Cement and Concrete Research 89 (2016) 320–331

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

3D Monte Carlo simulation of backscattered electron signal variation across pore-solid boundaries in cement-based materials

M.H.N. Yio, H.S. Wong *, N.R. Buenfeld

Concrete Durability Group, Department of Civil and Environmental Engineering, Imperial College London, SW7 2AZ, UK

ARTICLE INFO

Article history:
Received 21 June 2016
Revised 9 September 2016
Accepted 9 September 2016
Available online xxxx

Keywords:
Backscattered electron imaging
Pore structure
Cement-based materials
3D Monte Carlo simulation
Image analysis
Pore segmentation

ABSTRACT

Three-dimensional (3D) Monte Carlo simulation was used to study the variation of backscattered electron (BSE) signal across pore-solid boundaries in cement-based materials in order to enhance quantitative analysis of pore structure. The effects of pore size, depth and boundary inclination angle were investigated. It is found that pores down to 1 nm can generate sufficient contrast to be detected. Visibility improves with larger pore size, smaller beam probe size and lower acceleration voltage. However, pixels in shallow pores or near pore boundaries display higher grey values (brightness) than expected due to sampling sub-surface or neighbouring solid material. Thus, cement-based materials may appear less porous or the pores appear smaller than they actually are in BSE images. Simulated BSE images were used to test the accuracy of the Overflow pore segmentation method. Results show the method is generally valid and gives low errors for pores that are 1 μm and greater.

1. Introduction

The microstructure of cement-based materials plays a critical role in controlling the performance of concrete structures. In particular, the pores (and cracks) inherent in the microstructure influences the durability of concrete structures as they provide channels for ingress of deleterious species (such as chloride ions, carbon dioxide, and sulphate ions) causing a range of degradation mechanisms. The pore structure, which ranges over six orders of magnitude from nanometre to millimetre, also controls strength, elasticity and other important engineering properties such as creep and shrinkage. As such, there is a huge interest in characterising the pore structure of concrete.

Backscattered electron (BSE) microscopy has long been established as a versatile technique for quantitative characterisation of concrete microstructure. This is because the technique is capable of providing actual images of the microstructure at very high resolution and allows different phases to be distinguished based on their brightness [1]. Phase brightness is a function of the collected BSE coefficient, which increases monotonically with mean atomic number of the phase. Hence, in a BSE image of epoxy-impregnated polished cement paste, the unreacted cement particles appear the brightest, followed by hydration products such as calcium hydroxide (CH) and calcium silicate hydrate (C-S-H), while the epoxy-filled pores and cracks appear the darkest. Some applications of quantitative BSE imaging in cement and concrete research include measuring reaction degrees, estimating mix composition and assessing deterioration. Quantitative BSE microscopy has also been used to characterise many other types of porous materials including bone [2], rocks [3] and alloys [4].

Two critical aspects of quantitative microscopy are the accuracy of feature segmentation and resolution, i.e. the smallest feature that can be reliably measured. Segmentation is usually carried out by selecting the appropriate upper and lower grey level threshold values from the brightness histogram that correspond to the phase of interest. However, the process can be ambiguous and prone to error [5]. This is partly because pixels near boundaries tend to exhibit gradual transition in grey values due to mixing of signals from neighbouring phases. As a result, different phases may share similar grey values making it very difficult to define the thresholds that can satisfy all boundary conditions. In quantitative microscopy, it also important to know the size of the smallest feature that can be reliably imaged and measured. This not only defines the capability of a particular instrument/technique, but also the accuracy and potential errors of the measurement. Furthermore, understanding factors that influence resolution helps optimisation of the imaging technique for a particular application.

Monte Carlo simulation of electron-solid interactions offers a unique means to study signal transition across phase boundaries [6,7] where experiments would not be possible. Such simulations could help improve image segmentation and establish the theoretical resolution for a particular phase of interest. The Monte Carlo technique uses a stochastic process to simulate the elastic and inelastic scattering of electrons in any solids and across any boundary types. Each electron trajectory is monitored in a stepwise manner from its entry point until the electron is either absorbed by the sample or backscattered. This technique has been developed over the last five decades to provide a theoretical foundation underpinning electron microscopy and X-ray microanalysis, and

* Corresponding author.
E-mail address: hong.wong@imperial.ac.uk (H.S. Wong).

http://dx.doi.org/10.1016/j.cemconres.2016.09.008
0008-8846/

to assist quantitative interpretation of SEM images. Details of the physics behind the technique can be found in [8,9].

