Scanning Electron Microscopy in Concrete Petrography

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SCANNING ELECTRON MICROSCOPY IN CONCRETE PETROGRAPHY[1]

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ABSTRACT

Scanning electron microscopy has distinct advantages for characterization of concrete, cement, and aggregate microstructure, and in the interpretation of causes for concrete deterioration. Scanning electron microscope imaging facilitates identification of hardened cement paste constituents with greater contrast, and greater spatial resolution than for optical methods and provides ancillary capability for element analysis and imaging. Quantitative information may be extracted from these data, such as composition, phase abundance and distribution. Sample preparation and demonstration of some of the common imaging techniques and extraction of data using image processing and analysis are presented.

INTRODUCTION

The study of concrete microstructure has benefited greatly from the use of microscopic examination and in particular, scanning electron microscopy. Scanning electron microscopy imaging and X-ray microanalysis techniques have been developed for imaging the complex microstructure of concrete and provide images with sub-micrometer definition. Through combination of the information available in the backscattered electron and X-ray images, an accurate segmentation of the image into its constituent phases may be achieved. The application of scanning electron microscopy (SEM) enhances our ability to characterize cement and concrete microstructure, and will aid in evaluating the influence of supplementary cementing materials, evaluation of concrete durability problems, and in the prediction of service life. In this paper, the use of the

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scanning electron microscope will be explored through a discussion of specimen preparation and the demonstration of the commonly used imaging techniques. Their application to examination of concrete microstructure, the identification and quantitative measurement of phases will be illustrated.

The Scanning Electron Microscope

The SEM scans a focused beam of electrons across the specimen and measures any of several signals resulting from the electron beam interaction with the specimen. Images of topography can be used to study particle size, shape, surface roughness, and fracture surfaces, while polished surfaces are used for determination of phase distribution and chemical composition. X-ray microanalysis provides quantitative spot chemical analysis as well as maps of element distribution. Images are monochrome because they reflect the electron or X-ray flux resulting from the beam/specimen interaction. Backscattered electron and X-ray imaging are the most useful imaging modes for quantitative scanning electron microscopy. Computer-based image processing and analysis (IA) makes routine quantitative imaging possible.

Secondary Electron Imaging: Secondary electrons (SE) are low-energy electrons resulting from an inelastic collision of a primary beam electron with an electron of a specimen atom. Because of their low energy, they are readily absorbed and only those produced near the surface escape, resulting in an image of surface topography. The apparent shadowing in the image is a result of the absorption of the secondary electrons by intermediary parts of the specimen.

Figure 1 illustrates SE imaging of fracture surfaces of hardened cement paste. At early-ages cement pastes typically have sufficiently large void spaces that well-formed crystals can develop, while at later ages, the well-formed crystal shapes are generally found only in regions of very high porosity or in air voids. In the upper image one can see plates of calcium hydroxide, exhibiting a typical hexagonal habit, and ettringite needles. The lower image, a cement paste after 7 days hydration, illustrates ettringite with its needle-like habit, blocky calcium hydroxide crystals showing their characteristic cleavage parting along the basal plane, a Type I calcium-silicate-hydrate gel (C-S-H) identified by its short needle-like form and and fine bundles of Type I C-S-H, platy-Type II C-S-H, and ettringite needles. Type II C-S-H, more foil-like in appearance. SE imaging is principally applied in the examination of early-age paste microstructure, high-magnification imaging of

