscale histogram was stretched to cover the entire greyscale, but not over-saturated at the low and high ends of the spectrum (Section 3.2.4). The pore phase was segmented using the Overflow method (Chapter 4); the inflection point of the cumulative brightness histogram was taken as the upper threshold grey value for pores. The anhydrous cement phase was segmented by using the minimum point between the peaks for hydrated paste and anhydrous phase as the lower threshold value (Fig. 4.1 b & d). Bond cracks appearing at the interface and air voids were excluded from the analysis. We decided not to analyse the calcium hydroxide (CH) phase due to problems in segmentation. The grey values for CH and other hydrated phases tend to overlap significantly and it is very difficult to confidently isolate these based on grey value alone. As noted by Scrivener et al. [1988], the distance measured on a random plane section will overestimate the true normal distance from the aggregate surface. In this work, no attempt was made to correct for this effect and all distances are reported as measured.

Fig. 8.6 shows the distribution of anhydrous cement particles and detectable porosity from the aggregate-paste interface at one pixel strip width for C 0.4. Results are expressed as area percentage of the cement paste. Fig. 8.6 (A) clearly shows a deficit in cement grains near the boundary compared to bulk paste. The very pronounced anhydrous cement gradient is due to disrupted packing of cement grains against much larger aggregate particles, i.e. the ‘wall-effect’, which is generally regarded as the basis of the ITZ phenomena. The anhydrous cement fraction increased steadily from 1% at the boundary to around 14% at 50 μ m away.

However, the distribution of detectable porosity from the interface, shown in Fig. 8.6 (B), gave interesting results. At less than 5 μ m away from the interface, there appears to be a sudden drop in detectable porosity, giving the impression that the aggregates are surrounded by a thin layer of paste that is almost as dense as the bulk paste. We note that this feature has not been reported before, possibly because previous studies were at lower resolution. Nevertheless, the general trend is conventional; porosity decreases with increasing distance from the interface and the value at the boundary is approximately twice that of the bulk region. From Fig. 8.6 (B), it appears that the ITZ extends to around 50 μ m away from the aggregate surface, with respect to both anhydrous cement and detectable porosity gradients.

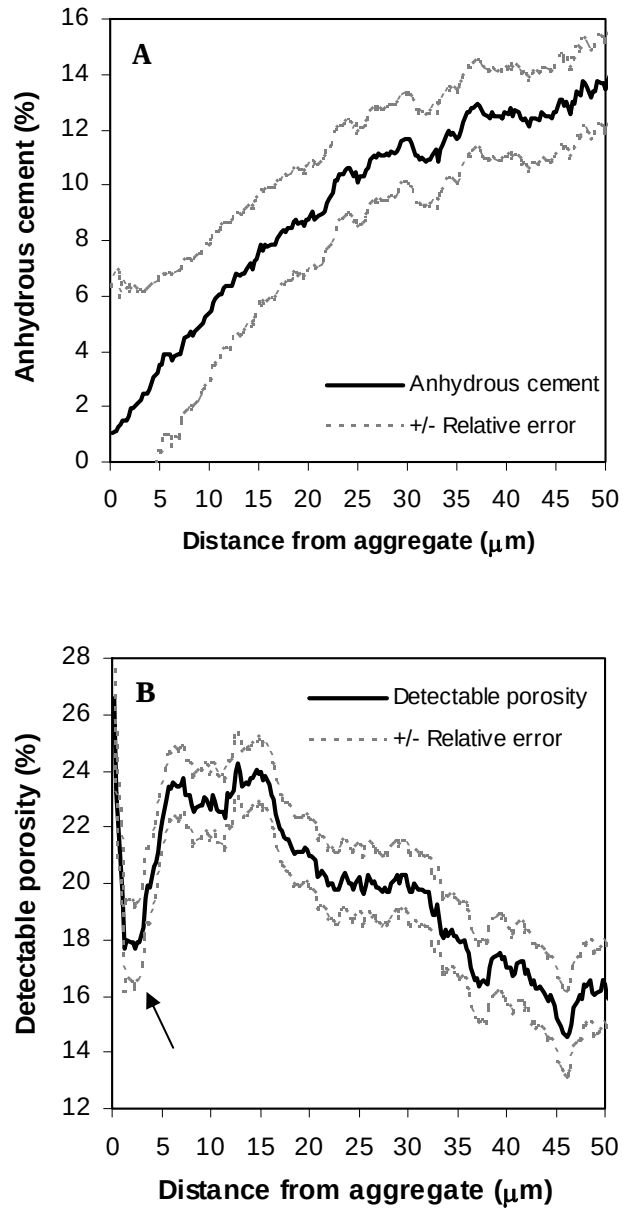


Figure 8.6 Detectable anhydrous cement (A) and porosity distribution (B) plots at single pixel strip width, measured from the aggregate-paste interface for sample C 0.4. Arrow in Fig (B) shows the effect of CH deposits on aggregate surfaces, on the porosity gradient. Values are the average of 30 frames.

After a thorough check on all the images and individual porosity gradients, we observed three types of ITZ characteristics; these are shown in Fig. 8.7. The first appears to be a very porous ITZ, with a strong porosity gradient and the detectable porosity at the interface is almost three times that of the bulk paste. This may be similar to the ITZs originally reported by Scrivener et al. [1988]. The second is much denser with large amounts of CH deposited on the aggregate surface. The detectable porosity gradient is weak and there is a sudden drop in porosity at less than $5\mu\text{m}$ from the aggregate surface due to the presence of CH. This may be similar to that reported by Diamond & Huang [1998, 2001]. The third type contains a mixture of ‘porous’ and ‘dense’ ITZs; the porosity gradient is evident, but is not as strong as the first example. Obviously, the ‘average’ porosity gradient of the ITZ will depend on the relative proportion of the ‘porous’ and ‘dense’ ITZs contained in the sample set. However, the presence, size and shape of CH deposits are very irregular; we observed that some aggregate particles are almost completely lined with CH in the 2D observation plane, while others are entirely free of it. Therefore, the sampling method will also have an influence on the measured ‘average’ porosity gradient. For example, results obtained from studies that adopt a uniform random sampling method, e.g. Scrivener et al [1988] will be different from those that select an aggregate particle and then capture a succession of adjacent images around the chosen grain, e.g. Diamond & Huang [1998, 2001]. This could be the reason why in the study by Diamond & Huang [2001], high porosity was not observed within the first $5\mu\text{m}$ of the aggregate surface.

Fig. 8.8 shows the distribution of anhydrous cement and detectable porosity from the aggregate-cement paste interface for M 0.6. For this sample, the deficit of cement grains near the aggregate-cement paste interface is also evident, but with a less pronounced gradient compared to C 0.4. This is likely due to two reasons: a) M 0.6 has lower original cement content per unit volume paste, approximately 35% vol. compared to 45% vol. for C 0.4; and b) M 0.6 was cured for a longer period, hence a larger fraction of the original cement would have been reacted prior to image analysis. The anhydrous cement distribution plot displayed another interesting characteristic: there appear to be four distinctive ‘zones’ in the curve, and these are marked I, II, III and IV in Fig. 8.8 (A) corresponding to sections of the curve at distances of $0\text{--}10\mu\text{m}$, $10\text{--}25\mu\text{m}$, $25\text{--}35\mu\text{m}$ and $35\text{--}50\mu\text{m}$ from the aggregate surface respectively. The unreacted cement fraction increased steadily from 1-2% for the first $10\mu\text{m}$ (Zone I), then remained relatively constant for the next $15\mu\text{m}$ (Zone II). From $25\text{--}35\mu\text{m}$ (Zone III), a rapid increase in unreacted cement fraction is observed, followed by a gradual increase to about 7.5% at $50\mu\text{m}$ (Zone IV).

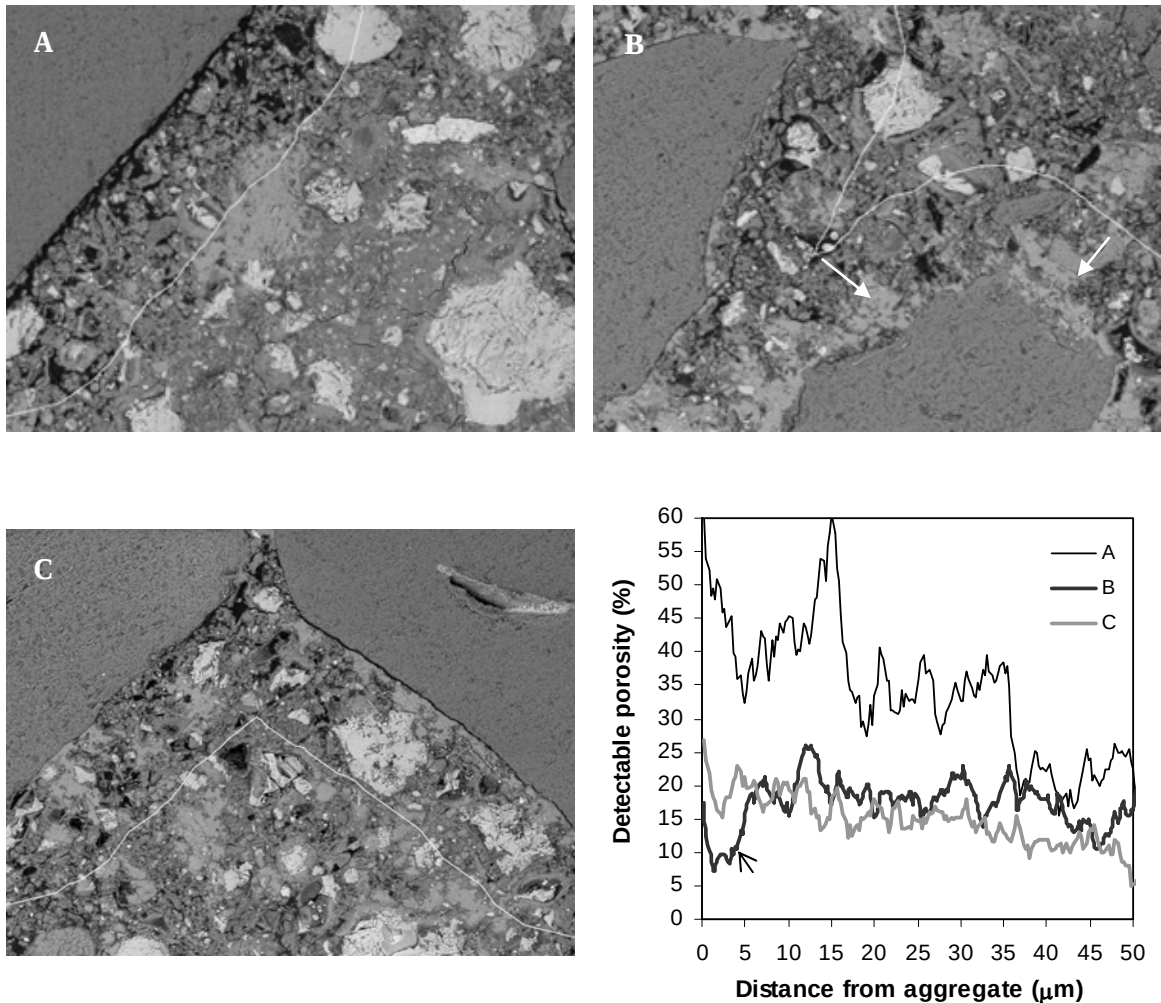


Figure 8.7 Detectable porosity distribution plots showing different ITZ characteristics observed in C 0.4: A) very porous ITZ; B) relatively dense ITZ with large amount of CH deposits on the aggregate surface (arrowed); and C) mixture of porous and dense ITZs. The averaged result will depend on the relative proportion of the porous and dense ITZ. Note that the bond cracks visible in A and C are not tallied. White border represents the 50 μ m strip (field of view: 267 x 200 μ m).

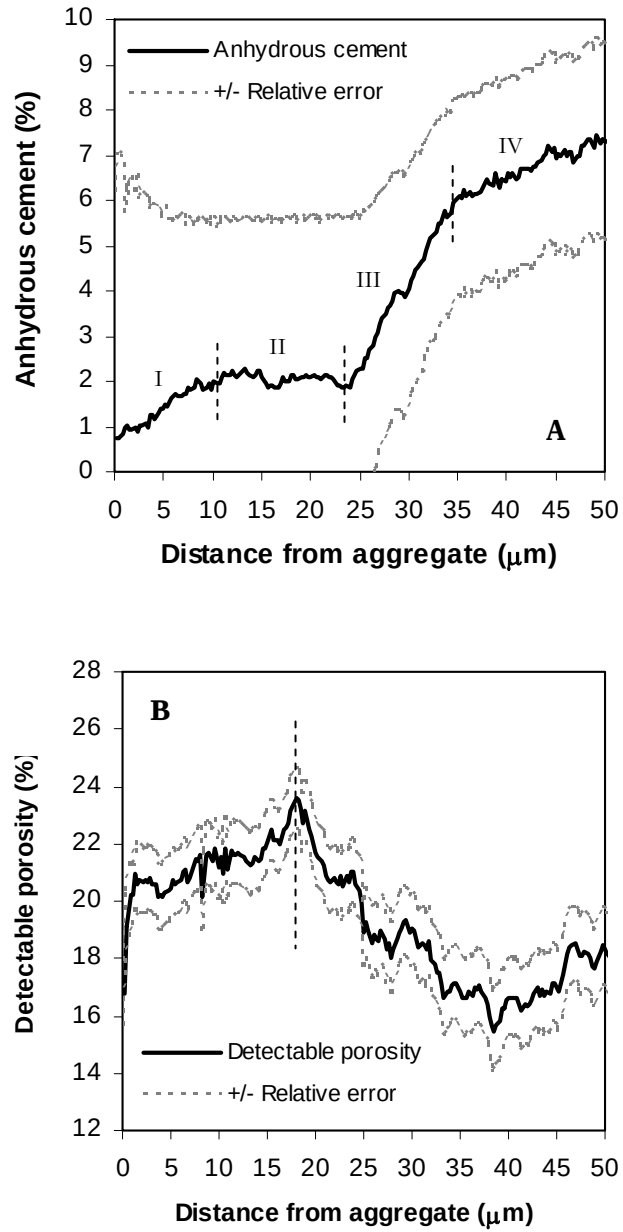


Figure 8.8 Detectable anhydrous cement (A) and porosity distribution (B) plots at single pixel strip width, measured from the aggregate-paste interface for sample M 0.6. Values are the average of 30 frames.

This distinctive anhydrous cement distribution curve could be a result of prolonged hydration on the initial particle-packing effects of multi-sized cement grains. To illustrate this, we assume that the initial cement particle size distribution can be sub-divided into three major size groups: small, medium and large grains. Upon casting, the smaller grains will pack closer to the aggregate surface than larger ones. The smaller grains would also have higher surface area per unit volume and therefore, hydrate faster than the larger grains. After a certain curing period, the small grains will be consumed entirely by hydration, leaving behind the medium and large anhydrous cores that react at a slower rate. The observed four distinctive zones are a result of particle packing effects arising from the remaining medium and large-sized anhydrous cores. Since the medium grains will pack closer to the aggregate (Zones I and II), there would be a region farther out that is depleted of the medium grains (Zone III) [Scrivener, 2004b]. The rapid rise in unreacted cement fraction in Zones I and III is attributable to packing effects of the medium and the large grains respectively, the plateau stage in Zone II suggests a region dominated by medium grains only, while the milder slope in Zone IV comes from the packing effect of the medium and large grains, as the ‘bulk’ region is approached. Fig. 8.9 is a schematic representation of this effect.

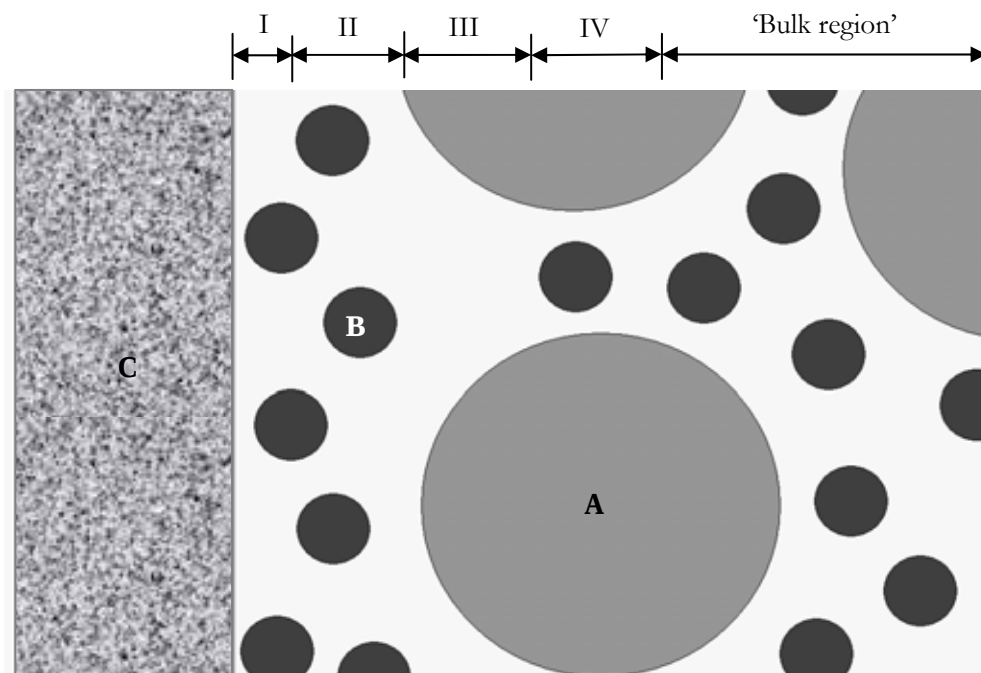


Figure 8.9 Schematic showing the packing effects of two different sized unreacted cement grains (A & B) against a large aggregate particle (C), after a period of hydration that has consumed the smaller grains. Adapted from Crumbie [1994].

A similar phenomena was observed in the Ph.D. thesis of Crumbie [1994] and subsequently reported by Scrivener et al. [1999, 2004b]. In that study, Crumbie [1994] made ITZ measurements in OPC concretes of w/c ratio 0.4 at ages 1 and 28 days, and 1 year. For all samples tested at 28 days, Crumbie [1994] observed a secondary minimum at a distance of about 40 μ m from the aggregate surface in the average anhydrous cement distribution plot. This was attributed to long-range packing effects for cement particles larger than about 15 μ m [Scrivener, 1999]. According to Scrivener et al. [2004b], a more detailed effect of disrupted packing on the grading of the cement particles becomes clear as hydration proceeds. Smaller grains pack closer to the interface so there is a region farther out that is depleted of small grains, while the larger grains in this region react at a slower rate between 1 and 28 days. The secondary minima reported by Crumbie [1994] is not seen here, possibly because of differences in the cement particle size distribution as well as the w/c ratio of the samples tested. Nevertheless, it is very likely that the observations made in this study and in that of Crumbie [1994], allude to the same phenomena.

The detectable porosity distribution from the aggregate surface for M 0.6 is shown in Fig. 8.8 (B). Here, the effect of calcium hydroxide deposits on the porosity gradient is again evident and appears to be more significant than it is for the case of C 0.4. On average, this 'CH influence zone' appears to extend up to 20 μ m from the aggregate surface, compared to 5 μ m for C 0.4. Fig. 8.10 shows examples of different ITZ porosity characteristics that arise as a result of varying amounts of CH deposits on the aggregate surface. Generally, it is observed that the thickness of the CH deposits is greater, and its variability between frames is higher, when compared to C 0.4. In certain cases, for example in Fig. 8.10 (D), the CH deposits can extend up to the mid-point between adjacent aggregate particles. Such large CH deposits observed in M 0.6 are to be expected because of the higher initial porosity at the aggregate-paste interface due to a higher w/c ratio and also a greater probability of microbleeding occurring on the aggregate surface. Thus, there is an increased migration/diffusion of calcium and hydroxyl ions from 'bulk' regions to the interface, which favours more deposition of CH in this region [Scrivener et al., 2004b].