In cement and concrete research, Wong and Buenfeld [10] have carried out Monte Carlo simulations to study the shape and size of the interaction volume, spatial and energy distribution of backscattered electrons and characteristic X-rays in cement-based materials. However, the study was limited to two-dimensional simulations of single phases and to tungsten thermionic emitters that have now been surpassed by field emitters. In this paper, we present three-dimensional Monte Carlo simulations to investigate how BSE signal varies across pore-solid boundaries in cement-based materials. A range of pore size, depth and orientation were simulated. Other variables included emitter type, beam accelerating voltage and probe diameter. The aim of the work was to better understand signal transition across pore-solid boundaries in order to enhance quantitative analysis of pore structure. Results were used to establish the resolution of BSE microscopy for pore analysis and to test accuracy of the Overflow pore segmentation method [11].

2. Simulation

2.1. 3D Monte Carlo simulation

3D CASINO (Version 3.2) was used to perform the simulations throughout this study. The Monte Carlo simulation software is an update of the 2D version developed by [12,13]. A comprehensive description of the software is given in [14]. In the current version, electron trajectories can be traced in three-dimensions in complicated models built from basic shapes and planes. This allows pore structure of different configurations to be investigated. Another important feature is the ability to perform areal scanning to generate realistic BSE images. This is particularly useful for testing and verifying quantitative image analysis. The software allows users to choose various simulation settings including the physical model, number of electrons, angle of incident beam, accelerating voltage, probe diameter etc. Furthermore, the accuracy of the software has been validated by [14] based on a comparison between simulated and measured backscattered coefficients of a silicon sample at beam energies below 5 keV.

In this study, the Mott model and the modified Bethe equation were adopted for modelling elastic scattering, and deceleration and energy loss of electrons respectively. In order to ensure that the obtained results were statistically significant, a large number of electrons was simulated per analysis. Unless otherwise stated, 4×10^5 electrons were simulated per spot for point and line scans. This yields a relative error of 0.16% ($\approx 1/n^{0.5}$, where n is the number of electrons). For areal scans, the number of electrons was halved to 2×10^5 per spot to reduce computation time, but still keeping a small relative error of 0.22%. The computational time for a typical simulation consisting of 124 points using 4×10^5 electrons at 10 keV was approximately 5.5 h on a workstation (Intel® Xeon® CPU E5-1650, 3.2 GHz processor). The angle of the incident beam was set perpendicular to the sample surface since this is the most common configuration for quantitative BSE imaging. The trajectory of each electron was traced until its energy fell below 50 eV or until it left the sample surface. The probe diameters used and their corresponding accelerating voltages are presented in the following Section.

2.2. Probe diameter

Four different types of emitter were simulated in this investigation to cover the range of emitters available in practice. These were tungsten and lanthanum hexaboride thermionic, Schottky and cold field emitters. The probe diameter for each emitter was derived based on the method proposed by [15]. The method uses practical brightness, which determines the actual amount of current in the probe, to calculate the source image size (d_I). The total probe diameter (d_p) was obtained by adding d_I together with other contributions including diffraction (d_A), chromatic (d_C) and spherical (d_S) aberrations using the root-power-sum (RPS) method as shown in Eq. (1). In order to eliminate assumptions concerning the electron probe profile, the full width median (FW50) values were adopted for all contributions. Further explanations of this are given by [15].

$$d_p = \sqrt{\left[\left(d_A^4 + d_S^4\right)^{1.3/4} + d_I^{1.3}\right]^{2/1.3} + d_C^2} \tag{1}$$

Table 1 shows the calculated probe diameters for all emitters at increasing beam energies of 5, 10, 15, 20, 25 and 30 keV. The calculated probe diameters ranged between 1 and 150 nm, and decreased with increasing beam energy as expected. Field emitters produced the brightest source and smallest probe diameters. Detailed calculations and assumptions involved are presented in Appendix I.