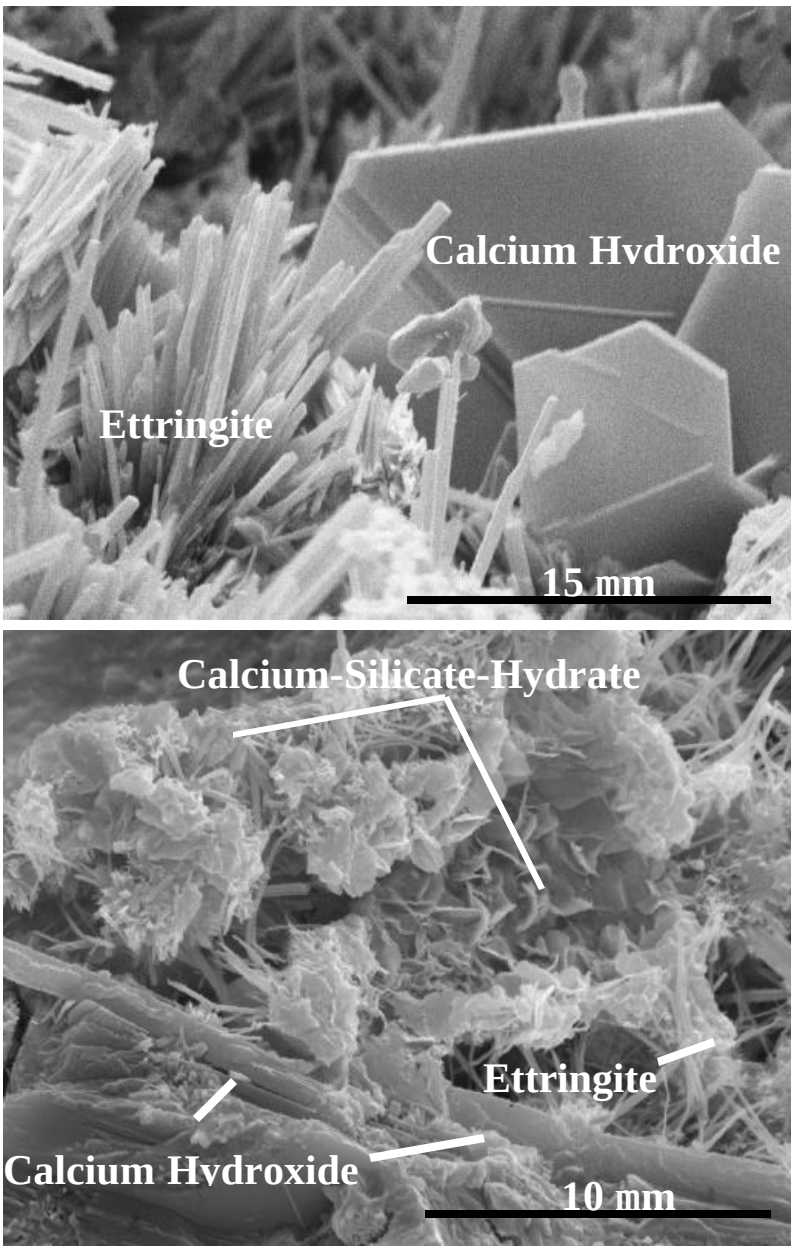

Figure 1. Secondary electron images showing the hexagonal habit of calcium hydroxide, needle-like habit of ettringite, and the sheet-like habit of calcium-silicate-hydrate. In the upper image, crystal growth into a void, where space restrictions are minimal, allowing development of euhedral forms. The lower image, being a more mature paste with limited space, exhibits crystal forms are more subhedral to anhedral. Here one may identify the plate-like CH morphology and fine bundles of Type I C-S-H, platy-Type II C-S-H, and ettringite needles.

microstructural features, and for examining aggregate texture. Knowledge of the morphological and compositional characteristics of the hardened cement paste constituents is invaluable for their identification. While SE imaging is useful for examining surface texture and crystal morphology, the rough surface makes measurements of phase abundance and distribution unreliable. As the hardened cement paste matures, filling of the void spaces eliminates the well-formed crystals shown in these figures with the resulting microstructure appearing nondescript. Backscattered electron and x-ray imaging are ultimately more useful in examination of these microstructures.

Backscattered Electron Imaging: Backscattered electrons (BE) are high-energy beam electrons that have been scattered by the specimen. The BE image contrast is generated by the different phases' compositions relative to their average atomic number, and is observed by the differential brightness in the image. Anhydrous cement appears brightest followed by calcium hydroxide, calcium silicate hydrate, and aggregate; voids appear dark (Figure 2).

Two morphological forms of calcium hydroxide are common, elongated crystals and massive. The elongated crystals are cross-sections of the hexagonal plates. These exhibit characteristic cleavage parting along basal planes and may represent early-formed CH where relatively unrestricted growth allowed the formation of the ideal hexagonal habit. The term massive CH (without form) may be used where the fine-grained habit shows no crystal form. This material fills voids in the C-S-H, and so, is probably a later-occurring product of the hydration process.

SEM analysis using backscattered electron and X-ray imaging requires a highly polished surface for optimum imaging and X-ray microanalysis. Rough-textured surfaces diminish the image quality by reducing contrast and poor feature definition [2]. Additionally, the lack of a polished specimen makes quantitative estimates arduous, as the surface is no longer planar.