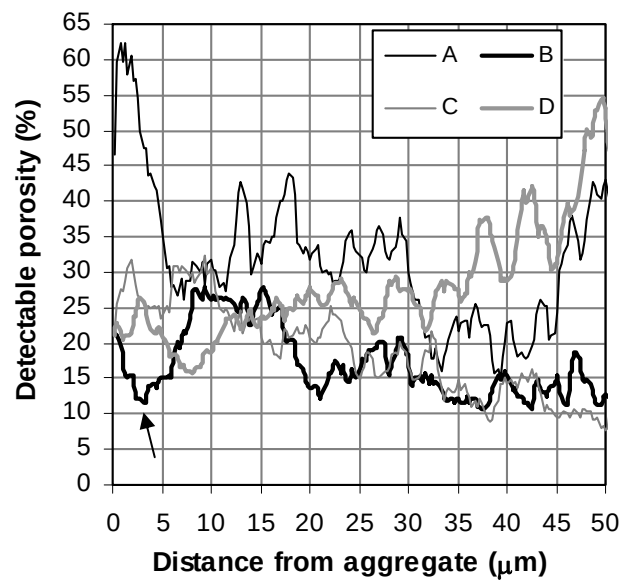
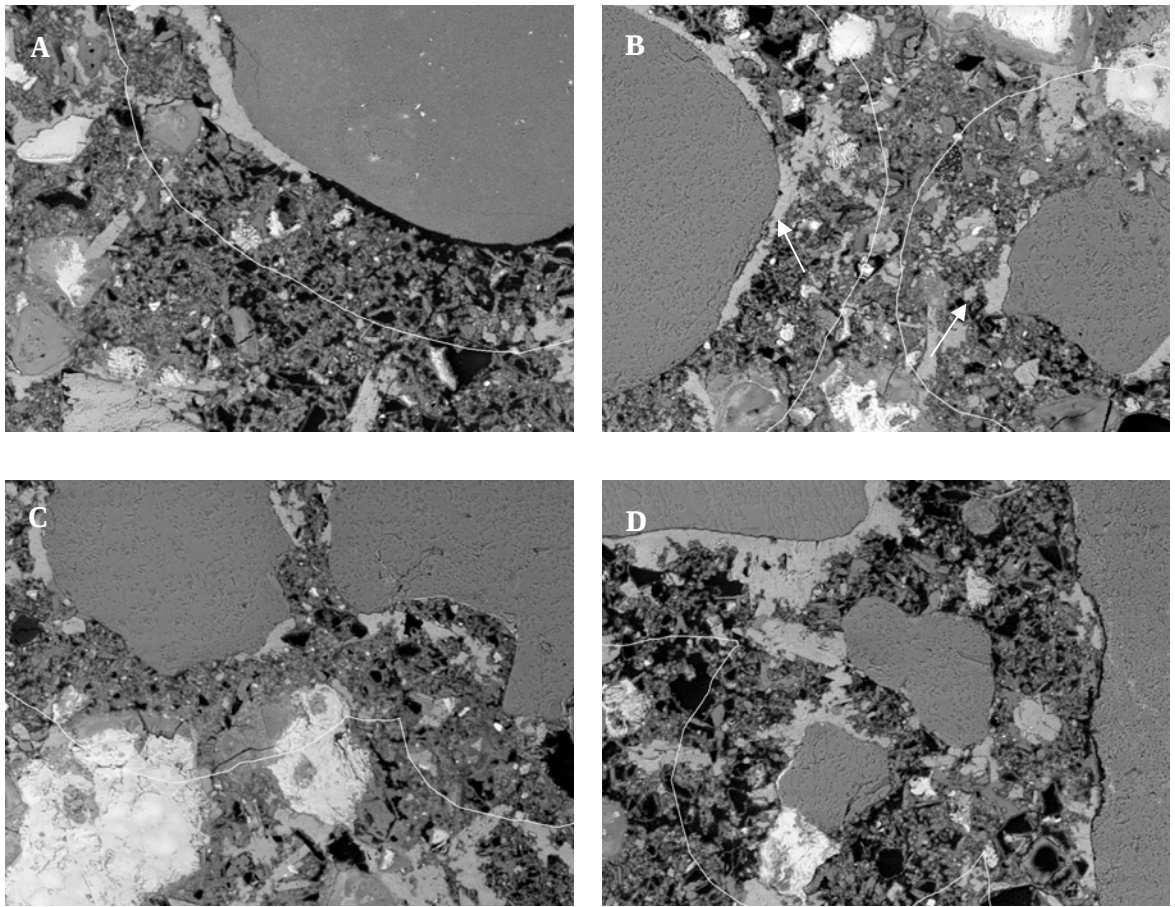


Figure 8.10 Detectable porosity distribution plots showing different ITZ characteristics in sample M 0.6 as a result of varying amounts of CH deposit on the aggregate surface. White border represents the 50µm strip (field of view: 267 x 200µm).

8.4 Heterogeneity of the ITZ

The image analysis results presented in the previous section are averaged values taken over many frames captured at different locations. Although the averaged results display specific trends that are physically explainable and attributable to a particular process, the individual result of a localised area may not display such trends and indeed, is usually very variable. Despite the fact that the deficiency in anhydrous cement and excess in detectable porosity at the ITZ is evident in the averaged results, there is however, a significant variability from location to location. Therefore, the reader should be cautious when interpreting these results, and must bear in mind the spatial variability and inherent heterogeneity of the ITZ.

The issue of local variation in the microstructure within the ITZ has been noted before, for example, in the work by Diamond & Huang [1998], Diamond [2001b] and Scrivener et al. [2004b]. This can be straightforwardly deduced by making qualitative observation on individual micrographs, for example by observing the variations in the microstructural features of the ITZ in the images presented in Fig. 8.7 and Fig. 8.10. Nevertheless, in order to achieve a better understanding of the heterogeneous nature of the ITZ, a quantitative characterisation of this variability is much needed. In the previous section, the EDM method was used to determine the distribution of average porosity and anhydrous cement content at the ITZ, at a single pixel step from the aggregate surface up to a distance of 50 μ m away, using measurements from thirty equally spaced locations. This provides us with data to perform a simple quantitative investigation on the spatial variability of the microstructural gradients observed at the ITZ.

To characterise variability of a measured feature, we will compute its coefficient of variation, which is defined as the standard deviation divided by the mean and expressed as a percentage. The coefficient of variation provides a relative measure of dispersion of data around the mean value; when the coefficient of variation is small, the data scatter (i.e. variation) compared to the mean is small and vice-versa. Hence, plotting the coefficient of variation of the average detectable porosity or anhydrous cement against distance from the aggregate surface, gives an idea of the spatial variability of the ITZ.

Fig. 8.11 shows the coefficient of variation for anhydrous cement and detectable porosity, plotted against distance from the aggregate surface for C 0.4 and M 0.6. The coefficient of variation ranges between 60 and 140% for anhydrous cement and between 30 and

60% for detectable porosity. It is important to note that the coefficient of variation is substantially higher than the expected variation due to counting statistics, i.e. the standard error, which is approximately 1 to 2% for porosity and 1 to 6% for unreacted cement (Fig. 8.6 and Fig. 8.8). This shows that the variation in the measured property is a real and an inherent feature of the microstructure.

In both samples, the coefficient of variation for anhydrous cement is significantly larger than for porosity. The higher coefficient of variation for anhydrous cement is partially due to its spatial variability, as well as its relatively large particle size. This is because the size of the measured particle relative to the image area can have an effect on its sampling frequency. In Fig. 8.11, it can be seen that the coefficient of variation for detectable porosity is particularly high in the first 5 μm for C 0.4, and in the first 10 μm for M 0.6, and this is likely a result of the variability of the CH deposits on the aggregate surfaces. It is noted that the size of the 'CH influence zone' as observed in Fig. 8.11 (A) matches the one in the porosity gradient in Fig. 8.6 (B). In addition, it is interesting to observe that for M 0.6, the peaks in the anhydrous cement curve at approximately 20-30 μm and 35-50 μm in Fig. 8.11 (B) correspond to Zone III and IV respectively, in Fig. 8.8 (A).

Although the samples investigated here are significantly different in terms of mix composition and maturity, as reflected in the measured average porosity and unreacted cement gradients, it is very interesting to note that their respective distributions produced a similar range of coefficient of variations. This suggests that the spatial variability at the ITZ may behave in a consistent and characteristic way and hence, not only that the degree of heterogeneity is quantifiable, but may also be predictable. If this is true, then spatial variability may form another type of microstructure characterisation method. The average gradients together with the coefficient of variations may provide additional information to generate new models of the microstructure, or to calibrate and to improve upon existing models. This seems premature and we certainly do not discount the probability that the results could be a fortuitous coincidence, therefore, this warrants further investigation.

Using the EDM phase analysis method, we have obtained new information regarding the nature of the ITZ, as presented in this and the previous section. Whilst this is encouraging, it must be stressed that the number of samples investigated so far is limited and thus, the results should be viewed as preliminary. Additional testing over a wide range of materials is necessary to confirm these findings. Nevertheless, the high variability in the microstructural gradients at the ITZ is real and as emphasised by Diamond & Huang [1998, 2001], should be given consideration in computer models that attempt to simulate the micro-

structure of cement-based materials. Clearly, a more detailed analysis of the spatial variability in the ITZ, covering samples of a range of mix composition and maturity, is much needed before this can be achieved. It may also be worthwhile to study the microstructural gradients and spatial variability of phases that occurs in a pure paste system using the EDM approach. The results can be compared with those obtained from equivalent mortar and concrete samples. This presents another approach to study how the presence of aggregate particles can affect the microstructure of cement-based materials.

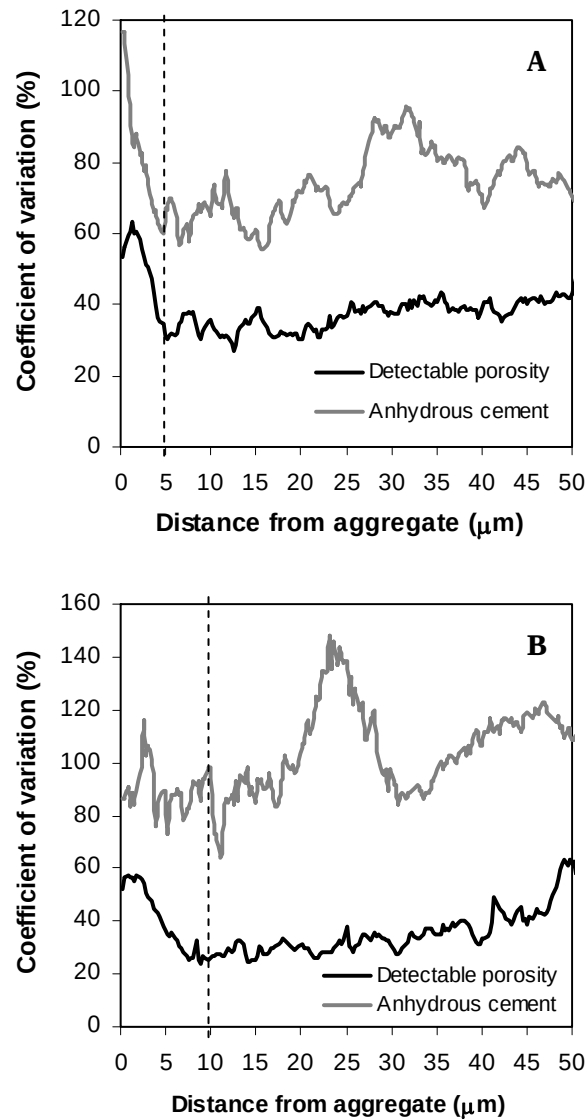


Figure 8.11 Coefficients of variation for the average detectable porosity and unreacted cement plotted against distance from aggregate surface for A) C 0.4; and B) M 0.6.

8.5 Role of ITZ in molecular transport

In order to model accurately molecular/ionic transport in the microstructure of cement-based materials, it is necessary to identify the phases where transport predominates, and the extent to which, and circumstances under which, flow occurs preferentially via a certain interconnected phase, bypassing others. If it is known that transport occurs via the interconnection of a certain phase only, for example, through the interconnection of microcracks or the ‘porous ITZs’, then effective medium and percolation theories may be called upon to model such behaviour. However, if flow occurs ‘evenly’ through the microstructure, then global descriptors of the pore structure, such as the pore volume fraction, specific surface, tortuosity, et cetera, may suffice as input values to analytical models for transport prediction. Clearly, this is not an easy question to answer, and it is likely that in most cases, transport occurs via a combination of both mechanisms.

For many years, the interfacial transition zone has been a phase of particular interest to researchers keen on modelling the behaviour of cement-based materials. It is well-known that the microstructure at the ITZ is different from the ‘bulk paste’. It is also known that the microstructure at the ITZ is inferior, from the observation that under continuous loading, microcracking occurs predominantly at the ITZ. Researchers have believed that the difference in microstructure has a significant effect on the mechanical and durability properties of concrete. Hence, the common view that the ITZ is the weakest link in concrete. This idea resulted in the development of many conceptual three-phase microstructure models, where the ITZ is treated as an isolated phase of a definite thickness around aggregate grains, and is accorded with either a fixed property level or functional gradient, but exhibited uniformly around all aggregate particles [Nielsen & Monteiro, 1993; Winslow et al., 1994; Bourdette et al., 1995; Bentz & Garboczi, 1999].

Since the ITZ is on average, more porous than the ‘bulk paste’, it is usual to postulate that the local penetrability is higher at the ITZ. Thus, it would be expected that in certain cases where there is a high ITZ content, adjacent ITZs would overlap, forming a continuous porous link. The fraction of connected ITZ increases with increasing aggregate content, and when the ITZ fraction is beyond a certain critical threshold, the interconnected porous ITZ will span the entire sample, i.e. percolation occurs, providing an easy path for mass/ionic movement. Thus, models that assume a uniform thick porous ITZ layer surrounding aggregate particles, will predict that beyond a critical aggregate level, the percolation of the inter-

connected porous ITZ will lead to a sudden increase in mass/ionic transport properties. In an example of such models [Winslow et al., 1994], it was predicted that for an ITZ thickness of 20-40 μm , the critical sand volume fraction in mortars where 100% of the porous ITZ is percolated is around 50-60%. This suggests that even for a modest ITZ thickness of 20 μm , interfacial zone percolation will occur in almost all typical construction concrete mixes.

As highlighted in the literature review in Section 2.1.2, the deleterious effect of the ITZ on mechanical properties of cement-based composites is well known, but its effect on transport properties and durability performance is less straightforward. ITZ percolation models predict a critical threshold aggregate content above which transport should increase significantly. The percolation of overlapping ITZs was first indicated by mercury intrusion porosimetry tests [Feldman, 1986; Winslow & Lui, 1990] and has been inferred from SEM observations of samples intruded with Woods' metal [Scrivener & Nemat, 1996]. However, it has been shown that mercury intrusion porosimetry tests, due to the drying and high pressures involved, may be destructive to the microstructure of cement-based materials [Feldman, 1984; Olson et al., 1997; Gall , 2001].

Experimental transport studies do not provide clear evidence for ITZ percolation. Studies by Costa et al. [1990], Ping et al. [1991], Houst et al. [1993], Winslow et al. [1994], Halamickova et al. [1995], Princigallo et al. [2003], and the general observation that the penetrability of mortars/concretes is generally one to two orders of magnitude greater than that of cement pastes, supports the idea of ITZ percolation. However, other studies done by Delagr ve et al. [1997, 1998], Carcasses et al. [1998] and Buenfeld & Okundi [1998], have suggested otherwise. This conflicting experimental data from various sources reflects the inherent complications involved in isolating the effects of the ITZ on transport properties. This is partly because different compositional parameters are varying together when the aggregate volume fraction is changed. In addition, sample preparation for transport testing requires some form of cutting and drying, and these may have artificially induced microcracking at the ITZ, exaggerating its effect on the measured molecular/ionic transport properties.

8.5.1 Experimental

To investigate the effect of ITZ on molecular transport properties, mortar samples with a range of sand volume content were cast and tested. Three series of mortars were prepared; the first was an OPC mortar at w/c ratio 0.5, the second was an OPC mortar at w/c

ratio 0.3, and the third was an OPC-silica fume blended mortar at w/c ratio 0.3 with 8% silica fume replacement. For comparison purposes, equivalent paste samples at the same w/c ratio and with the same binder system were also prepared. The samples represent normal and 'high-performance' mixtures. Silica fume acts as a pozzolanic micro-filler and quantitative microscopy studies [Scrivener et al., 1988b] have shown that it can promote densification of the ITZ pore structure. Hence, this was included in order to investigate the effects of the resulting 'improved ITZ' on molecular transport.

A medium graded siliceous sand (Thames Valley) was used. The sand volume fraction was varied between 10% and 70%. A sulphonated naphthalene-based superplasticising admixture was used to improve the workability of stiff mixes, particularly at low w/c ratio and high sand content. Trials were made to determine the superplasticiser content required to achieve sufficient workability for compaction. Any further increase in sand content was found to be unfeasible because it resulted in very stiff mixes that could not be compacted well enough. Insufficient compaction will modify the ITZ characteristics as well as introduce additional porosity, making it difficult to isolate the contribution of ITZ if any increase in transport is observed. The mixture proportions are given in Table 8.2.

In order to accentuate (any) effects of the ITZ on molecular transport, the samples were cured for a short period (3 days) and tested at a relatively young age (~90 days). Cylindrical samples (100Φ x 250mm) were cast, demoulded after 24 hours and then immediately sealed in cling film for curing at 20°C. After 3 days of curing, the samples were unwrapped and sectioned to produce three 50mm thick discs for mortars (20mm thick discs for pastes), for transport testing. The top and bottom face, approximately 30mm thick, of each cylinder was discarded. Transport tests were carried out on bulk rather than surface material to avoid complications in interpretation of results arising from microstructural gradients at the surface zone [Buenfeld & Okundi, 1998].

Moisture remaining in pores has an influence on transport properties, so samples must be dried and conditioned to a standard moisture state (Section 3.1.4). However, the ITZ is known to be structurally weaker than bulk paste and prone to microcracking if severe drying treatments are used. At high sand volume contents, these artificially induced microcracks may interconnect and could significantly affect the transport results. Therefore, in this study, care was taken to avoid a high thermal gradient in the sample and excessive moisture loss particularly during the initial stages of drying. After curing, the discs were unwrapped and allowed to dry in an incubator at 50% relative humidity, 20°C for 7 days. Then, the discs were transferred to an oven and dried at gradually increasing temperatures up to 50°C, over

saturated ZnCl_2 . After a total conditioning period of around 90 days, the rate of mass loss was less than 0.01%/day, and this was taken as the equilibrium condition. The discs were then cooled to room temperature in a vacuumed desiccator containing silica gel and tested sequentially (3 replicates) for oxygen diffusivity, oxygen permeability and water absorption. Detailed procedures for these tests are given in Section 3.4.

	Mixture	Cement (kg/m ³)	SF (kg/m ³)	Free w/c	SP (%)	Sand (kg/m ³)	Sand vol. (%)
1.	M 0.5 – 10	1094	-		-	260	10
	M 0.5 – 40	729	-		-	1040	40
	M 0.5 – 50	608	-		-	1300	50
	M 0.5 – 55	547	-	0.5	-	1430	55
	M 0.5 – 60	486	-		-	1560	60
	M 0.5 – 65	425	-		0.50	1690	65
	M 0.5 – 70	365	-		0.75	1820	70
2.	M 0.3 – 10	1446	-		-	260	10
	M 0.3 – 30	1124	-		-	780	30
	M 0.3 – 40	964	-		0.25	1040	40
	M 0.3 – 45	883	-	0.3	0.25	1175	45
	M 0.3 – 50	803	-		0.50	1300	50
	M 0.3 – 55	723	-		0.75	1430	55
	M 0.3 – 60	642	-		1.0	1560	60
	M 0.3 – 65	562	-		1.2	1690	65
3.	M 0.3 SF – 10	1330	116		-	260	10
	M 0.3 SF – 30	1034	90		0.25	780	30
	M 0.3 SF – 40	887	77		0.50	1040	40
	M 0.3 SF – 45	813	71	0.3	0.50	1170	45
	M 0.3 SF – 50	739	64		0.75	1300	50
	M 0.3 SF – 55	665	58		1.0	1430	55
	M 0.3 SF – 60	591	51		1.2	1560	60
4.	P 0.5	1216	-	0.5	-	-	-
	P 0.3	1606	-	0.3	-	-	-
	P 0.3 SF	1478	128	0.3	-	-	-

Table 8.2 Mixture proportions for mortar (1, 2, 3) and paste (4) samples, for molecular transport testing. Notation: SF = silica fume, SP = superplasticiser.

8.5.2 Results and discussion

Results for oxygen diffusivity, oxygen permeability and water sorptivity, plotted against sand volume fraction for mortars and pastes are shown in Fig. 8.12. In Fig. 8.13, the transport coefficients are normalised to the values for pastes. As expected, the transport coefficients are higher for mixtures with a higher w/c ratio. Mixtures containing silica fume recorded the lowest transport coefficients for all sand volume fractions; this is in line with well-established findings that silica fume acts as a pozzolanic micro-filler that refines the pore structure, thereby reducing the transport properties of cement-based materials.