2.3. 3D models of pore-solid boundaries in cement-based materials

A total of 119 simulations representing a range of pore sizes and geometries were carried out. The pores were assumed to be filled with a low viscosity araldite resin ($C_{10}H_{18}O_4$) of 1.14 g/cm^3 specific gravity. This is because samples are usually impregnated with resin to preserve the delicate microstructure and produce atomic contrast for BSE imaging. Calcium silicate hydrate (C-S-H) was taken to represent the solid since this is the main binding phase and hydration product forming in the originally water-filled spaces during cement hydration. However, simulating the C-S-H phase is challenging because it has variable composition and disordered structure [16–19]. For simplicity, the general formula $x\mathrm{CaO}\cdot\mathrm{SiO_2}\cdot y\mathrm{H_2O}$ was used. The Ca/Si ratio of C-S-H in hardened cement pastes generally range between 1.2 and 2.3, with the mean value close to 1.75 [17]. The H_2O/SiO_2 ratio and C-S-H density depend on moisture state. However, high-resolution BSE imaging is usually performed on dried samples in vacuum. For C-S-H with a monolayer of water at 11% relative humidity, an approximated chemical composition of $1.7\mathrm{CaO}\cdot\mathrm{SiO_2}\cdot 2.1\mathrm{H_2O}$ and specific gravity of 2.47 g/cm^3 have been suggested [19]. These values were used throughout the study and it is

Table 1
Calculated practical brightness (B_{prac}), diameter of source image (d_I), contributions from chromatic (d_C) and spherical (d_S) aberrations and diffraction (d_A), and resulting total probe diameter (d_p) for different emitters at increasing accelerating voltages (E). W, LaB_6 and ZrO represent tungsten, lanthanum hexaboride and zirconium oxide respectively.

	E (keV)	B_{pract} (A/m^{2}sr)	d_I (nm)	d_C (nm)	d_S (nm)	d_A (nm)	d_p (nm)
Thermionic (W)	5	3.44E+08	153.54	6.80	0.45	1.87	154.07
	10	6.88E+08	108.57	3.40	0.45	1.32	108.89
	15	1.03E+09	88.65	2.27	0.45	1.08	88.90
	20	1.38E+09	76.77	1.70	0.45	0.93	76.98
	25	1.72E+09	68.66	1.36	0.45	0.83	68.85
	30	2.06E+09	62.68	1.13	0.45	0.76	62.85
Thermionic (LaB_6)	5	4.17E+09	44.09	3.40	0.45	1.87	44.78
	10	8.34E+09	31.18	1.70	0.45	1.32	31.62
	15	1.25E+10	25.46	1.13	0.45	1.08	25.80
	20	1.67E+10	22.05	0.85	0.45	0.93	22.34
	25	2.08E+10	19.72	0.68	0.45	0.83	19.98
	30	2.50E+10	18.00	0.57	0.45	0.76	18.24
Schottky Field Emitter (ZrO/W)	5	2.35E+11	5.88	0.55	0.07	1.87	6.89
	10	4.69E+11	4.16	0.28	0.07	1.32	4.87
	15	7.04E+11	3.39	0.18	0.07	1.08	3.97
	20	9.38E+11	2.94	0.14	0.07	0.93	3.44
	25	1.17E+12	2.63	0.11	0.07	0.83	3.08
	30	1.41E+12	2.40	0.09	0.07	0.76	2.81
Cold field emitter (W)	5	3.41E+12	1.54	0.18	0.05	1.87	2.91
	10	6.83E+12	1.09	0.09	0.05	1.32	2.06
	15	1.02E+13	0.89	0.06	0.05	1.08	1.68
	20	1.37E+13	0.77	0.05	0.05	0.93	1.45
	25	1.71E+13	0.69	0.04	0.05	0.83	1.30
	30	2.05E+13	0.63	0.03	0.05	0.76	1.19