Sample preparation uses an epoxy to permeate the material's pore system. Specimens are then cut or ground to expose a fresh surface, which is then polished using a series of successively finer grades of diamond paste. This polishing stage removes the cutting and grinding damage, exposing a cross section of the material's microstructure. Epoxy impregnation of the pore system serves two purposes: A) it fills voids and, upon curing, supports the microstructure, restraining it against shrinkage cracking, and B) it enhances contrast between the pores, hydration products, and cementitious material.

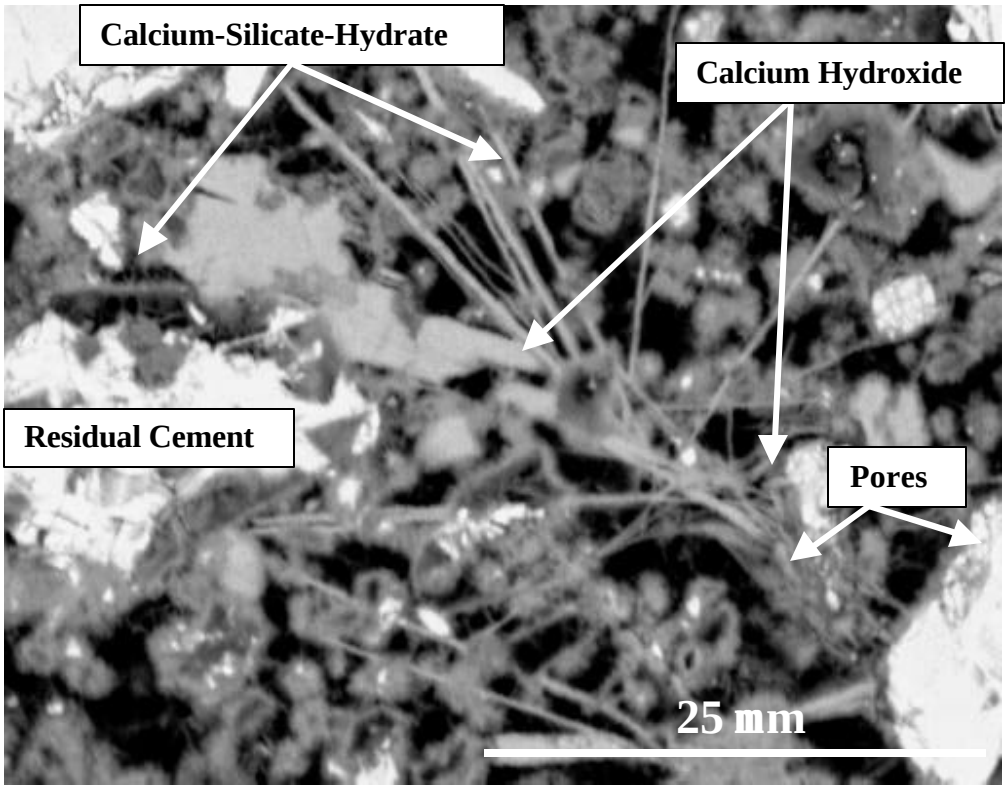

Figure 2. BE imaging of hardened cement paste at 1 day. Identification of calcium hydroxide is made by its relative brightness (between CSH and anhydrous cement), morphological characteristics (cross-sections of the plate-like crystals), and spot chemical analysis (calcium and oxygen). The BE image from a planar cross section, is amenable to both image analysis and x-ray microanalysis.

X-Ray Microanalysis: X-radiation is produced when a specimen is bombarded by high-energy electrons. X-ray microanalysis systems generally employ an energy-dispersive detector with the other detector type being a wavelength detector. The energy-dispersive detector has the advantage of collecting the entire spectrum at one time while the wavelength detector acquires the spectrum sequentially. The X-ray energy level is displayed as the number of counts at each energy interval and appears as a set of peaks on a continuous background (Figure 3). The positions of the peaks are characteristic of a particular element, so identifications are made by examination of peak positions and relative intensities. The X-ray signal can be used for: A) spectrum analysis to determine which elements are present and in

what concentration; B) line scan analysis to display the relative concentration changes along a line; and C) X-ray imaging (XR) of element spatial distribution and relative concentrations, to aid in phase identification. Mass concentration to a few tenths of a percent can be detected using an energy dispersive X-ray detector with relative accuracy of quantitative analysis (using certified standards) about ±20% for concentrations around 1%, and ±2% for concentrations greater than 50%. More details on x-ray microanalysis may be found in Goldstein et. al [1].