Comparing the test results for mortars only, we find that the oxygen diffusivity, oxygen permeability and water sorptivity, consistently decreased with increasing sand volume fraction. This shows that in mortars, the porous hydrated cement paste is the only interconnected phase that allows mass transport to occur. The sand particles are denser than the hydrated cement paste hence these act as isolated and relatively impermeable solids in the microstructure. When more and more sand particles are added into the mixture, the volume fraction of the interconnected porous cement paste is reduced. At the same time, the tortuosity of the transport path is increased by the presence of more sand particles. These factors result in a consistent reduction in transport properties as the sand volume fraction increased.

From the results plotted in Fig. 8.12 and Fig. 8.13, there is no indication of a critical sand volume threshold, above which, transport increases significantly due to percolation of interconnected IT'Zs. This study covers a wide range of sand volume fraction, up to 70%, and is sufficient, considering that the critical sand volume fraction for IT'Z percolation is predicted to be around 50-60% [Winslow et al., 1994]. As mentioned previously, mortars with sand content greater than those presented here were not tested in this study because they could not be adequately compacted. In addition, the mortars investigated represent young samples, but there is no reason to expect a different behaviour in mature samples. Since the IT'Zs are more porous at early ages, percolation should have occurred in young samples if the IT'Z percolation hypothesis is true, and not later.

However, when comparing the transport results of pure cement pastes with mortars, we observe an inconsistent trend. The oxygen permeability of pure cement pastes is found to be lower than mortars of the same series, whereas for oxygen diffusivity and sorptivity, except for the case of w/c ratio 0.5, the transport coefficients are higher in pastes than in mortars. The reason for this is, unfortunately, not clear. It appears that addition of a small

amount of sand particles can have a drastic effect on the transport properties. However, we cannot discount the possibility that the inconsistent behaviour is due to experimental errors. Despite the care taken during conditioning, drying shrinkage-induced damage may still have occurred in the samples, particularly at the ITZ. In permeability testing, which involves pressure-induced flow, results are usually very sensitive to microcracks because flow will occur preferentially in the large interconnected cracks rather than in the smaller capillary pores. On the other hand, for diffusion and water absorption-type tests, the transport mechanism is governed by random molecule-molecule collisions and capillary pore suction respectively, so mass transport occurs more evenly through the entire pore structure compared to pressure-induced flow. This results in a less notable difference in the diffusivity and sorptivity coefficients between samples of varying degrees of damage. Thus, this could explain the larger permeability coefficients obtained for mortar samples compared to the pure cement pastes.

An implicit assumption that was made in the preceding discussion is that the cement paste porosity is identical in each series regardless of the sand volume content. That is to say, that the cement paste porosity is invariant with the sand content, and is only dependent on the w/c ratio and the binder system for each series. In the mix proportions, the aggregate water absorption is accounted for and thus, it should not be expected that the decrease in the measured transport properties could also be due to the decrease in free w/c ratio as the sand volume fraction increased. Nevertheless, the validity of this assumption needs to be verified. To do this, we compare the paste porosity for all samples measured by the water absorption test. The paste porosity is taken as the total water absorbed by the sample, corrected for aggregate absorption, and divided by the paste volume in the sample. The result, plotted in Fig. 8.14, does not appear to indicate a decreasing trend in the total paste porosity with increasing sand content. In fact, the paste porosity for mortars is almost equivalent to the porosity recorded for pure cement pastes. Thus, the above assumption is likely to be valid

The study on mortars indicates that the effects of decreasing paste volume and decrease in total porosity outweigh any effects of increased mass transport in the porous ITZ. Therefore, transport properties are controlled by the volume fraction and microgeometry of the entire pore structure in the cement paste, not by localised microstructure gradients at the ITZ. As shown in the previous section, the pore structure at the ITZ is highly heterogeneous in nature and spatially variable. Although there is an average porosity gradient at the ITZ, this is not exhibited uniformly around all aggregate particles. Since computational models of the ITZ invariably assume a uniformly thick porous ITZ layer surrounding aggregate particles, neglecting its spatial variability, these simulations have produced results contrary to experimental observations.

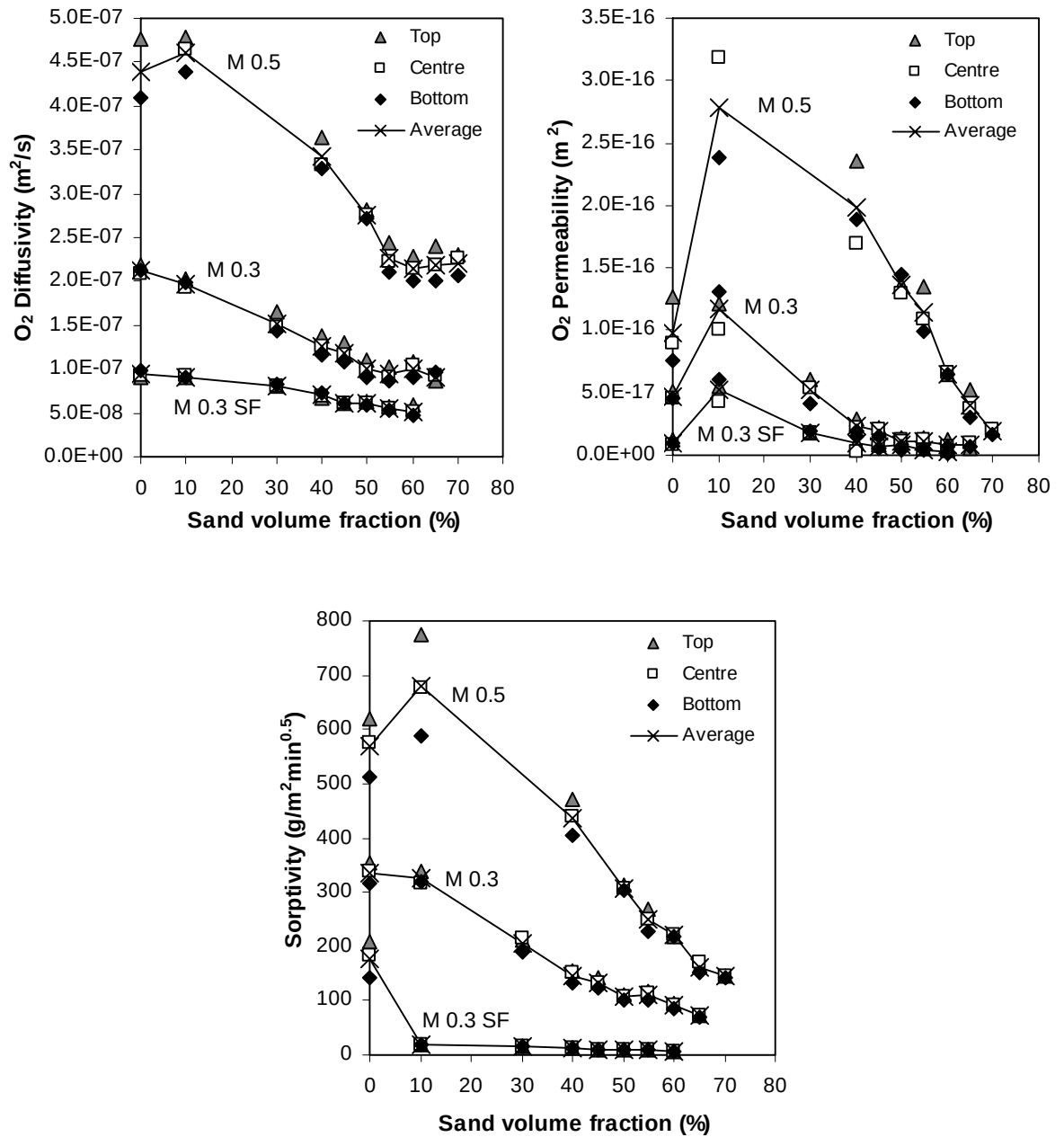


Figure 8.12 Oxygen diffusivity, oxygen permeability and water sorptivity plotted against sand volume fraction.

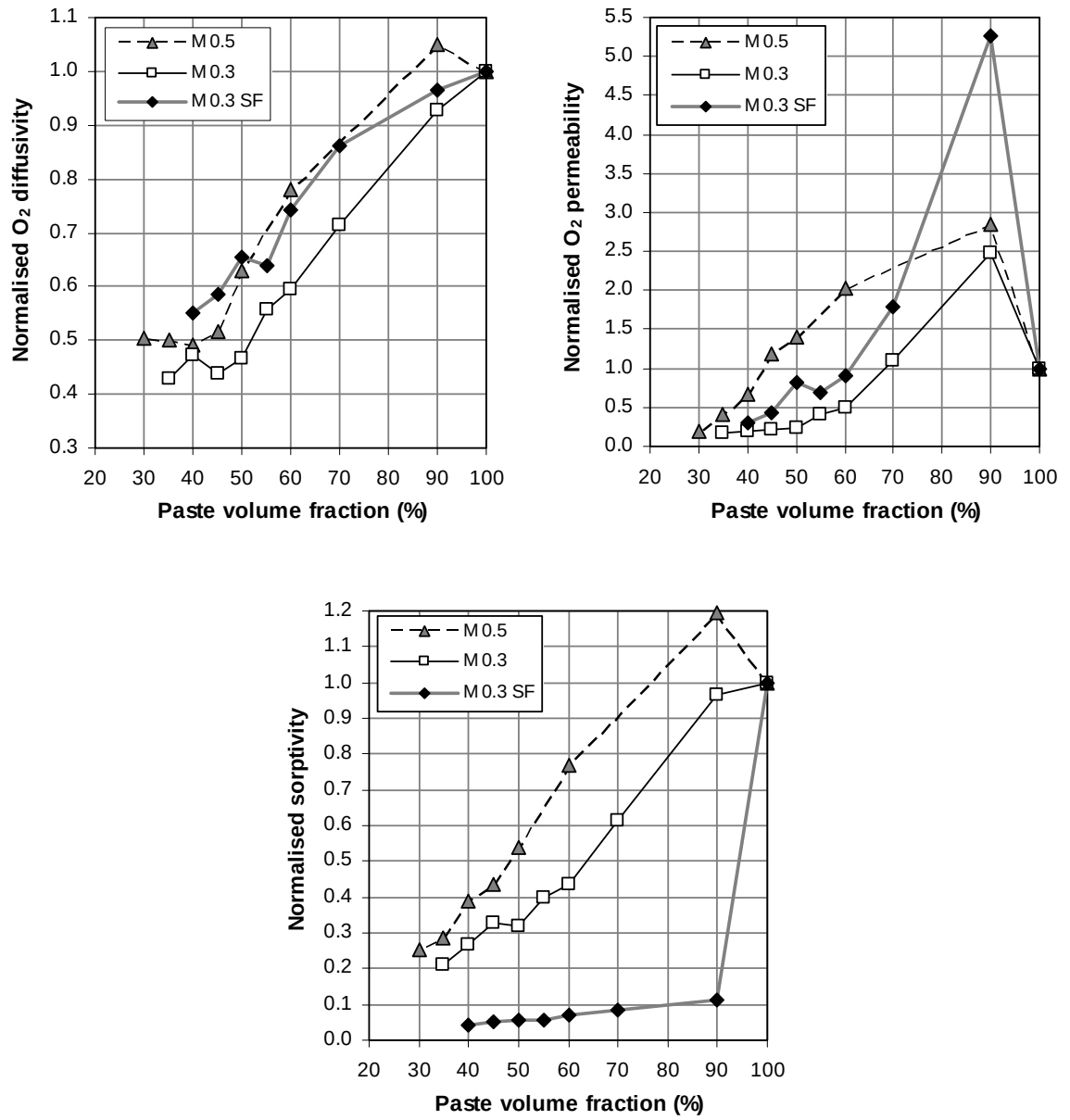


Figure 8.13 Normalised transport coefficients plotted against paste volume fraction.

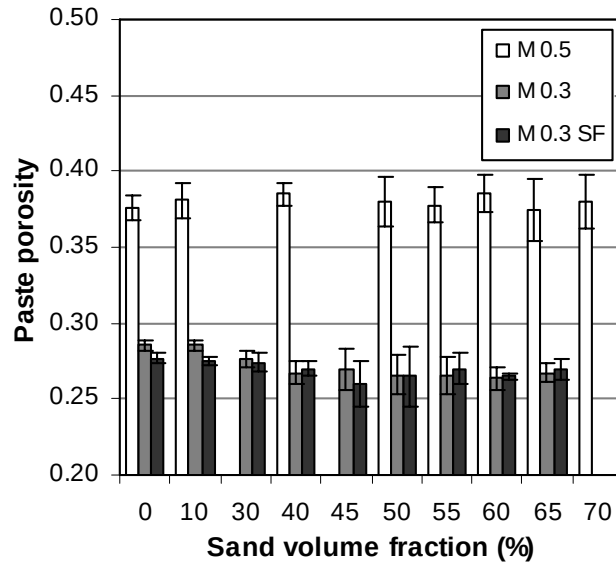


Figure 8.14 Cement paste porosity measured from water absorption test. Error bars represent plus/minus one standard deviation.

8.6 Conclusions

A new image analysis method for investigating microstructural gradients at interfaces in composite materials is presented. The method uses Euclidean Distance Mapping to generate microstructural gradient plots at single-pixel strip width. The new method is faster than conventional dilation-subtraction strip analysis, and is not constrained by feature geometry and boundary conditions. Therefore, a truly random and unbiased sampling procedure can be achieved. The new method was applied to investigate microstructural gradients at the interfacial transition zone of an ordinary Portland cement concrete and mortar sample. The results showed that although the overall ITZ can be characterised by a strong gradient in anhydrous cement and detectable porosity, this is highly variable from location to location. The higher sensitivity of the new method enabled it to detect previously unreported effects of calcium hydroxide deposits on the aggregate surface on the porosity gradient. The measured 'average' characteristic of the ITZ via image analysis is dependent upon the extent of CH deposition at aggregate surfaces and also on the adopted sampling procedure. Molecular transport testing on mortars revealed a consistent decrease in oxygen diffusivity, oxygen

permeability and water absorption, as the aggregate content (ITZ fraction) increases, indicating that the effects of decreasing paste volume (i.e. total porosity) and increase in transport path tortuosity outweigh any effects of increased transport in the porous ITZ. However, computational models that assume a uniform thick porous ITZ surrounding all aggregate particles in order to study mass/ionic transport by using percolation theories predict a critical aggregate volume threshold, above which, transport should increase significantly due to overlapping of ITZs. This departure from experimental results may be explained by the observed spatial variability of the ITZ porosity gradient and its dependence on calcium hydroxide deposits, which has not been accounted for in these models.

Chapter 9

Predicting molecular transport properties from image analysis

Two ordinary Portland cement mortars at w/c ratio of 0.35 and 0.70 were prepared, cured and conditioned to produce a range of pore structure characteristics. Image analysis was used to characterise the pore structure in terms of simple morphological parameters such as resolvable porosity and specific surface area of the pores. These were found to be highly correlated to measured transport coefficients (diffusivity, permeability and sorptivity), suggesting the feasibility of image analysis to derive valuable quantitative information describing the pore structure that can be used as input values for a transport prediction model. A model incorporating tortuosity and constrictivity was used to predict oxygen diffusivity and a variant of the Kozeny-Carman model was used to predict oxygen permeability. The diffusion model tended to over-predict for the lower w/c ratio mortar, but the general agreement was reasonable, with 90% of the estimated values within a factor of two from the measured values. The modified Kozeny-Carman model, however, over-predicted all permeability values with an error of between half to one order of magnitude.

9.1 Introduction

This is an exploratory study of the feasibility of using image analysis on backscattered electron images to extract quantitative information on pore structure that can be used to develop simple transport prediction models. Transport properties govern the rate of all major deterioration processes and the service life of cement-based materials, hence, much effort has been dedicated to their prediction. Experimental methods for investigating pore structure are divided into indirect methods such as mercury porosimetry, that rely on measurements of a secondary or derived property (Section 2.2), and direct methods such as microscopy, that produce an image of the microstructure that reveals the morphology and spatial relationship of the various phases (Section 2.3). Measurements made on a 2D image can to some extent, be related to the 3D structure via stereology rules (Section 2.4) [Underwood, 1970; Russ & Dehoff, 1999].

Since the rate of mass transport is governed by the interconnected pore space, it follows that the pore parameters derived from microscopy may be used to predict transport properties. Indeed, there are many examples of such work particularly in the field of geological sciences, where research is aimed at understanding the transport of oil and gases, contaminants and solutes in soils and rock formations. However, there are not many examples of similar work on cement-based materials, possibly because of their greater complexity, compounded by limitations in instrumentation. Two examples of studies involving microscopy to predict transport properties of cementitious materials are the recent works by Hu & Stroeven [2003], who used BSE imaging to determine the critical pore size to predict permeability via general effective media theory, and Koster et al. [2006], who derived water permeability and vapour diffusivity from 3D microtomographic images via network modelling. Both studies were performed on hardened cement pastes. In this contribution, we will attempt to use 2D pore parameters from BSE images to estimate the gaseous diffusivity and permeability coefficients of mortar samples. Mortars were chosen for this preliminary study because they resemble concretes by having sand particles and aggregate-paste interfaces, but are more homogeneous due to the exclusion of large aggregate particles

Properties that are relevant to molecular transport are the volume of interconnected pores, surface area of the solid-void interface, pore shape, constrictivity, tortuosity and connectivity of the pores. However, a BSE image is only a two-dimensional representation of a three-dimensional structure. While porosity and specific surface area are easily obtainable from a 2D section, it is impossible to define and measure the shape, connectivity and tortuosity from a 2D image. Researchers have often relied on other properties, for example the formation factor (ratio of resistivity of the saturated porous medium to the resistivity of the pore water), to characterise connectivity and tortuosity. 3D imaging such as microtomography and confocal microscopy may provide valuable insights on higher-order parameters like connectivity and tortuosity. However, although such parameters can describe simple pore configurations effectively, their concept is difficult to implement on complex porous media.

As emphasised earlier, the inherent limitation of any imaging technique is the size range that is available for quantitative analysis. This presents two complications: first, the ability to resolve and measure the smallest features present, and second, the size of the field of view necessary to obtain a statistically valid representation of the microstructure (Section 3.2.5). As shown by Monte Carlo simulations presented in Chapter 6, measurement errors increase substantially as the feature size approaches the image resolution. Increasing the magnification can improve the resolving ability up to the resolution limit of a particular imaging system, but a high magnification will result in a small field of view, and hence, a larger

number of images must be analysed. A small field of view also limits the size of the largest feature that can be quantified accurately, regardless of the total number of images analysed. One must always remember that such limitations exist when using image analysis for quantitative work.

9.2 General considerations

Careful thought was given in selecting the type of transport tests to be carried out. For an investigation of this kind, it is important that the transport mechanisms to be studied do not alter the pore structure during the test itself and that the transported matter should be inert to the sample. Hence, tests that involve prolonged exposure to water, carbon dioxide or chloride ions were deemed unsuitable. Application of high-pressure was also avoided to minimise risk the of specimen damage.

Most deterioration processes begin with movement of the contaminant through the exposed surface; therefore, transport testing should include a cast surface. However, the surface zone is affected by microstructural gradients from particle packing effects, a result of which is higher cement content near the surface than in the bulk material. This will cause the calculated transport coefficients to be erroneous because the assumption of material homogeneity required in the underlying theory is not attained [Buenfeld & Okundi, 1998]. Other factors such as the type of formwork, mould oil and curing regime are also likely to affect the penetrability of the surface material [Buenfeld & Okundi, 1998]. In view of these factors, transport testing will be carried out on bulk material that is free from surface heterogeneities.

In this study, samples were tested following the sequence of oxygen diffusion, oxygen permeation and water absorption. This sequence of testing is advantageous because the same disc can be used for all tests since successive test results are not affected by the previous test. Also, note that with these three tests, we measure three distinctly different types of transport mechanisms. Oxygen transport is relevant in view of its importance to reinforcement corrosion while water ingress via capillary suction is a major transport phenomenon occurring in concrete structures. In the water absorption test, the sorptivity coefficient can be calculated using data obtained from the first few hours of water uptake, thus the effect of further hydration on pore structure during this period is assumed negligible.

The gaseous diffusivity and permeability, and water sorptivity are dependent upon the degree of pore saturation, therefore samples must be conditioned to a standard moisture state prior to testing so that meaningful comparison can be made (Section 3.1.4). However,

the question remains as to which humidity is the most suitable to be adopted for this study. Conditioning at high humidity may be more practical because less time is required to reach equilibrium compared to conditioning at low humidity. However, a sample conditioned to high humidity contains many saturated pores that are effectively blocked and do not contribute to transport, but may be imaged and analysed during microscopy. Another factor to be considered is the effect of the conditioning regime on the microstructure itself. Ideally, the drying process should not alter the pore structure and so, drying at extreme temperatures should be avoided.

In a digital image, pores finer than the resolution limit are not measured and thus, if the conditioning regime can be devised to ensure all pores smaller than this are saturated, then the issue of not accounting for the smaller capillaries does not arise. However, if the size of the largest saturated pore is greater than the resolution limit, then some of the measured pores from the images actually do not contribute to transport. In summary, the largest saturated pore size should ideally match the image resolution, but this is not easy to achieve as there are no reliable means to control the drying process in such a way that ensures this. Also, the drying process does not necessarily progress evenly from the largest to the smallest pore because of ink bottle effects.

Previous work suggests that the influence of pore saturation on the transport properties of cement-based materials is only significant when the internal relative humidity (RH) level is greater than about 60%. Parrott [1994] found that the air permeability and water absorption for a range of concretes (w/c: 0.46, 0.59, 0.72) were very sensitive to the moisture content at RH above 60%. Ollivier et al. [1995] investigated many gas permeability results found in the literature; it was observed that large increases in permeability occurred when drying from saturation down to 75% RH, but further drying to about 40% RH had little effect. Similar observations can be made on experimental data obtained by Gallé et al. [1997] and Jacobs [1998]. These findings suggest that most capillary pores are emptied when the internal humidity is around 60%, thus specimens should be dried to at least this level in order to minimise the influence of pore saturation. When dried further, the increase in penetrability is only very slight, and is probably partially associated with changes in the pore structure, for example cracking, rather than solely the emptying of the pores [Ollivier et al., 1995].

To investigate the influence of RH on transport properties, two pastes that had been cured for more than 7 years, one containing slag (BBFS: OPC = 3:1) and another containing fly ash (PFA: OPC = 3:1) at w/c 0.35 and 0.42 respectively were conditioned to various degrees of pore saturation and tested for oxygen diffusivity, oxygen permeability and water

sorptivity (Section 3.4). A well-hydrated sample was chosen in order to exclude the possibility that the variation in measured transport coefficients may be attributed to further hydration caused by the differences in conditioning humidity. Three replicate discs (100mm diameter, 20mm thick) were sectioned from the pastes and were conditioned for a 6 months period at 20°C and at RH of 0%, 35%, 55%, 75% and 86%; these were achieved using silica gel and saturated salt solutions of MgCl_2 , $\text{Na}_2\text{Cr}_2\text{O}_7$, NaCl and KCl respectively. The incubators were kept free of CO_2 using soda lime. The RH of each incubator was constantly monitored and the silica gel/saturated salt solutions were replaced when necessary. By the end of the conditioning period, the rate of mass loss was less than 0.02% per day.

Fig. 9.1 shows the effect of conditioning humidity on the measured transport coefficients. The results show that the transport coefficients are strongly dependant on the conditioning humidity, particularly at RH levels greater than about 55%. At RH lower than 55%, the increase in transport coefficients is negligible, probably because most of the pores relevant to transport (capillary pores) have already been emptied. This observation is consistent with the study by Powers & Brownyard [1948] on water vapour absorption isotherms of cement pastes, who found that the capillary pores only begin to condensate at RH greater than about 45%. The results in Fig. 9.1 also suggest that the remaining gel pores are too small to have any significant effects on mass transport. Another observation is that the variability of the gaseous transport coefficients seems to be somewhat higher for partially dried samples. This suggests that the remaining moisture in pores may have an effect on the consistency of the transport test, for example, the sample may be drying out while the test is being performed. Thus, considering these factors, it was decided that the samples tested in this study would be conditioned at least to equilibrium with 55% RH at 20°C, in order to minimise the influence of pore saturation.

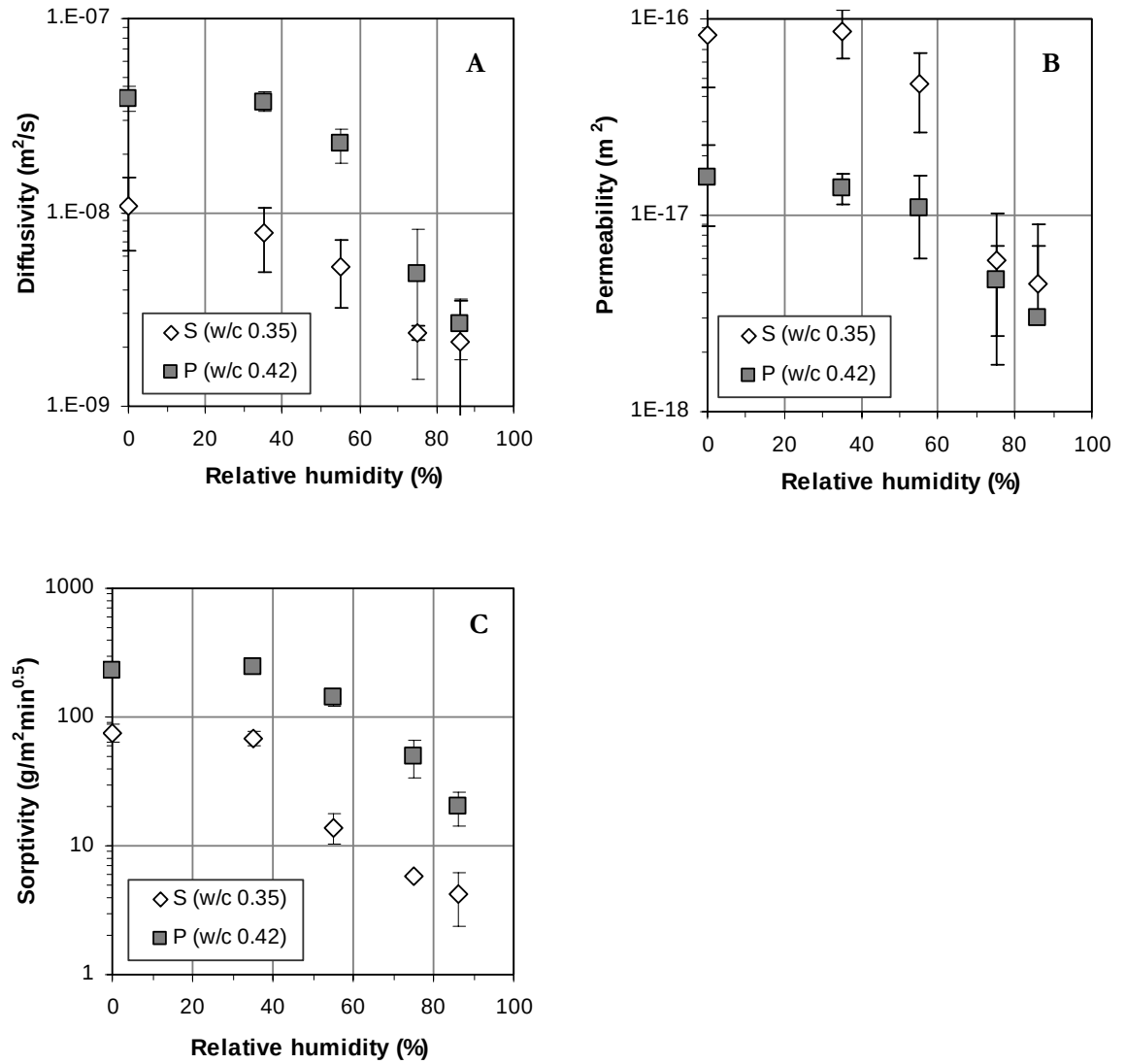


Figure 9.1 Effect of conditioning humidity on A) oxygen diffusivity; B) oxygen permeability; and C) sorptivity of mature pastes (> 7 years) containing GBBS (Mix S) and PFA (Mix P) at w/c 0.35 and 0.42 respectively. Plotted values are an average of three measurements. Error bars represent plus/minus one standard deviation.

9.3 Experimental

9.3.1 Specimen preparation, curing and conditioning

Ordinary Portland cement and medium graded (BS 882: 1992) siliceous sand were used to prepare two mortar mixtures according to the proportions given in Table 9.1. The decision to use very high and low w/c ratio was based on the intention to study samples of a wide range of pore structure characteristics and to determine the limits of applicability and sensitivity of the derived pore structure-transport relationships. The sand volume fraction was 63%. A naphthalene sulphonated type superplasticizer was used for M 0.35 at a dosage of 0.5% by weight of cement. The mortars were mixed following the procedure outlined in Section 3.1.3. The higher w/c ratio mortar showed signs of bleeding, but no efforts were made to quantify the amount of mix water lost.

Fig. 9.2 shows the sequence of the adopted methodology. Cylindrical specimens (100mm ϕ x 250mm) were cast, demoulded after 24 hours and sealed cured in cling film at 20°C. After an initial curing period, each cylinder was sectioned to produce three 50mm thick discs and two 10mm thick discs. The 50mm thick discs were used for transport testing while the 20mm thick discs were used for quantitative microscopy. The end discs, approximately 30mm thick, were discarded.

Several curing and conditioning regimes, shown in Table 9.2, were applied in order to produce specimens with a range of maturity and pore structure characteristics. As mentioned earlier, the samples needed to be dried to at least 55% RH at 20°C (Fig. 9.1) in order to minimise the effect of pore saturation on the measured transport coefficients. Therefore, the discs were conditioned by either drying at 55% RH (at 20°C using saturated Na₂Cr₂O₇) or at elevated temperatures of 50°C and 105°C until constant mass, taken when the rate of mass loss was not more than 0.01% per day. Some samples were dried at elevated temperatures in order to deliberately induce microcracks. For conditioning at 50°C, the oven humidity was maintained at 10% by using saturated ZnCl₂; this provides about the same vapour density as the vapour density at 55% RH and 20°C so that a similar equilibrium moisture state was achieved at the end of the conditioning regime. Drying at 105°C would remove all evaporable water in about 3-14 days. Conditioning at 55% RH (20°C) required about 6 months while conditioning at 50°C (10% RH) took about 90 days for the samples to achieve constant mass.

Mixture	Cement (kg/m ³)	Sand (kg/m ³)	Free w/c ratio
M 0.7 (Mortar A)	365	1635	0.70
M 0.35 (Mortar B)	550	1635	0.35

Table 9.1 Mixture proportions for transport prediction study

Mixture	Sample designation	Curing period (days)	Conditioning regime
M 0.7	A 1: M 0.7 (2d) 105C	2	105°C
	A 2: M 0.7 (2d) 50C	2	50°C at 10% RH
	A 3: M 0.7 (2d) 20C	2	20°C at 55% RH
	A 4: M 0.7 (28d) 105C	28	105°C
	A 5: M 0.7 (28d) 50C	28	50°C at 10% RH
	A 6: M 0.7 (28d) 20C	28	20°C at 55% RH
M 0.35	B 1: M 0.35 (2d) 105C	2	105°C
	B 2: M 0.35 (28d) 105C	28	105°C
	B 3: M 0.35 (28d) 50C	28	50°C at 10% RH
	B 4: M 0.35 (28d) 20C	28	20°C at 55% RH

Table 9.2 Curing and conditioning regimes.

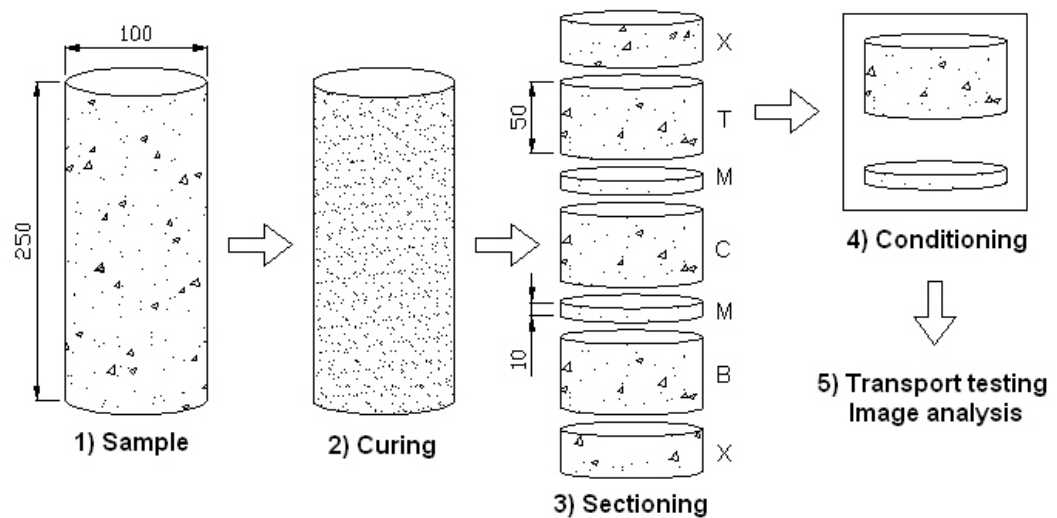


Figure 9.2 Flow chart for sample preparation and testing. Discs marked ‘M’ are for microscopy, ‘T’, ‘C’ and ‘B’ (Top, Centre and Bottom) are for transport testing. End discs (‘X’) are discarded. All dimensions in mm.

Since the samples were to be transport tested at room temperature, care had to be taken to ensure that the moisture content did not increase when the oven-dried samples were cooled. To ensure this, the oven-dried samples were transferred into a vacuumed desiccator and allowed to cool naturally to room temperature. The discs were taken out of the desiccator only when required for testing. Checks by weighing found negligible mass increase. Discs that were conditioned at RH 55% were wrapped in cling-film for another week to allow for moisture redistribution before transport testing and imaging.

9.3.2 Molecular transport testing

Three replicate discs were tested following the sequence of oxygen diffusion, oxygen permeation and water absorption. All specimens were tested at the same age (30 weeks) and at room temperature. Oxygen diffusivity (Section 3.4.1) was determined using the method suggested by Lawrence [1984]. Oxygen permeability (Section 3.4.2) was determined by measuring the steady-state flow rate at three input pressures of 0.5, 1.5 and 2.5 bars. The apparent permeability was calculated following Darcy's equation at each pressure, from which the intrinsic permeability coefficient was determined by using Klinkenberg [1941] correction. The water absorption test (Section 3.4.3) was performed by monitoring the mass gain due to capillary absorption of deionised water with time. The mass of absorbed water per unit area of the inflow face was plotted against the square root of time. A best-fit line was drawn for the first 15 readings (approximately 6 hours of measurement) and the slope of this is reported as the sorptivity coefficient. The coefficients of regression of the least squares fit in the Klinkenberg correction and water absorption plot were always greater than 0.99.

9.3.3 Backscattered electron imaging

After conditioning, the discs for microscopy were sectioned using a diamond saw to produce block specimens (40 x 20 x 10mm) at approximately mid-distance from the centre to the edge. A non-aqueous solution was used as a lubricating fluid. The blocks were vacuum-impregnated with epoxy, then ground and polished to a $\frac{1}{4}$ μm finish (Section 3.2.1.). The final flat-polished blocks were coated with carbon using an evaporative coater prior to imaging. A JEOL 5410LV scanning electron microscope operated at 10keV accelerating voltage, 10mm working distance and high vacuum was used for imaging. Twenty images were collected per sample at 500x magnification. The images were digitised to 1940 x 1455

pixels, giving a field of view of $240 \times 180 \mu\text{m}$ at a pixel spacing of $0.124 \mu\text{m}$. This magnification is commonly used for studying pore structure and was chosen as a compromise between adequate resolution and sampling size (Section 3.2.5). Areas of the microstructure to be imaged were selected randomly so that pastes at the ITZ and bulk pastes were both represented. In order to ensure random and unbiased sampling (Section 3.2.6), the microscope stage was programmed to move in a grid fashion, stopping at twenty predefined, equally spaced coordinates. Thus, the frequency of an image containing either the ITZ, bulk paste or both will solely depend on the aggregate distribution and volume fraction. Areas near the sample edge were not imaged to avoid sampling mortar that may have been saw-damaged.

9.3.4 Image analysis

BSE images of a mortar sample captured at 500x magnification will most likely contain some fraction of sand particles, which will vary significantly from frame to frame. The sand particles must first be removed from the original image (Section 4.41) before thresholding and measurement of the pore phase can be carried out. This is because the aggregate greyscale values overlap with that of the hydrated cement paste and this complicates the thresholding of the pore phase. The sand particles themselves may contain pores, but since they are relatively impermeable compared to the hydrated cement paste (Fig. 8.12), the aggregate pores should not be measured. Therefore, the sand particles are excluded in the analysis and all measurements on the pore structure are made relative to the cement paste.

A pore binary image was then produced by grey-level thresholding using the Overflow method presented in Chapter 4. The segmented pores consist of capillaries, micro-cracks and hollow-shells. Air voids and bond failures at the aggregate-paste interface were excluded since the former do not contribute to transport while the latter is an artefact of specimen preparation. The unreacted cement phase was segmented by taking the minimum point between the peaks for hydrated paste and anhydrous cement as the lower threshold value (Fig. 4.1).

Two important pore structure parameters that are easily obtained from a 2D image are the porosity and the specific surface (Section 2.4). Porosity is the volume fraction of the void phase while specific surface is the internal surface area of the solid-pore interface per unit volume. The specific surface, when normalised to the pore volume, is equivalent to the inverse of the hydraulic radius, a parameter that relates to the degree of pore refinement or pore complexity. For two materials having the same porosity, but different specific surface

areas, the one that has a higher specific surface will have a larger number of finer pores, and/or a more tortuous boundary. Thus, it would be expected that transport increases with porosity, but decreases with specific surface.

Measuring area and boundary length in a digital image can be an error-prone operation because of the finite pixel size and image resolution, particularly for small features. When imaged at higher magnification or at a better resolution, more irregularities of the feature boundary become visible; the measured perimeter and area changes and becomes a better approximation of the true value. Monte Carlo simulation presented in Chapter 6 (Fig. 6.15) showed that for the current microscope set-up and image magnification, measurement errors due to finite pixel size and image resolution are not significant for pores larger than $1\mu\text{m}$, but the error increases for pores smaller than this and becomes substantial ($>50\%$) when the pores are smaller than the probe size ($\sim 0.1\mu\text{m}$). In addition, small features may also be noise generated from image capture and segmentation. Therefore, to reduce these errors and uncertainties concerning measurement of small particles, a size filter was applied on the pore binary image that excludes features smaller than 10 pixels. Hence, the smallest detected pores have an equivalent circular diameter of $0.44\mu\text{m}$. Monte Carlo simulation predicted a measurement error of about 25% associated with pores at this size, which decreases to $\sim 5\%$ for pores at $1\mu\text{m}$ and $< 1\%$ for pores larger than $5\mu\text{m}$ (Fig. 6.15).

The area fraction of segmented pores (Φ_p) and unreacted cement particles (AH_p), and the specific surface (S_p) are calculated from the following equations:

$$\Phi_p = \frac{\sum_1^n A^o}{\sum_1^n A_p} \quad \text{Eq. 9.1}$$

$$AH_p = \frac{\sum_1^n A_{AH}}{\sum_1^n A_p} \quad \text{Eq. 9.2}$$

$$S_p = \frac{4}{\pi} \frac{\sum_1^n \Gamma}{\sum_1^n A^o} \quad \text{Eq. 9.3}$$

Where A° , A_p , A_{AH} and Γ are the measured pore area, paste area, unreacted cement area and pore perimeter respectively. The suffix 'p' indicates that the area fraction of segmented pores and unreacted cement particles are normalised to the paste area, while the specific surface is normalised to the pore area. We found no significant change in the measured porosity and specific surface area by analysing more than about 20 images. The degree of hydration (α) can be estimated as follows:

$$\alpha = 1 - \frac{AH_p}{AH_o} \quad \text{Eq. 9.4}$$

Where AH_p is the area fraction of the unreacted cement phase obtained from image analysis (Eq. 9.2) and AH_o is the volume fraction of the initial cement content (normalised to the paste volume fraction), which is 0.31 and 0.47 for Mortar A and Mortar B respectively.

9.4 Results

9.4.1 Porosity, specific surface and degree of hydration

Fig. 9.3 shows the change in the detectable paste porosity and specific surface with the number of frames analysed. It is observed that a relatively stable value for detectable paste porosity and specific surface can be attained after analysing about twenty images. This suggests that the accuracy of the measurements will not be significantly improved even if more images, taken at the same resolution, were to be analysed.

The average values for paste porosity, specific surface and degree of hydration are given in Table 9.3. Note that the largest pore that was detected has an equivalent circular diameter of about 50 μm . The paste porosity and specific surface ranges from 8.9 to 33.5% and 2.4 to 5.5 μm^{-1} respectively, while the degree of hydration ranges from 0.59 to 0.89. As expected, a lower w/c ratio and a longer curing time resulted in smaller porosity. For samples at the same w/c ratio, the paste porosity decreases with increase in degree of hydration. Samples with similar w/c ratio and curing age, but conditioned at 20°C and 55% RH have a slightly higher degree of hydration compared to those conditioned at 50°C and at 105°C. Generally, the specific surface increases as the porosity decreases from A1 to B4, indicating pore refinement.

It is interesting to note that the samples from M 0.35 that were conditioned at 105°C (B1, B2) showed only a 0.7% decrease in paste porosity for a 12% increase in degree of hydration between 2 and 28-day curing. Similarly cured and conditioned samples from M 0.7 (A1, A4) showed a 12.9% decrease in paste porosity for a 26% increase in degree of hydration. This suggests that the additional hydration that occurred between 2 and 28-day curing for M 0.35 produced more densification of the C-S-H phase than densification of the capillary pores. This could be due to the finer and less connected capillary pore system in the low w/c ratio mix, which inhibits migration and deposition of hydration products into the capillary pores. However, it is also possible that some densification occurred on the finer capillary pores that were below the image resolution limit, and hence, was not detected.

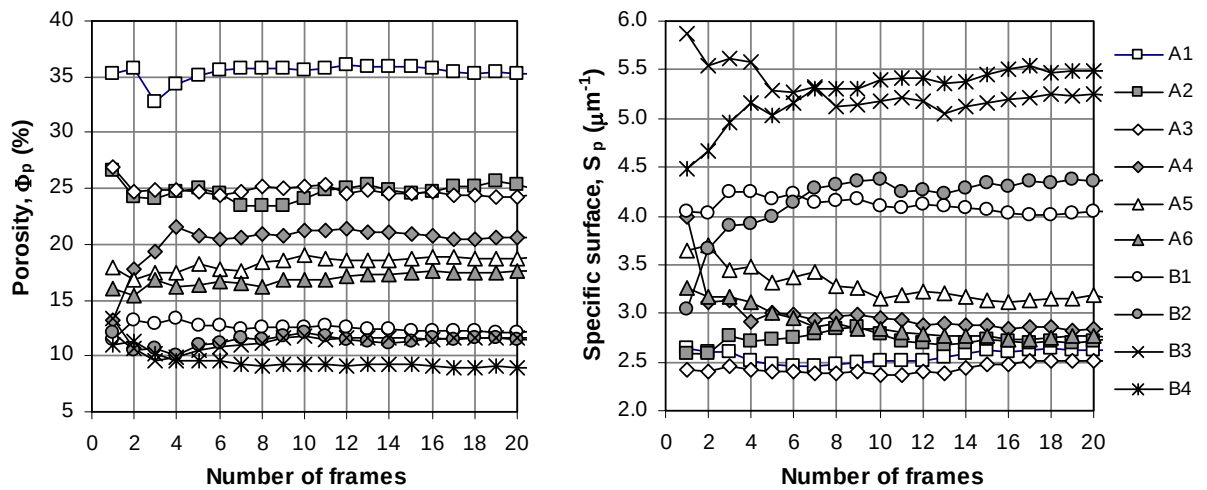


Figure 9.3 Variation of detectable porosity and specific surface with the number of frames analysed. A relatively stable value was obtained after analysing twenty frames.

Mix *	A 1	A 2	A 3	A 4	A 5	A 6	B 1	B 2	B 3	B 4
Φ_p (%)	33.5 (7.3)	24.6 (1.6)	24.3 (1.4)	20.6 (0.1)	18.1 (5.7)	17.6 (0.6)	12.4 (2.3)	11.7 (3.4)	11.3 (3.6)	8.89 (2.1)
S_p (μm^{-1})	2.59 (1.4)	2.82 (3.5)	2.44 (3.9)	2.94 (5.0)	3.32 (7.7)	2.87 (6.1)	4.06 (0.7)	4.39 (0.6)	5.06 (5.1)	5.51 (0.3)
α	0.59 (1.3)	0.60 (2.5)	0.68 (1.7)	0.85 (1.1)	0.87 (2.0)	0.89 (1.2)	0.59 (1.2)	0.71 (1.9)	0.72 (6.6)	0.74 (3.5)

*Values in parentheses represent coefficient of variation (%).

Table 9.3 Average values for paste porosity, specific surface and degree of hydration.

It may be instructive to compare the detectable paste porosity and specific surface values measured from image analysis to those obtained via other means. Day & Marsh [1988] measured the porosity of a various cement pastes cured in saturated limewater using several indirect methods, such as oven drying at 105°C to assess the non-evaporable water content, oven drying followed by resaturation with water, methanol and propanol, solvent exchange using methanol and propanol, and mercury intrusion porosimetry (MIP). The study found that for any particular paste/curing combination, there was a wide range in the porosity values estimated by the various methods. Results from MIP showed that after 28 days of curing in saturated limewater at 20°C, the w/c 0.71 OPC pastes had a porosity of 49%, while the w/c 0.3 OPC pastes had a porosity of 20%. In another study, Cook & Hover [1999] used MIP to determine the porosity of OPC pastes that were cured in saturated limewater at 23°C for up to 56 days. They found that the w/c 0.7 pastes had a porosity of 52% at 3 days and 42% at 28 days, while the w/c 0.3 pastes had a porosity of 22% at 3 days and 17% at 28 days.

By taking into account the slight differences in w/c ratio and curing regimes used in both studies, the MIP porosity values reported in these earlier studies can be considered to be within a similar range, but are substantially larger than the values obtained in this study using image analysis (Table 9.3), by a factor of 2 to 3. This discrepancy is not surprising because image analysis only measures a narrow range of pore sizes. As emphasised earlier, capillary pores smaller than the image resolution are excluded. Also, some large pores may not be counted because these are either inadequately sampled due to the image size and number of frames, or are intentionally excluded if it was considered a priori that these are isolated voids having little or no contribution to mass transport (for example air voids). In contrast, indirect methods cover a wider range of pore sizes including (perhaps) gel pores, small capillary pores and large air voids that are less relevant to mass transport.

Comparison between specific surface areas measured by image analysis with other methods such as gas sorption (N₂ or water vapour), small angle scattering using neutrons (SANS) or X-rays (SAXS), and nuclear magnetic resonance (NMR) relaxation would lead to an even greater discrepancy. For example, these methods normally give specific surface areas in the region of 50 to 150m²/g (N₂ sorption), 100 to 200m²/g (SANS), 200 to 600m²/g (SAXS) and up to as high as 900m²/g (NMR) for 28-day cured OPC pastes with w/c ratios 0.35 to 0.70 [Thomas et al, 1999]. Note that the surface areas are normalised to the weight of D-dried paste. Normalising to the pore volume fraction should give specific surface areas in the region of 200 to 4000μm⁻¹, which are about 2 to 3 orders of magnitude greater than the values reported in this study. The extremely high surface area obtained by these methods is because a large fraction of the reported value comes from gel pores in the hydration prod-

ucts, while the surface area contributed by capillary pores is relatively small. In addition, these methods (except for gas sorption) include isolated pores in their surface area measurements, while image analysis only determines the surface area of interconnected pores that are intruded by epoxy from the external surface.

Perhaps, a more appropriate comparison would be against the theoretical volume fractions as predicted by Powers' model [Powers & Brownyard, 1948], but bearing in mind that changes in cement composition over the last five decades may affect its validity for the cement used in this study. In Fig. 9.4, we compare the detectable paste porosity to Powers' capillary porosity of an equivalent cement paste, at the same w/c ratio and degree of hydration. The Power's capillary porosity is calculated using Eq. 4.3. This equation was derived by taking the specific volume of cement and non-evaporable water as $0.32\text{cm}^3/\text{g}$ and $0.75\text{cm}^3/\text{g}$ respectively, the non-evaporable water content as 0.23g/g reacted cement, the physical bound water (gel water) content as 0.19g/g reacted cement and the chemical shrinkage as $6.4\text{ml}/100\text{g}$ reacted cement.

Although the image porosity includes micro-cracks and hollow-shells in addition to capillary pores, all the image porosity values are found to be lower than the Powers' capillary porosity. The magnitude of difference ranges from about 15 to 50%, with higher errors associated with samples of higher w/c ratio. Unfortunately, the fraction of micro-cracks and hollow-shells was not determined because of difficulties in segmentation. Assuming that Powers' model is correct, the result suggests that many capillary pores are smaller than the image resolution and hence, were not detected. The underestimation could also be due to the fact that image analysis only measures the fraction of interconnected, epoxy-filled pores. Isolated capillary pores cannot be intruded by the epoxy and therefore, are not detected in the BSE images because of lack of atomic contrast (Chapter 7). On the contrary, Powers' model accounts for all capillary pores regardless of their connectivity. However, it is odd to find more discrepancy at higher w/c ratio. For Mortar A, the large deviation from Powers' capillary porosity could be due to bleeding effects, which may have reduced the effective w/c ratio by the bleed water evaporating from the sample or forming large cavities, so that assigning a w/c of 0.70 in the Powers' model erroneously overestimates the capillary porosity. The bleed water cavities are irregularly shaped, much like entrapped air voids from poor compaction, and therefore, are not sampled (by intent or otherwise) because these large isolated voids are not likely to make much contribution to transport.

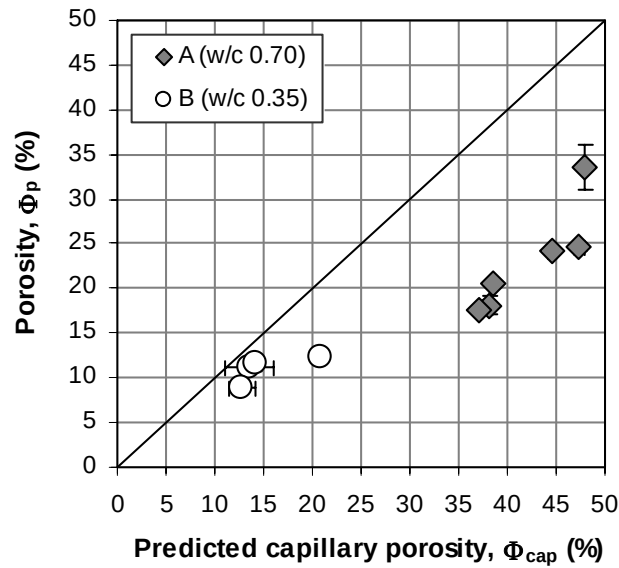


Figure 9.4 Comparison between detectable paste porosity and theoretical capillary porosity as predicted by Powers' model [Powers & Brownyard, 1948].

9.4.2 Correlations between transport properties and pore structure

Table 9.4 shows the average transport coefficients for each sample (three replicates). The results are consistent with the expectation that mass transport decreases with reduction in w/c ratio and with longer curing age. For similarly cured samples, conditioning at 105°C is the most severe regime with respect to its adverse effect on transport properties, followed by conditioning at 50°C and at 20°C, 55% RH. Rapid drying stops hydration earlier and this produces a coarser pore structure than it would otherwise. This is reflected in the measured porosity and degree of hydration values shown in Table 9.3. Drying at high temperature also generates high thermal gradients that may cause microcracking.

Fig 9.5 shows BSE images of samples that were conditioned at either 105°C or 20°C. These are selected from the set of images used for image analysis (Section 9.3.3) and can be considered to be representative of the typical microstructure observed from the image set for the particular sample. The BSE images give a general idea of how w/c ratio, curing age and conditioning regime affects the pore structure, and provides evidence of microcracking in samples conditioned at 105°C. The microcracks do not appear to have a preferred orientation, but some are connected to aggregate particles, suggesting that they originate from the ITZ. It is also interesting to note that the 2-day cured, 0.7 w/c ratio sample (A1) showed

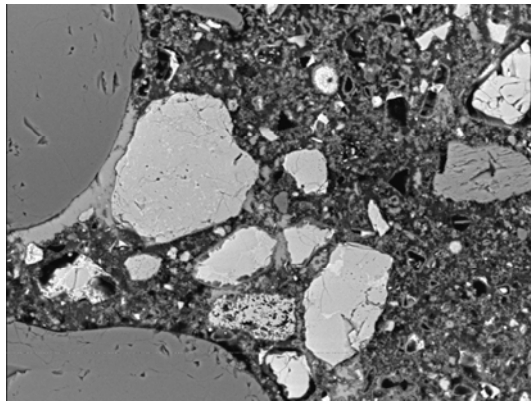
less microcracking compared to the 28-day cured samples (A4 and B2). This suggests that a highly porous sample has a lower cracking tendency, but it is also likely that the microcracks are obscured by the very porous nature of the sample. Generally, samples conditioned at 50°C were less affected by microcracking than those conditioned at 105°C.

Microcracks are anisotropic features with a high degree of heterogeneity and thus, it is not possible to accurately characterise them from a random 2D section using image analysis. Nevertheless, we can indirectly deduce the effect of microcracking by comparing the transport properties of similarly cured samples, but conditioned at either 105°C or 20°C. The results, plotted in Fig. 9.6, show that the effect of microcracking on transport properties is far more significant for M 0.35 than for M 0.70. Note that the large difference in transport properties between B2 and B4 cannot simply be attributed to the difference in degree of hydration, which is relatively small (Table 9.3). This suggests that in a low w/c ratio sample, microcracks play a more significant role in mass transport because they increase the volume and connectivity of the pore structure. In a high w/c ratio sample, microcracks have a lesser effect on transport properties since a highly porous and connected capillary pore structure is already existing in the sample.

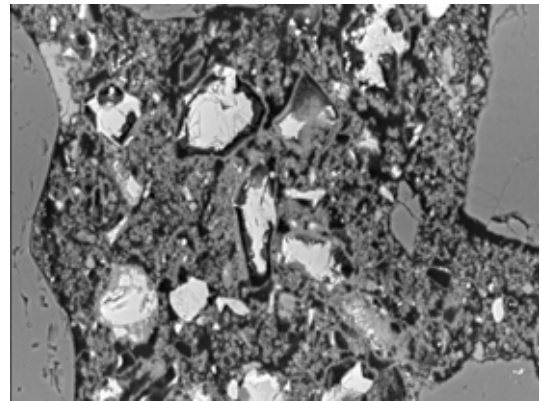
Sample	O ₂ diffusivity (m ² /s)	O ₂ permeability (m ²)	Sorptivity (g/m ² min ^{0.5})
A 1: M 0.7 (2d) 105C	6.28 x 10 ⁻⁷ (2.5%)	1.21 x 10 ⁻¹⁵ (17.7%)	710 (4.8%)
A 2: M 0.7 (2d) 50C	5.82 x 10 ⁻⁷ (8.0%)	8.13 x 10 ⁻¹⁶ (34.8%)	592 (7.4%)
A 3: M 0.7 (2d) 20C	5.35 x 10 ⁻⁷ (10.0%)	7.85 x 10 ⁻¹⁶ (45.2%)	573 (8.3%)
A 4: M 0.7 (28d) 105C	4.36 x 10 ⁻⁷ (10.8%)	4.27 x 10 ⁻¹⁶ (68.9%)	428 (1.5%)
A 5: M 0.7 (28d) 50C	3.38 x 10 ⁻⁷ (4.8%)	2.47 x 10 ⁻¹⁶ (15.1%)	314 (3.0%)
A 6: M 0.7 (28d) 20C	2.64 x 10 ⁻⁷ (9.4%)	3.79 x 10 ⁻¹⁶ (32.6%)	308 (1.7%)
B 1: M 0.35 (2d) 105C	2.23 x 10 ⁻⁷ (13.4%)	4.12 x 10 ⁻¹⁷ (53.8%)	205 (1.6%)
B 2: M 0.35 (28d) 105C	1.65 x 10 ⁻⁷ (6.1%)	3.78 x 10 ⁻¹⁷ (14.7%)	165 (3.5%)
B 3: M 0.35 (28d) 50C	1.16 x 10 ⁻⁷ (5.1%)	2.09 x 10 ⁻¹⁷ (34.1%)	108 (0.8%)
B 4: M 0.35 (28d) 20C	3.73 x 10 ⁻⁸ (5.5%)	3.59 x 10 ⁻¹⁸ (30.7%)	41 (2.1%)

*Values in parentheses represent coefficient of variation.

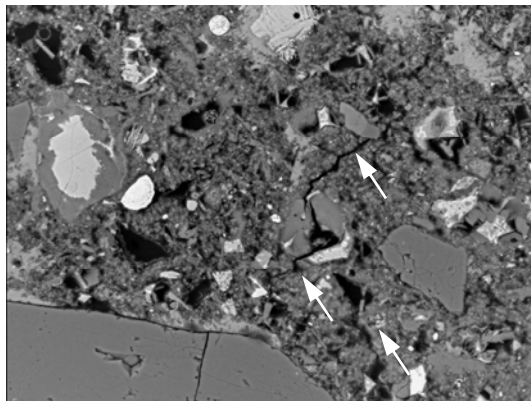
Table 9.4 Average transport coefficients



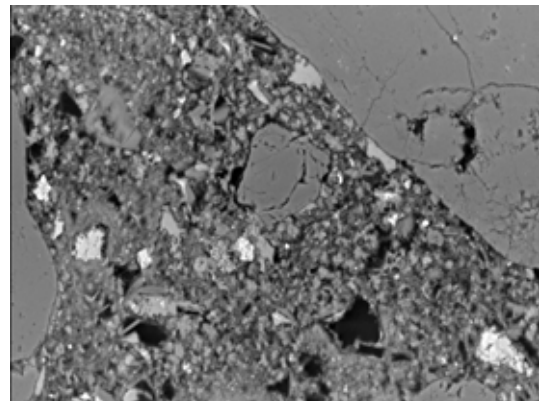
a) A1: M 0.7 (2d) 105C



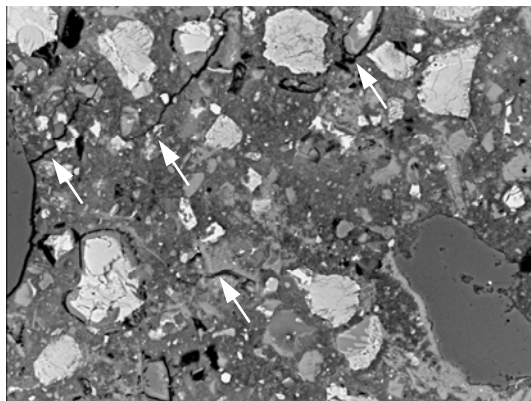
b) A3: M 0.7 (2d) 20C



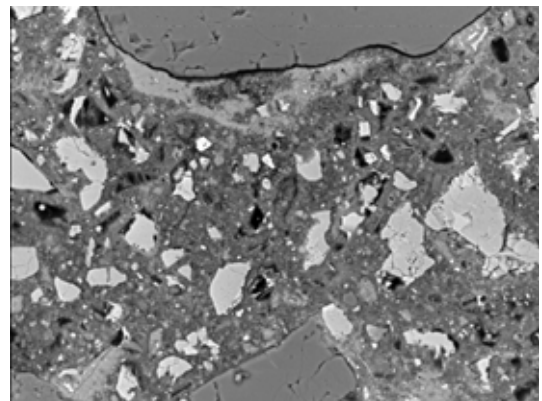
c) A4: M 0.7 (28d) 105C



d) A6: M 0.7 (28d) 20C



e) B2: M 0.35 (28d) 105C



f) B4: M 0.35 (28d) 20C

Figure 9.5 BSE images of samples conditioned at 105°C and 20°C. Samples conditioned at 105°C were found to be affected by microcracking (arrowed). (500x magnification, field of view: 240 x 180µm).

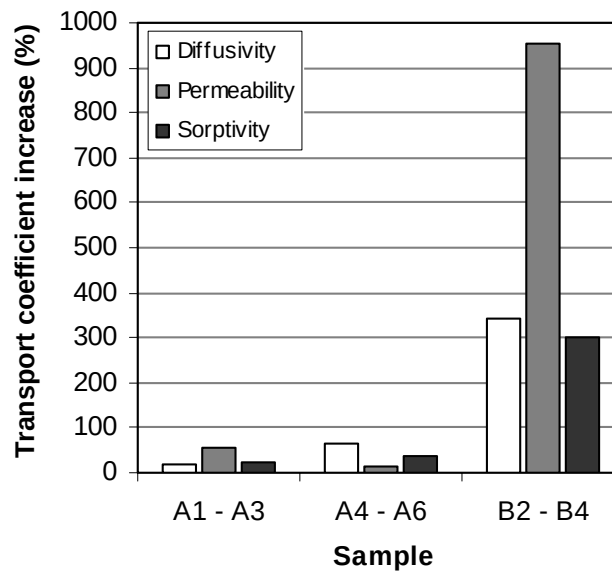


Figure 9.6 Percentage increase in transport coefficients as a result of conditioning at 105°C. The transport properties of M 0.35 are more affected by microcracking compared to M 0.7.

When the image porosity and specific surface values are plotted against transport coefficients in Fig. 9.7, strong correlations can be observed. Since the permeability coefficients cover more than 2 orders of magnitude, they were plotted on a logarithmic scale in order to display the data points. The regression lines were obtained using simple curve-fitting to either a linear, power, logarithmic, exponential or polynomial equation, whichever giving the highest coefficient of regression. Both diffusivity and sorptivity are found to have a positive linear correlation with porosity, while permeability is related to porosity by a power function. All transport coefficients are correlated to the specific surface by an inverse power function. The coefficient of regression (R^2) is greater than 0.85 in all cases.

The result suggests that despite the apparent limitation of image analysis, which only picks up a narrow range of pore sizes after having intentionally left behind the larger air voids (apart from the fact that it is two-dimensional), the pores that are included appear to have a strong influence on transport properties. The detectable porosity and specific surface values have high predictive potentials for transport properties and they may be used as input values for a pore structure-transport model, as will be shown in the following sections.

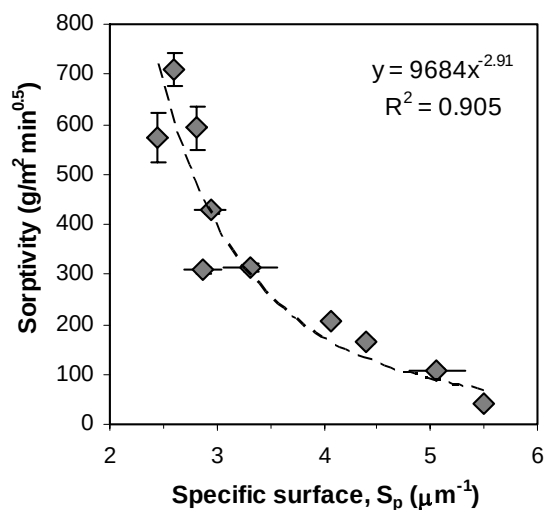
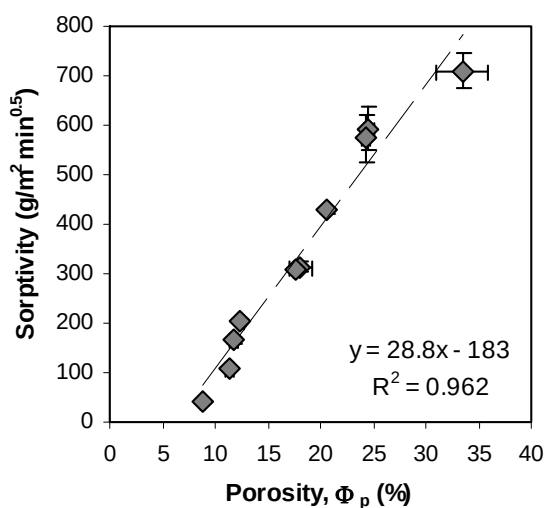
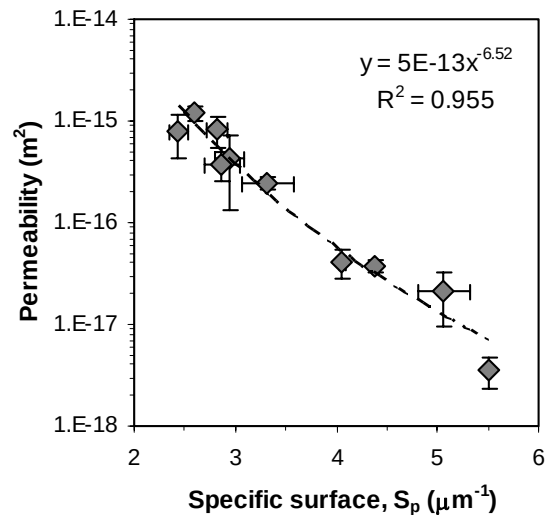
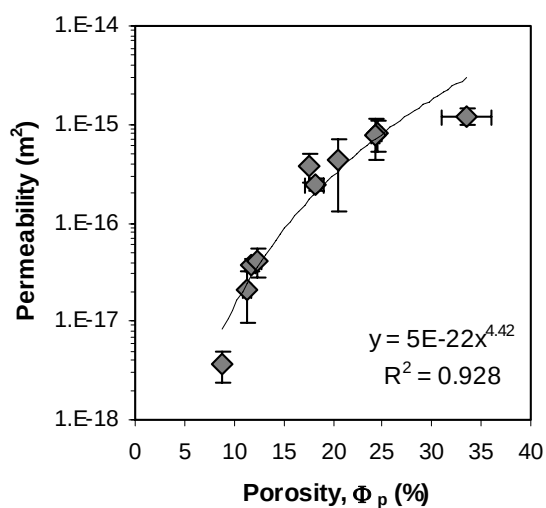
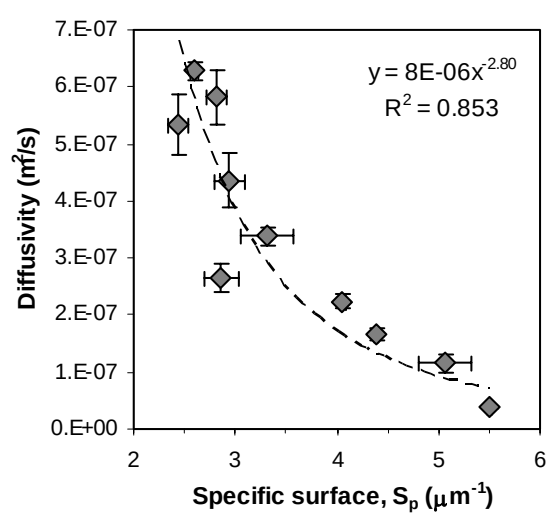
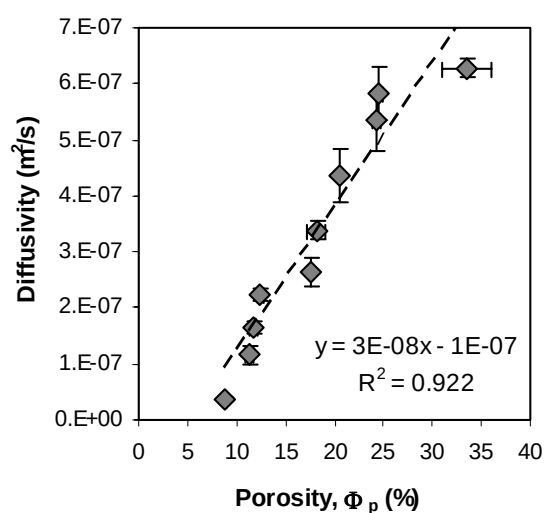


Figure 9.7 Relationships between transport coefficients and Φ_p or S_p . Error bars indicate plus-minus one standard deviation.

9.4.3 Predicting diffusivity from pore structure

The effective diffusion coefficient of a non-reactive species in a homogeneous isotropic porous medium, D (m²/s), may be related to its free diffusivity in the absence of the porous material, D_o (m²/s), by the following equation [Van Brakel & Heertjes, 1974]:

$$D = D_o \frac{\delta \Phi}{\tau^2} \quad \text{Eq. 9.5}$$

Where Φ is the porosity, and τ and δ are dimensionless parameters accounting for tortuosity ($\tau \geq 1$) and constrictivity ($0 < \delta \leq 1$) of the porous media. In effect, the above relationship attempts to scale D_o to D by including factors that correct for the reduced available volume for diffusion (Φ), the increased transport path length due to the ‘crookedness’ of the actual pore channels (τ), and the variation in cross-section of a pore channel over length (δ).

Tortuosity is traditionally defined as the ratio of the effective travel distance of a molecule through the pore channel to the shortest straight flow path through the medium [Epstein, 1989], i.e. $\tau = L_e/L$. In mortars, the tortuosity of the hydrated paste that is formed because of the presence of aggregate particles can be used as an estimate for the tortuosity of the true transport path. This approach, of course, assumes that because aggregate particles have very much lower porosity than the paste, they act as solid impermeable particles. This is a reasonable assumption because results presented in Section 8.5 (Fig. 8.12) showed a consistent reduction in transport properties with increase in sand content in mortars. This indicates that the aggregate particles are of very low permeability and that mass transport properties are controlled by the volume fraction and microgeometry of the pore structure in the cement paste.

Using stereology, Stroeven [2000] showed that the paste tortuosity is invariant to the aggregate size distribution and can be calculated from the aggregate volume fraction, V_a :

$$\tau \text{ (paste)} = 1 + 0.5V_a \quad \text{Eq. 9.6}$$

For the present study, $V_a = 0.63$ gives a value of 1.315 for the paste tortuosity. We shall use this, but recognise that it is only a lower-bound estimate for the tortuosity of the true transport path. This is because the true tortuosity should equal the paste tortuosity plus the capillary pore tortuosity, i.e. the above equation should, in theory, include a factor (≥ 1) representing the ‘natural’ tortuosity of the capillary pores in a paste specimen (when $V_a = 0$). This factor is unknown, but is expected to be a function of Φ and approaches unity when porosity is high, i.e. $\lim(\tau) = 1$ when $\Phi \rightarrow 1$. Nonetheless, when V_a is large, as in the case of this study, the error caused by exclusion of this factor is not expected to be very great. For comparison, theoretical modelling based on various random capillary pore network models has produced τ values of $\sqrt{2}$ (≈ 1.44) [Carman, 1937; Peterson, 1958] and $\sqrt{3}$ (≈ 1.73) [Bhatia, 1985; Dykhuizen & Casey, 1989]. Other values for tortuosity, for example, $\sqrt{\pi/2}$ (≈ 1.25), have been reported [Haughey & Beveridge, 1969].

To estimate the constrictivity factor, the pore channels can be idealised as tubes of circular cross-section with radius that varies in a sinusoidal fashion along the length of the channel, i.e. $r(z) = r_o - \alpha \cos(2\pi z/\lambda)$, where α is the amplitude and λ is the wavelength of the radius variation. Constrictivity is then defined as the hydraulic conductance of the sinusoidal pore divided by the hydraulic conductance of a cylindrical pore with an average radius r_o . Bernabé & Olson [2000] showed that this can be written as a function of the ratio of minimum to maximum pore radius ($r_{\min}/r_{\max}$) along the sinusoidal pore:

$$\delta = \frac{G}{G_o} = \frac{2(1 - (\alpha/r_o)^2)^{7/2}}{2 + 3(\alpha/r_o)^2} = \frac{256\rho^{7/2}}{(1 + \rho)^4(5\rho^3 + 3\rho^2 + 3\rho + 5)} \quad \text{Eq. 9.7}$$

where $\rho = (r_o - \alpha)/(r_o + \alpha) = r_{\min}/r_{\max}$. Fig. 9.8 shows the variation of δ with ρ according to Eq. 9.7. Therefore, δ can be obtained from Eq. 9.7 using a suitable estimate for $r_{\min}/r_{\max}$. We were unable to measure this from 2D images, so we shall refer to Cargill [1984] who reported a value of 0.57 for a pore space formed by a simple cubic arrangement of mono-dispersed spheres and a value 0.29 for a more compact hexagonal packing. The average of these two values will be used, giving a constrictivity factor of 0.44.

The oxygen diffusivity in air, D_o , is calculated from the Chapman-Enskog equation [Thompson, 2000]:

$$D_o = \frac{1.8824 \times 10^{-3} \sqrt{T^3 (m_a^{-1} + m_b^{-1})}}{P \sigma_{ab}^2 \Omega_D} \quad \text{Eq. 9.8}$$

Where T (K) is the temperature, P (kPa) is pressure, m_a and m_b are the molecular weights of oxygen and air, σ_{ab} (nm) is the collision diameter, and Ω_D is the collision integral. For air at 293K and atmospheric pressure, the oxygen diffusivity is $2.0 \times 10^{-5} \text{ m}^2/\text{s}$.

To use Eq. 9.5 for diffusivity prediction, the image analysis porosity, Φ_p , has to be converted to overall porosity Φ , by taking into account the aggregate content, i.e. $\Phi = (1 - V_a) \Phi_p$. Fig. 9.9 shows the predicted diffusivity plotted against experimental values. The model tends to over-predict for the lower w/c ratio mortar, but the general agreement is reasonable, with 90% of the estimated values within a factor of two, and 100% within a factor of five from the measured values. The vertical bars in Fig. 9.9 represent the range of predicted diffusivity, should the true value for δ lie within $\pm 30\%$ of the chosen value (i.e. δ : 0.31 to 0.57; ϱ : 0.36 to 0.50) and for τ , from + 0 to 60% of the chosen value (i.e. τ : 1.315 to 2.104), hence covering most of the typical values of ϱ and τ reported in the literature. Given such a wide range for δ and τ , the predicted diffusivities are still within half an order of magnitude from the measured values.

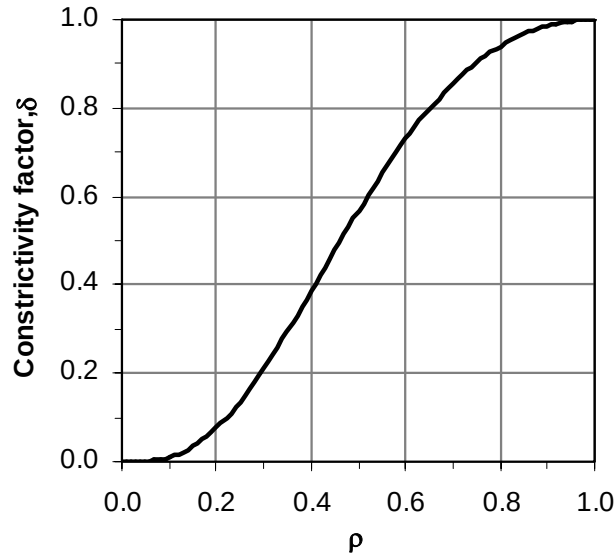


Figure 9.8 Variation of constrictivity factor, δ , as a function of the ratio of minimum to maximum pore radius, ϱ , for a sinusoidal pore channel [Bernabé & Olson, 2000].

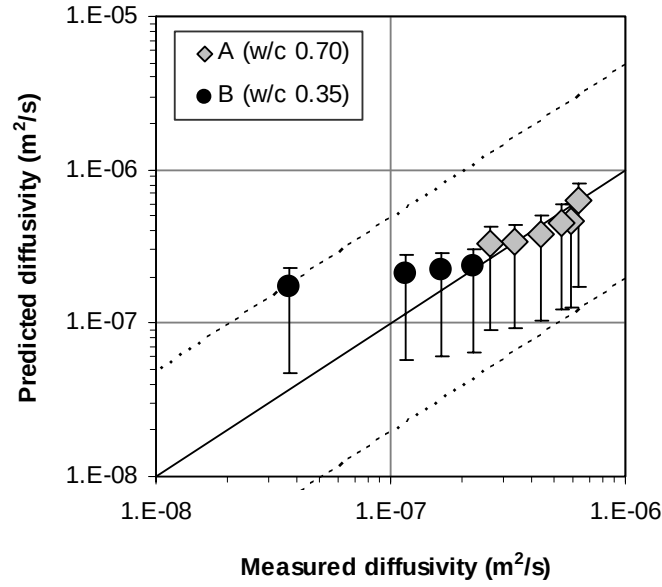


Figure 9.9 Predicted and measured values of oxygen diffusivity. 90% of the predicted values were accurate to within a factor of two and 100% to within a factor of five in relation to the measured values.

9.4.4 Predicting permeability using a Kozeny-Carman model

Relations between fluid permeability, porosity and specific surface are generally termed as Kozeny-Carman (K-C) models [Carman, 1956] and these were derived based on hydraulic radius theory for simple pore geometries. The basic example is considering flow, Q (m^3/s), through a single straight cylindrical tube of radius r (m), which is given by the Hagen-Poiseuille equation $Q = -(\pi r^4/8\eta)(\delta P/\delta z)$, where η (Ns/m^2) is the fluid dynamic viscosity and $\delta P/\delta z$ (N/m) is the pressure gradient along the tube. Note that the Hagen-Poiseuille equation is an exact solution of the Navier-Stokes equation for a straight circular tube. For a single cylindrical tube embedded in a block of solid material with cross-sectional area A (m^2),

Darcy's law gives $Q = - (kA/\eta)(\delta P/\delta z)$. Thus, by comparing Hagen-Poiseuille's equation with Darcy's law, it follows easily that the effective permeability, k (m^2), is:

$$k = \frac{\pi r^4}{8A} \quad \text{Eq. 9.9}$$

The porosity of the sample Φ is equivalent to $\pi r^2/A$, and the specific surface area, s (m^{-1}), is given by the tube surface area per unit volume of the sample, i.e. $s = 2\pi r/A$. Hence, Eq. 9.9 can be rewritten as a power function of Φ and s , giving:

$$k = \frac{\Phi^3}{2s^2} \quad \text{Eq. 9.10}$$

Eq. 9.10 is the original form of K-C model for the case of smooth-walled cylindrical pores where the tortuosity τ of the pore channel is unity. Derivation for a sample with n number of non-intersecting parallel cylindrical tubes of a particular radius distribution also yields a similar equation. Berryman & Blair [1987] showed that Eq. 9.10 is also valid for the case of straight tubes with arbitrary ellipsoidal cross-sections. For pores with tortuosity τ , Walsh and Brace [1984] showed that:

$$k = \frac{\Phi^3}{2\tau^2 s^2} \quad \text{Eq. 9.11}$$

The above equation assumes that the pores are of constant cross-sections, thus, it is proposed to include a term, δ , to take into account for the effect of constrictions in the pore throat. Considering that $s = \Phi S_p$ and $\Phi = (1 - V_a) \Phi_p$, we then have:

$$k = \frac{(1 - V_a)\delta}{2\tau^2} \frac{\Phi_p}{S_p^2} \quad \text{Eq. 9.12}$$

Eq. 9.12 can be interpreted as a relationship between permeability and the average hydraulic radius ($= 1/S_p$), with parameters that scale the permeability of a non-intersecting capillary tube model to include factors for complexity of the actual porous medium. Note that the factor 2 in the denominator is the originally derived shape factor for straight, circular pores.

Thus, the tortuosity and constrictivity factors act to transform the circular pore shape factor to a value that is supposedly representative of the actual pore geometry. Provided that τ and δ can be estimated realistically, the modified K-C model in the form of Eq. 9.12 contains no adjustable parameters. Eq. 9.12 can also be written in a form that involves the formation factor F . By taking the analogy between electrical conductivity and diffusion, and referring to Eq. 9.5:

$$F = \frac{\sigma_o}{\sigma} = \frac{D_o}{D} = \frac{\tau^2}{\delta\Phi} \quad \text{Eq. 9.13}$$

Substituting Eq. 9.13 in to Eq. 9.12 gives:

$$k = \frac{1}{2FS_p^2} \quad \text{Eq. 9.14}$$

Assuming that the pores are saturated with air that is of the same composition as ambient air, the formation factor based on measured oxygen diffusivity ranged from 30 to 530 for all the specimens; this is within the range of values that have been reported previously. For example, Tumidajski & Schumacher [1996] reported resistivity-based formation factors of between 83 and 314 for mortars at w/c ratios of 0.60 and 0.42, after curing for 7 and 28 days respectively.

Figs. 9.10 and 9.11 show the predicted permeability based on Eq. 9.12 and Eq. 9.14. The vertical bars in Fig. 9.10 represent the range of predicted values, given a $\pm 30\%$ error in δ and $+0-60\%$ error in τ . Both equations consistently overpredict with increasing error as the magnitude of permeability decreases. The model incorporating formation factor performed slightly better, with values predicted to within an order of magnitude. This is probably because inclusion of the formation factor in Eq. 9.14 has improved on the estimated tortuosity and constrictivity values.

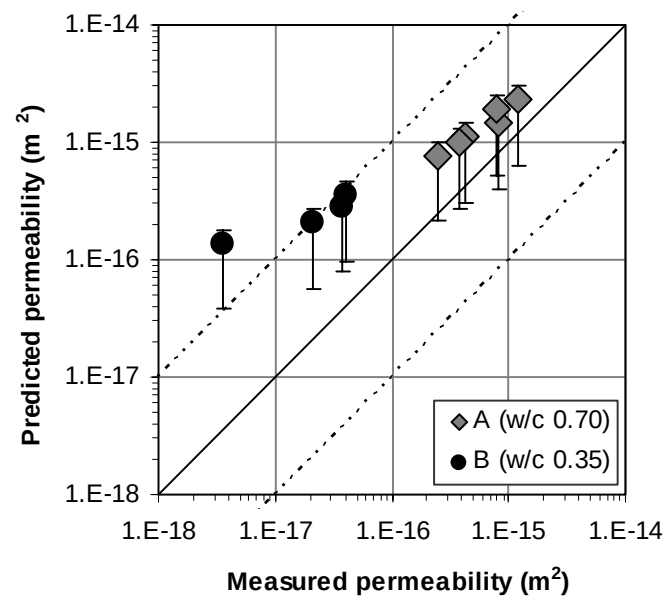


Figure 9.10 Predicted and measured values for permeability, using Eq. 9.12.

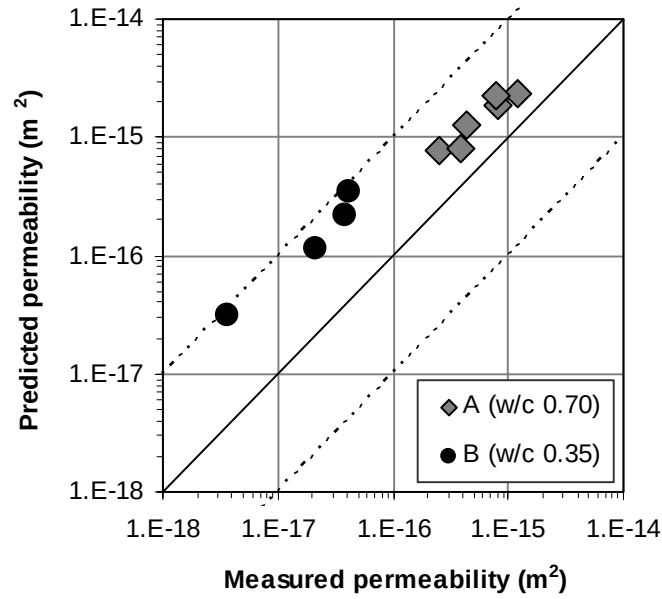


Figure 9.11 Predicted and measured values for permeability, using Eq. 9.14.

9.5 Discussion

As mentioned earlier, we would like to emphasise that this is an exploratory study of the feasibility of using image-derived pore parameters as inputs to simple analytical models for the prediction of transport properties of cement-based materials. Mortars were chosen for this preliminary study because they resemble concretes by having sand particles and aggregate-paste interfaces, but are more homogeneous by the exclusion of large aggregates. The decision to use very high and low w/c ratio was based on the intention to study samples of a wide range of pore structure characteristics and to determine the limits of applicability and sensitivity of the derived pore structure-transport relationships. Although only a small number of samples were tested, their transport properties cover a wide range of values (>1 order of magnitude for diffusivity and sorptivity, ~2.5 orders of magnitude for permeability). This reflects on the efficacy of the curing and conditioning regime to produce samples with a range of pore characteristics.

The major assumptions made in this study are: a) that all pores and cracks segmented from the image are interconnected, b) the image resolution is sufficient to include all pores contributing to transport and c) that the pores and cracks have the same relative im-

portance to transport. The first assumption is reasonable because only pores that are filled with epoxy are visible in a BSE image and therefore, the segmented pores do not contain any isolated pores. Whilst it is impossible to measure connectivity, we can at least be certain that all the pores tallied from image analysis are interconnected. However, the second and third assumptions are not strictly valid because features smaller than the resolution limit have not been detected and cracks probably have a higher relative contribution to transport in a severely damaged sample. Nevertheless, the strong correlation obtained between the measured pore properties with transport coefficients and the relatively good prediction obtained shows that the range of pore size analysed is relevant.

The image porosity includes hollow-shell pores, but their actual role in transport is not known. Since hollow-shell pores appear to be enclosed by a layer of dense hydration products, it is generally assumed that transport does not occur through these voids, although no conclusive experimental evidence exists. However, our recent 3D observation using laser scanning confocal microscopy [Head et al., 2005] found that many of these hollow-shell pores are, in fact, connected to the capillary pores. The size and degree of connectivity between the hollow-shell and capillary pores increase with w/c ratio and reduces with age. Therefore, hollow-shell pores may contribute to transport particularly for very porous or high w/c ratio systems. To investigate this further, the image porosity and specific surface can be measured again by excluding the hollow-shell pores and if this results in a weaker correlation, this would indicate that the hollow-shell pores are indeed important to transport. However, isolating the hollow-shell pores from other capillary pores is not a trivial procedure despite them being visually distinct. A reliable segmentation method for hollow shells must first be developed, and work in this area is currently in progress.

The diffusivity and permeability for the 0.35 w/c ratio mortar were consistently over-predicted, with increasing error as the sample porosity decreased. These errors cannot only be explained by measurement errors from image analysis due to the finite pixel size and image resolution effect, which are comparatively modest. For example, Monte Carlo simulation predicted a maximum measurement error of about 25% (for a $0.4\mu\text{m}$ pore). Thus, using simple error analysis, this overestimation in length of the smallest segmented pore should only translate to an over-prediction of about 50 to 100% for diffusivity and permeability.

Because of the finite image resolution, pores smaller than $0.44\mu\text{m}$ were not included. However, these fine pores may play an important role in transport especially in the dense mortar. Improving the image resolution will be able to capture these, and measuring these will increase the specific surface significantly, but will have only a marginal effect on the po-

rosity, therefore the net result would be an improved prediction of permeability (see Eq. 9.12 and Eq. 9.14).

Another possible reason for the over-prediction is that at low pore volume fraction, the paste tortuosity significantly underestimates the true tortuosity since the actual transport path deviates more from the paste tortuosity as the pore structure become finer. This could explain why a better prediction was obtained for the higher w/c ratio sample. The over-prediction could also be a result of the influence of hollow-shell pores. For dense pastes, a large fraction of the observed pores represents hollow-shells that are ‘preserved’ as hydration proceeds. In dense pastes, hollow-shells are isolated from each other and the degree of connectivity with capillary pores is smaller, so transport may be governed only by the capillaries. Therefore, an improvement in the transport prediction is likely to be achieved if hollow-shells are excluded in the analysis for dense pastes.

Although the tortuosity and constrictivity factors used in this study have not been measured directly, it is shown that errors in the estimated values of δ and τ do not strongly affect the predictions. 3D imaging techniques, such as laser scanning confocal microscopy, are expected to provide valuable information about these, for instance, a better estimate for $r_{\min}/r_{\max}$. As mentioned earlier, the connectivity of the pore structure has been neglected in this study. However, tortuosity should in theory, be very closely related to connectivity; a highly connected pore structure of a random porous material should have a low tortuosity due to shortening of the effective transport path length and vice versa. This suggests that if tortuosity can be accurately determined, the error associated with not having connectivity as a parameter in the model will not be large.

As mentioned earlier, the specific surface area is an important factor influencing transport. Conventional techniques for determining specific surface area such as gas sorption, small angle scattering using X-rays or neutrons, and nuclear magnetic resonance, tend to give very high values for cement-based materials because the surface area of the gel pores is included as well. By using image analysis, Berryman & Blair [1986] measured the Φ and S values for several porous materials (glass beads and sandstones) using two-point correlation functions, and the measured values were subsequently used to estimate fluid permeability from a modified form of the Kozeny-Carman equation. They found that the predicted values agreed well with the experimental values (within 10-30%) for sandstones with a permeability range of tens to several hundreds of mD (about 10^{-14} to 10^{-13}m^2). More recent work by Blair et al. [1996] on several different porous glass and a variety of sandstones using similar techniques found that the values agreed to within a factor of 2 for most samples, and 3 for

all samples. Thus, it appears that the specific surface measured using image analysis provided a better input for the Kozeny-Carman model, because the finer gel pores were excluded due to the finite resolution of the digital image. However, there is yet to be any known application of the Kozeny-Carman model on cement-based materials.

Quenard et al. [1998] combined results from mercury intrusion porosimetry and BSE imaging with advanced multi-scale computational modelling techniques involving 3D reconstruction from 2D images and renormalisation using a cubic lattice pore network model, to predict vapour diffusivity and air permeability of lime-silica brick, clinker brick and Baumberger sandstone. The transport properties of the materials investigated ranged from $1 \times 10^{-15} \text{m}^2$ to $3.9 \times 10^{-14} \text{m}^2$ for air permeability and $5.6 \times 10^{-7} \text{m}^2/\text{s}$ to $1.1 \times 10^{-6} \text{m}^2/\text{s}$ for vapour diffusivity, which correspond to the most porous samples in the present study. The reconstruction technique and subsequent image-based computations by solving Stoke's equation using a finite-difference method and Laplace's equation using a conjugate gradient technique gave computed air permeability and vapour diffusivity within a factor of 2 of the measured values. The renormalisation technique gave permeabilities that were close to measured values (<50% error) but for diffusivity, the discrepancies were much higher, around an order of magnitude. It appears then, that the accuracy of the analytical models presented in this study is comparable to the more sophisticated computational models presented by Quenard et al. [1998]. However, we believe there is still much room for improvement, for example by increasing the image resolution to include finer pores and by using 3D confocal imaging to obtain better estimates for tortuosity and constrictivity.

9.6 Conclusions

Mortar specimens of a very high and low w/c ratio were cured and conditioned in several ways to produce specimens with a range of pore structure and transport properties. Using image analysis on backscattered electron images, porosity and specific surface values were determined, and these were found to correlate very well with the measured oxygen diffusivity, oxygen permeability and water sorptivity. This shows that despite the limitations of two-dimensional image analysis, it is still a viable tool for extracting quantitative information of the pore structure that can be used as input values for a transport prediction model. A model incorporating tortuosity and constrictivity was used to predict oxygen diffusivity and a variant of the Kozeny-Carman model was used to predict oxygen permeability. To estimate the effect of constrictions on penetrability, the pore channels were idealised as tubes of cir-

cular cross-sections of sinusoidally varying radius. For mortars, the paste tortuosity, which is a function of aggregate volume content, gives a lower-bound estimate of the true transport path tortuosity. It was found that the diffusion model tends to over-predict for the lower w/c ratio mortar, but the general agreement was reasonable, with 90% of the estimated values within a factor of two from the measured values. The Kozeny-Carman model, however, over-predicted all permeability values with an error of between half to one order of magnitude.

Chapter 10

Thesis summary including main conclusions

The aim of this thesis was to develop backscattered electron microscopy and image analysis methods for characterising and quantifying the pore structure in cement-based materials, so that a better understanding of its nature and influence on molecular transport properties can be achieved. The study hoped to adopt a more rigorous approach towards quantitative backscattered electron microscopy so that accurate and reproducible results are attainable. Backscattered electron microscopy, within its limits, can be an invaluable tool for cement and concrete research. The key lies in having the right sample preparation technique and a good understanding of the principles of electron microscopy, signal generation and image formation, to avoid misunderstanding and misinterpretation of the images.

In image analysis, the feature segmentation stage plays a crucial role. However, conventional methods for segmenting pores are subjective, hence, error prone and require many images to obtain statistically significant results. A new method to segment pores and cracks that eliminates operator judgement and requires fewer images was presented in this thesis. The method determines the upper pore threshold grey level from the inflection point of the cumulative brightness histogram. This value corresponds to the critical point where the segmented pore areas begin to ‘overflow’ to the surrounding paste. The technique resolves difficulties in defining the boundary of the pore phase, particularly for dense microstructures.

A Monte Carlo method was used to simulate the electron-solid interactions in cement-based materials. It was found that the size of the interaction volume and BSE sampling volume is a strong function of the beam energy, but is independent of the probe size for beam energies greater than 10keV. The maximum electron penetration depth ranges from 0.75 to 1.5 μm at 10keV and from 2.5 to 5.0 μm at 20keV. The distribution of BSE and characteristic x-rays within this interaction volume is not uniform, but is concentrated near the probe impact point. The maximum BSE sampling depth is approximately 30% of the interaction volume depth and its lateral dimension is almost equivalent to the interaction volume depth. The sampling volume of characteristic x-rays for each element depends on the beam energy and the critical excitation energy, and can be a substantial fraction of the interaction volume. For ettringite, the amount of material analysed in x-ray microanalysis is estimated to be in the order of 1 to 100 μm^3 at 10 to 20keV.

Monte Carlo simulation was further applied to study the variation of BSE signal across pore-solid boundaries. The study verified that the inflection point in the cumulative brightness histogram is a good estimate for the upper threshold grey value for pores, as proposed by the Overflow method. However, sampling of subsurface material can drastically change the pixel intensity and this limits the detection of pores shallower than $0.2\mu\text{m}$ at 10keV and $0.8\mu\text{m}$ at 20keV . This effect also causes solid phases to be incorrectly segmented when there is an underlying pore close to the surface. Large errors in image analysis can be expected when the measured feature size approaches the image resolution. The comparison between actual thickness and measured thickness of epoxy layers, after having been segmented using the Overflow method, showed good agreement for thicknesses greater than $1\mu\text{m}$. However, for values smaller than $1\mu\text{m}$, the error increases and is significant ($>50\%$) when the thickness of the epoxy layer is less than the probe size.

This thesis established that the recently reported phenomenon of patch microstructure is an artefact of sample preparation; the dense patch is a false impression caused by pastes that have been ground beyond the epoxy intrusion depth. For BSE imaging of cement-based materials, it is important to ensure that the pores are saturated with epoxy. The resin stabilises the microstructure and minimises damage during grinding and polishing, and provides contrast between the pore and solid phases. However, conventional epoxy impregnation under vacuum can only achieve a very shallow penetration depth. Thus, extreme care must be followed so that the sample is not ground beyond the epoxy penetration depth. This thesis proposed a modified epoxy impregnation method that achieves a deeper epoxy penetration, in the order of several millimetres, compared to hundreds of microns in the conventional technique. The deeper epoxy penetration gives more allowance for grinding and polishing, assuring that the finished surface remains saturated with epoxy.

A new image analysis method for investigating microstructural gradients at interfaces was presented. The method uses Euclidean Distance Mapping to generate microstructural gradient plots at single-pixel strip width, is faster than conventional dilation-subtraction strip analysis, and is not constrained by feature geometry and boundary conditions. The new method was applied to investigate microstructural gradients at the interfacial transition zone. The results showed that although the overall ITZ can be characterised by a strong gradient in anhydrous cement and detectable porosity, this is highly variable from location to location. The higher sensitivity of the new method enabled it to detect previously unreported effects of calcium hydroxide deposits on the aggregate surface on the porosity gradient. The measured 'average' characteristic of the ITZ via image analysis is dependent upon the extent of CH deposition at aggregate surfaces and on the adopted sampling procedure.

Molecular transport testing on mortars revealed a consistent decrease in oxygen diffusivity, oxygen permeability and water absorption, as the aggregate content (ITZ fraction) increases, indicating that the effects of decreasing paste volume (and total porosity) and increase in transport path tortuosity outweigh any effects of increased transport in the porous ITZ. However, computational models that assume a uniform porous ITZ surrounding all aggregate particles in order to study mass/ionic transport by using percolation theories predict a critical aggregate volume threshold, above which, transport should increase significantly due to overlapping of ITZs. This departure from experimental results may be explained by the observed spatial variability of the ITZ porosity gradient and its dependence on calcium hydroxide deposits, which has not been accounted for in these models.

The detectable porosity and specific surface of various mortar samples with a range of pore structure were measured using image analysis, and these were found to correlate very well with oxygen diffusivity, oxygen permeability and water sorptivity. This shows that despite the limitations of 2D image analysis, it is still a viable tool for extracting information about the pore structure that can be used as input values for a transport prediction model. A model incorporating tortuosity and constrictivity was used to predict diffusivity and a variant of the Kozeny-Carman model was used to predict permeability. To estimate the effect of constrictions on penetrability, the pores were idealised as tubes of circular cross-sections with a sinusoidally varying radius. For mortars, the paste tortuosity, which is a function of aggregate content, gives a lower-bound estimate of the true transport path tortuosity. It was found that the diffusion model tends to over-predict diffusivity for the lower w/c ratio mortar, but the general agreement was reasonable, with 90% of the estimated values within a factor of two from the measured values. The Kozeny-Carman model, however, over-predicted all permeability values with an error of between half to one order of magnitude.

Whilst this is a long way from being able to predict transport properties accurately, the study has given confidence to the notion that a more complete description of pore structure and micro-cracks will allow useful predictions of mass transport and of long-term performance. The main disadvantages of backscattered electron microscopy are that the pores are only characterised in two dimensions, and that the pore size resolved is limited by its spatial resolution. This thesis highlighted the need for increased resolution to capture finer pores that are important to transport, particularly for dense microstructures, and for three-dimensional imaging to obtain accurate topological (constrictivity, tortuosity and connectivity) information. The recently successful grant application for a field-emission scanning electron microscope and a laser scanning confocal microscope by the Concrete Durability Group at Imperial College London, will allow this to be further pursued.

Chapter 11

Recommendations for further research

This thesis has largely focussed on the development of backscattered electron microscopy and image analysis methods for quantifying the pore structure. The samples that were tested, although covering several w/c ratios, represented simple mixes and were by no means extensive. Most samples examined were relatively young (less than 28 days curing). Future work should apply the developed methods to a wider range of cement-based materials for a more comprehensive study of the pore structure, as well as to substantiate the findings of this study. This will give a better understanding of how the pore structure characteristics changes with mix ingredients and proportions, age, processing, exposure history and interaction with external species, and how they influence macroscopic behaviour.

This study has highlighted the need for higher image resolution in order to include fine capillary pores, as well as to reduce measurement errors of small resolvable features. A field emission scanning electron microscope with a brighter electron source that maintains a nanometre sized probe at high beam currents can achieve this. The Monte Carlo methods presented in this thesis can be used to assist in interpretation of these high-resolution images, as well as to establish the optimal imaging conditions and measurement limits.

The study also highlighted the need for 3D imaging to obtain accurate topological information (connectivity, tortuosity and constrictivity) of the pore structure. Laser scanning confocal microscopy (LSCM) can be used for high-resolution ($\sim 0.1\mu\text{m}$), 3D imaging of capillary pores and micro-cracks [Head & Buenfeld, 2005], albeit to a limited depth of about $10\mu\text{m}$. LSCM works by scanning in the lateral and vertical directions through an optically transparent material to obtain, non-destructively, sub-surface information. Pores impregnated with fluorescent resin give very bright intensities allowing capillary pores, hollow shells and micro-cracks to be imaged and isolated in 3D. If the imaging depth of LSCM proves to be a serious limitation for a particular application, then research efforts need to be placed on integrating the information obtained from multiple LSCM image stacks, or with other 3D imaging methods such as X-ray microtomography, which offer better imaging depths.

3D image analysis of pores is a relatively new subject. First, the raw data needs to be processed using filtering and deconvolution techniques to remove noise so that pores can be accurately segmented. A new segmentation method needs to be developed if the Overflow

method is no longer suitable for 3D images. The segmented pores can then be surface rendered and skeletonised to erode the pore space to single-voxel linked pathways that run along the geometric centre of the pore channels, and are connected at nodes (pore chambers). Pore throats are identified through a search of minima in the hydraulic radius of individual pore channels. Hence, the complex pore structure is reduced to a skeletal network, but retains the original topology. From this network model, topological information can be obtained. However, at present, these parameters remain conceptual and therefore much effort needs to be put into developing ways of making reliable measurements.

The EDM method for measuring microstructural gradients can be applied to other interfaces, for example the steel-cement paste interface in reinforced concretes, which is important in view of corrosion. The EDM method can also be extended to study the nearest-neighbour and nearest-surface distribution functions for all phases that exist in the microstructure (much like studying the spacing distribution of air voids). Information derived from these distributions may improve upon, or form a new basis for a microstructural simulation model. The EDM method can be further developed for application to 3D images so that the real, normal distances from a particular surface are measured.

This thesis showed that although the ITZ contains, on average, higher porosity than the bulk region, this is highly variable partly due to the presence of calcium hydroxide deposits on the aggregate surfaces. Molecular transport testing revealed that effects of decreased paste volume, higher transport path tortuosity and spatial variability of the ITZ outweigh any effects of increased transport in the porous ITZ. It would be interesting to study how the removal of these calcium hydroxide deposits via extensive leaching would affect the average porosity gradient, the associated spatial variability of the ITZ and transport properties. With extensive leaching, the porous ITZ may percolate in the manner similar to those predicted by computational models. It is also well known that the ITZ is structurally weaker and that microcracking occurs predominantly at the ITZ when under stress. Hence, it would also be interesting to investigate the percolative effects of these micro-cracks on mass transport.

For pore-transport modelling, a key issue is identifying the pore type and size range that is most relevant to transport. The effect of hollow-shell pores, air voids, cracks, as well as gel pores and their relative contribution to transport needs to be investigated. Concrete structures usually have micro-cracks originating from mechanical loading, drying or thermal cycling, therefore these must be considered in service-life prediction models in order to obtain reliable estimates. The expectation is that micro-cracks will facilitate molecular/ionic transport and that when they percolate, the effect will be large. However, this has not been

validated, let alone quantified by measurements. This is partly because cracks are difficult to characterise due to their high degree of heterogeneity. Future studies using 3D imaging may make advances in this area.

The 2D and 3D images represent localised ‘snapshots’ of the pore structure at different length scales. The challenge is to use the information contained in these to reconstruct a model that faithfully resembles the actual microstructure. However, this is not a simple process of aligning and stitching the various image formats to form a large composite image. This may be achieved by combining low order statistical parameters (volume fractions, n -point correlation functions), topology, fractal geometry and spatial variability (e.g. microstructural gradients at interfaces) of all phases, in addition to knowledge of cement hydration reactions and properties of constituent materials. The multi-scale global microstructure will serve as a platform to model not only molecular/ionic transport, but also various macroscopic phenomena such as crack initiation and growth, and deterioration at the pore-scale level.

Generally, there are two ways to predict mass transport from pore structure. The first approach is to use the measured pore parameters as direct inputs to ‘classical’ models such as Archie, Kozeny-Carman and Katz-Thompson. The major flaw of these models is that transport is related to an averaged descriptor of the pore structure and simplified assumptions such as treating pore space as non-intersecting cylindrical tubes are made while neglecting actual pore network topology. However, attempts can be made to improve these models by fitting parameters related to 3D topology. The second approach is to make direct flow computations from the topologically equivalent pore network. This is done by applying a net potential gradient across the pore network, numerically solving the flow flux and potential at each pore throat and computing the macroscopic conductance, i.e. permeability or diffusivity using Darcy’s or Fick’s law respectively. This, however, would require solution of a large system of linear equations. Thus, the feasibility of applying effective medium approximation to simplify and expedite exact network calculations needs to be investigated.

Transport coefficients can also be derived from direct simulation of flow through the actual 3D pore space obtained from confocal imaging. To calculate diffusivity or conductivity, finite-difference, finite-element and random walk simulation techniques can be used. Lattice-Boltzmann simulation or a finite-difference method to numerically solve the Navier-Stokes equation can be applied to predict permeability. Flow simulation can be carried out in saturated and partially saturated pores by taking into account surface adsorption and condensation in pores of high humidity. It is expected that this method would require extensive computation, but yield the most accurate results.

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Appendix I

Calculation for brightness, probe current and probe diameter

This section provides theoretical calculations for the brightness, probe current and probe diameter at different accelerating voltages for optimal imaging conditions for cement-based materials. The method is based on the one proposed by Goldstein et al. [2003], following the work of Smith [1956] and Pease & Nixon [1965]. The calculations are for tungsten hairpin-type scanning electron microscopes, and do not apply to other electron sources such as lanthanum hexaboride (LaB_6) or Schottky (ZrO/W) thermal field emission electron guns.

The electron gun is the heart of the electron microscope and its brightness, defined as the current density per unit solid angle, is the most important parameter controlling its performance at high magnification. Assuming other factors being equal, the electron probe current determines the magnitude of the emitted signals (secondary, backscattered, X-rays, etc), while the probe size and the sampling volume of the electron-solid interactions determine the spatial resolution of the electron microscope. Therefore, for optimal resolution, the electron optical system must be designed so that the largest possible probe current is obtained, but at the smallest possible probe size and sampling volume [Goldstein, 2003].

However, all imaging devices are constrained by fundamental statistical fluctuations in the signal, leading to limits of visibility. For any choice of imaging conditions, there will always be a level of contrast below which features are not visible. Thus, even with an optimal imaging strategy, certain phases will still not be visible under any imaging conditions within the operating parameters of the SEM. This is an inevitable limitation of the electron microscope, but recognising that such limitations exists and understanding how to optimise instrument parameters to achieve the best performance is critical for quantitative microscopy.

The maximum theoretical brightness for thermionic emitters, β ($\text{A}/\text{cm}^2\text{.sr}$), is a direct function of the accelerating voltage and can be calculated from the Langmuir [1937] equation:

$$\beta = \frac{J_c e E}{\pi k T} \quad \text{Eq. I.1}$$

Where J_c (A/cm²) is the emission current density at the cathode, e is the electronic charge ($=1.59 \times 10^{-19}$ C), E (V) is the accelerating voltage, k_B is the Boltzmann constant ($=1.38 \times 10^{-23}$ J/K), and T (K) is the emission temperature. The emission current density, J_c (A/cm²), from thermionic emission is given by the Richardson-Dushman equation:

$$J_c = A_R T^2 \exp\left(-\frac{W}{k_B T}\right) \quad \text{Eq. I.2}$$

Where A_R is the Richardson's constant ($= 120 \text{ A/cm}^2 \text{K}^2$ for thermionic emitters) and W is the work function ($= 4.5 \text{ eV}$ for tungsten). For a tungsten filament operating at a typical temperature of 2700K, the emission current density, J_c is 3.55 A/cm².

An important feature of the electron gun brightness is that it is conserved, that is to say that the brightness at any point in the microscope optical column is the same as the value measured at the electron source itself even as the individual values of probe current, size and convergence angle change. This can be expressed in the following equation, known as the 'brightness equation':

$$\beta = \frac{\text{current}}{\text{area} * \text{solid angle}} = \frac{i_p}{\left(\frac{\pi d_p^2}{4}\right) * \pi \alpha_p^2} = \frac{4i_p}{\pi^2 d_p^2 \alpha_p^2} \quad \text{Eq. I.3}$$

Where d_p is the probe diameter, i_p is the probe current, and α_p is the probe convergence angle, which is the half-angle of the cone of electrons converging onto the sample. The brightness equation presented above is the first of two important equations that allow for the development of a practical understanding of the electron-optical limitations of the SEM [Goldstein et al., 2003]. The second equation is the 'threshold equation', which is given next.

To achieve the highest resolution, d_p must be as small as possible while at the same time containing sufficient beam current to exceed the visibility threshold for the contrast produced by the features of interest. The visibility of a phase with respect to its surrounding depends on the difference in signal (number of electrons) detected when the beam is positioned on it and on the neighbouring regions, i.e. contrast. In order for two distinct phases to

be differentiated by an average observer, the change in signal due to contrast between the two phases has to exceed random noise by a factor of 5, i.e. $\Delta S > 5N$. This is known as the Rose [1948] criterion. To satisfy the Rose criterion, the probe current must be larger than a certain threshold value. The minimum probe current, I_p (A), that must be used to detect a certain level of contrast between two points in an image for a specific scan time and collection efficiency is given by the ‘threshold equation’ [Oatley, 1972]:

$$I_p > \frac{25e}{\epsilon C^2 t} \quad \text{Eq. I.4}$$

Where ϵ is the signal collection efficiency that depends on the signal yield from the electron-solid interaction and on the detector characteristics (angular size and energy response of the detector), i.e. the detector quantum efficiency, C is the signal contrast and t is the picture dwell time (=scan time/total pixels). According to Goldstein et al. [2003], the Rose criterion is not a fundamental physical law, but recent study by Bright et al. [1997] has confirmed its general validity. The Rose criterion can be taken as a conservative estimate of the threshold condition. Thus, the general imaging procedure is always to ensure that the beam current and scan times chosen are adequate, as computed from the Rose criterion, in order to guarantee visibility of the feature of interest.

For BSE imaging, the signal contrast between two phases is calculated from the backscattering coefficients, $C = (\eta_2 - \eta_1) / \eta_2$. Assuming that the microscope is set up to image an atomic contrast level of 2.5% with a detector collection efficiency of 0.1 and a scan time of 100s for a 1024 x 768 image, a probe current greater than 0.5nA must be applied. At this level, the epoxy-filled voids, hydrated cement paste (Aft, Afm and C-S-H), CH and ferrite can be differentiated from their brightness rightness intensity. This is generally observed in routine BSE imaging of cement-based materials.

Next, the aberration-free Gaussian probe diameter, which is the full-width at half-maximum height of the intensity distribution of the probe at the sample surface, is calculated. Because the electron brightness is conserved throughout the electron column, we can use the brightness equation to determine the Gaussian probe diameter at the sample surface. Hence, the brightness equation is rearranged to give:

$$d_G = \sqrt{\frac{4I_p}{\pi^2 \alpha_p^2 \beta}} \quad \text{Eq. I.5}$$

For a microscope with a final objective lens aperture of 100 μ m operated at a working distance of 10mm, α_p is 0.005rad.

In reality, the probe size is enlarged due to lens aberration. Based on work by Smith [1956], and Pease & Nixon [1965], the effective spot size d_p is equal to the square root of the sum of the squares of the Gaussian probe size and separate disc diameters due to chromatic aberration (d_c), spherical aberration (d_s) and aperture diffraction (d_d). This is given in the following equations:

$$d_p = \sqrt{d_G^2 + d_c^2 + d_s^2 + d_d^2} \quad \text{Eq. I.6}$$

Where $d_c = (\Delta E/E_o)C_c\alpha_p$; $d_s = 0.5 \times C_s\alpha_p^3$; and $d_d = 0.61\lambda_e / \alpha_p$

Where ΔE is the variation in the electron beam voltage (~ 2 eV for tungsten hair filament, [Broers, 1973]), E_o (eV) is the beam energy, C_c is the chromatic aberration coefficient (~ 1 cm), C_s is the spherical aberration coefficient (~ 2 cm) and λ_e (nm) is the electron wavelength, given by $\lambda_e = 1.24E_o^{-0.5}$.

Values for brightness, Gaussian probe diameter, lens aberrations and the effective probe diameters are given in the following table. Note that at normal-voltage operation (10-30kV), the final probe size is dominated the Gaussian probe diameter. At low-voltage operation (< 5 kV), the magnitude for the chromatic aberration and diffraction terms becomes relatively larger and plays an increasingly important effect.

E (keV)	β (A/m ² .sr)	d_G (nm)	d_c (nm)	d_s (nm)	d_d (nm)	d_p (nm)
5	2.7×10^8	177	20	1.3	2.1	178
10	5.4×10^8	125	10	1.3	1.5	126
15	8.2×10^8	102	7	1.3	1.2	102
20	1.1×10^9	88	5	1.3	1.1	89
25	1.4×10^9	79	4	1.3	1.0	79
30	1.6×10^9	72	3	1.3	0.9	72

Table I Calculated values of brightness (β), Gaussian probe diameter (d_G), chromatic aberration (d_c), spherical aberration (d_s), aperture diffraction (d_d) and effective probe diameter (d_p) at several accelerating voltages (E).

Appendix II

Standard error, relative standard error, confidence interval and number of fields required for statistical significance

It is common to find that repeated measurements of a particular object or feature do not produce identical results. Measurement variation stems from a variety of sources, such as the finite precision of the measuring tool (e.g. the finite pixel area in a digital image, signal noise) and the difficulty in defining what to measure (e.g. uncertainties in threshold selection). Another factor that limits the precision and accuracy of the measurements is variations due to a finite sampling process [Russ & DeHoff, 2001]. It is impossible to apply a strict measurement procedure to the entire population, i.e. to the entire surface of a polished block specimen, hence only a sample of the population is selected and measured. If the sampling process is done in a way that is representative of the population (i.e. random, uniform and isotropic), then the measurement results should allow us to infer something about the entire population. The methods that provide for a statistical characterisation of a finite data are presented in this section. However, these methods do not cover systematic variations that can arise from human errors, sampling bias et cetera.

Suppose we have captured a uniform random sample of n number of images, and for every individual image there is an associated measured quantity y_i (e.g. pore volume fraction), the sample mean, $\bar{y} = \frac{1}{n} \sum y_i$, is an unbiased estimator of the population mean μ . Note that for determining a sample mean where the reference space varies from one field to another (e.g. the average pore fraction in the cement paste for mortars or concretes where the cement paste area varies from one image to another), the correct unbiased estimator of the population mean μ is $\bar{y} = \sum A_i / \sum B_i$, where A_i and B_i represent counts for the phase of interest and the reference space respectively [Section 4.4.3].

The sample variance, s^2 , is defined as:

$$s^2 = \frac{1}{n-1} \sum_{i=1}^n (y_i - \bar{y})^2 \quad \text{Eq. II.1}$$

The sample variance is a measure of the distribution width and denotes the spread of the measured data. The sample variance is an unbiased estimate of the population variance, σ^2 , factored by $n/(n-1)$, which for large values of n , is effectively equal to σ^2 . The square root of the sample variance is known as the sample standard deviation, s , and is an unbiased estimate of the population standard deviation, σ . The mean, variance and standard deviation are the most basic tools in statistics for quantifying the location (mean) and dispersion (variance and standard deviation) of a population of values [Howard & Reed, 1998].

To obtain an idea of the spread of the data and its reliability, we make use of the coefficient of variation, $C.V.$, and the standard error, $S.E.$, which is estimated from the sample standard deviation:

$$C.V. = \frac{s}{\bar{y}} \quad \text{Eq. II.2}$$

$$S.E. = \frac{s}{\sqrt{n}} \quad \text{Eq. II.3}$$

Note that $C.V.$ relates to the variability of the values of y_i in the population, while $S.E.$ reflects the variability of the estimated sample mean $\bar{y}$ with respect to that population mean μ . It should also be noted that the increase in precision of an estimate, as quantified by the $S.E.$, reduces in proportion to the reciprocal of the square root of the number of sample n . Thus, the $S.E.$ is a measure of accuracy of an average, a smaller value of $S.E.$ reflects a higher accuracy of the mean. The $S.E.$ is dependent upon the sample size and would become smaller by increasing the number of sampling units.

For digital images recorded using backscattered electron microscopy, it will be inevitable that the recorded image will contain some amount of noise, or random fluctuations in the pixel brightness values that are not due to natural variations in the mean atomic number. One unavoidable source of noise is the counting statistics in the detector due to a small number of incident particles detected. The relative standard deviation for a given counting process is inversely proportional to the square root of the number of counts, i.e. pixels, tallied [Klug & Alexander, 1954]:

$$\sigma_{rel} = \frac{1}{\sqrt{N}} \quad \text{Eq. II.4}$$

Where σ_{rel} is the relative standard deviation and N is the number of counts tallied. This measure reflects only the variation due to the counting process itself, with a homogeneous population assumed to be present. For a sample with unknown homogeneity, any measured variability within the population is naturally increased by the fluctuation due to counting process. Thus, it is important to ascertain that the statistical variation due this counting process is much smaller than the variability in the population, as measured by the $C.V.$

It is important to understand the difference between the standard deviation, s , and the standard error, $S.E.$, of the calculated mean. The standard deviation is often used to denote the spread of the data. For a normally distributed data, 68% of the measured values are expected to fall within the range of $\bar{y} \pm s$, 95% within the range of $\bar{y} \pm 2 * s$ and 99% within the range of $\bar{y} \pm 3 * s$. The $S.E.$, however, reduces as the sample size increase, and gives an indication of the reliability of the result.

The $S.E.$ is used to generate a confidence interval, which gives a range of values, in the form of mean $\pm$ a value, in which we believe with a certain probability that the true value lies [Russ & DeHoff, 2001]. To obtain a confidence interval, we also need to know or assume the shape of the sampling distribution for the estimator. If the population mean is being estimated and the true population variance is unknown, then the Student's t-distribution is often used as a model of the sampling distribution [Russ & DeHoff, 2001]. This distribution is a modified form of the well known Gaussian distribution and changes width according to the number of sampling points n . Using the Student's t-distribution, a confidence interval for the estimated population mean can be written as:

$$\bar{y} \pm t_{1-\alpha, v} \frac{s}{\sqrt{n}} \quad \text{Eq. II.5}$$

Where $t_{1-\alpha, v}$ is the critical value of the t-distribution for v degrees of freedom ($= n - 1$) and is available in most statistics books. For example, for a sample size of $n = 30$, the critical t value at 95% confidence is 2.045. Hence, the 95% confidence interval can be written as:

$$\bar{y} \pm 2.045 \frac{s}{\sqrt{n}} \quad \text{Eq. II.6}$$

This means that we are 95% confident that the true population mean value will fall within the range of $\bar{y} \pm 2.045 * S.E.$. To put it in another way, the 95% confidence interval means

that the probability that the true mean of the population lies within this interval is 0.95. Therefore, the smaller the confidence interval, the more precise the estimate is.

The Student's t-distribution can also be used to determine the number of fields required per sample n , such that the sample mean $\bar{y}$, is within a certain δ % error from the true population mean μ , at a particular degree of confidence:

$$t_{1-\alpha, \nu} = \frac{\bar{y} - \mu}{s / \sqrt{n}} \quad \text{Eq. II.7}$$

$$n = \left(\frac{t_{1-\alpha, \nu} \times s}{\bar{y} - \mu} \right)^2 = \left(\frac{t_{1-\alpha, \nu} \times s \times 100}{\delta - \mu} \right)^2 \quad \text{Eq. II.8}$$

If the sample standard deviation, s , and mean, μ , is estimated from a sample size of 30, the critical t-value for a two-tailed test, $t_{0.025, 29}$ is equal to 2.045. Therefore, for an error of 10%, the number of fields required is given by:

$$n = \left(\frac{2.045 \times S}{0.1 - \mu} \right)^2 \quad \text{Eq. II.9}$$

Appendix III

Entropy maximisation

The entropy maximisation method proposed by Kapur et al. [1985] assumes that the entire histogram consists of two separate probability distributions; one for the object and the other for background. If s_0 is the assumed threshold for the object, the entropy (information content) of the black portion (object) is:

$$H_B = - \sum_{i=0}^{s_0} \frac{P_i}{P_s} \log_2 \left(\frac{P_i}{P_s} \right) \quad \text{Eq. III.1}$$

The entropy of the white portion (background) is:

$$H_W = - \sum_{i=s_0+1}^{255} \frac{P_i}{(1-P_s)} \log_2 \left(\frac{P_i}{1-P_s} \right) \quad \text{Eq. III.2}$$

Where $P_i = N_i / N$
 N_i = number of pixels with brightness intensity i
 N = total pixels in the image
 $P_s = \sum_{i=0}^s P_i$

The total entropy of the image is:

$$H_T = H_B + H_W \quad \text{Eq. III.3}$$

The value s_0 that maximises H_T is the threshold for object and background.

Appendix IV

Publications arising from this research

Journal papers

- [1] H.S. Wong, M.K. Head, N.R. Buenfeld, Pore segmentation of cement-based materials from backscattered electron images, *Cem. Concr. Res.*, 2005 (In press).
- [2] H.S. Wong, N.R. Buenfeld, Euclidean Distance Mapping for computing microstructural gradients at interfaces in composite materials, *Cem. Concr. Res.*, 2005 (In press).
- [3] H.S. Wong, N.R. Buenfeld, Patch microstructure in cement-based materials: Fact or artefact? *Cem. Concr. Res.*, 2005 (In press).
- [4] H.S. Wong, N.R. Buenfeld, M.K. Head, Estimating transport properties of mortars using image analysis on backscattered electron images, *Cem. Concr. Res.*, 2005 (Accepted).
- [5] M.K. Head, H.S. Wong, N.R. Buenfeld, Characterisation of ‘Hadley’ grains by confocal microscopy, *Cem. Concr. Res.*, 2005 (Accepted).
- [6] H.S. Wong, N.R. Buenfeld, Monte Carlo simulation of electron-solid interactions in cement-based materials, *Cem. Concr. Res.*, 2005 (In press).

Conference proceedings

- [1] H.S. Wong, N.R. Buenfeld, M.K. Head (2005), Estimating transport properties of mortars using image analysis on backscattered electron images, 10th Euroseminar on Microscopy Applied to Building Materials, June 22-25, University of Paisley.
- [2] M.K. Head, H.S. Wong, N.R. Buenfeld (2005), Characterisation of ‘Hadley’ grains by confocal microscopy, 10th Euroseminar on Microscopy Applied to Building Materials, June 22-25, University of Paisley.
- [3] N.R. Buenfeld, H.S. Wong (2005), Recent developments in backscattered electron imaging and image analysis of pores for predicting transport in concrete, Keynote paper, Workshop on Cementitious Materials as Model Porous Media: Nanostructure and Transport Processes, Monte Verita, Switzerland, July 2005.
- [4] H.S. Wong, M.K. Head, N.R. Buenfeld (2006), Quantitative image analysis of the pore structure of cement-based materials using backscattered electron imaging and laser scanning confocal microscopy, ‘Measuring, Monitoring, and Modelling Concrete Properties’, European Conference on Fracture, Alexandroupolis, Greece, July 3-7.