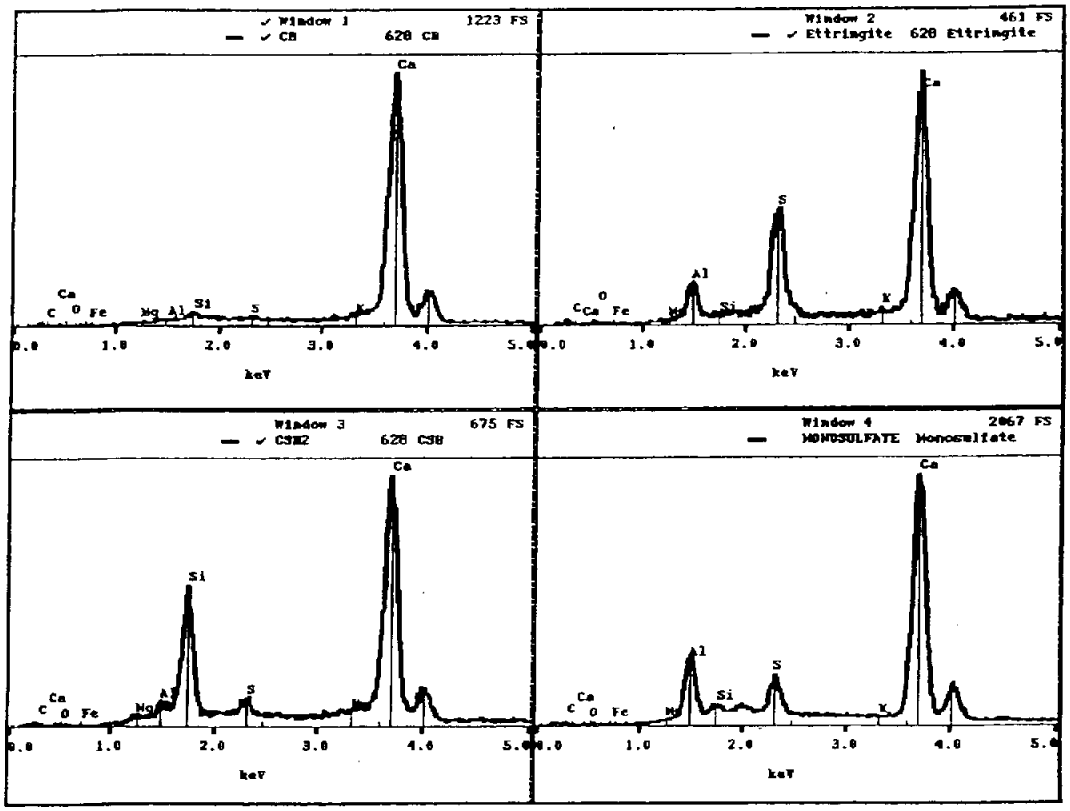

Figure 3. X-ray microanalysis is used for qualitative chemical analysis. These data, with morphological characteristic descriptions, may be used for phase identification through supposition of the element compositions and the relative peak intensities for selected elements.

In Figure 4, BE and X-ray (XR) images display constituents of hardened portland cement paste after about six months hydration. Compared to Figure 2, the large pores are greatly reduced as the hydration products fill the available space. Residual cement grains appear brightest followed the hydration products calcium hydroxide (CH), calcium-silicate-hydrate (CSH), and the darkest being the epoxy-filled pore spaces. Other constituents such as ettringite and monosulfate appear similar in gray level to that of CSH and the use of X-ray analysis and imaging simplifies their identification and imaging their distribution. Both of these phases do show greater uniformity and are a slightly darker gray than that of CSH and often exhibit a platy parting. Feature resolution is dependent upon instrument operating conditions, imaging mode and phase density. Secondary electron imaging resolution may approach nanometer-size while image resolution for the BE is approximately 0.25 μm and, for the x-ray images, about 1 μm.

Preparation of Cement Paste, Mortar, and Concrete Sections

Cement pastes, mortars, and concretes may be prepared in two ways: A) dry potting and B) wet potting. Dry potting is used when the specimen has been dried before, when drying shrinkage-related cracking is not of concern, or when a rapid preparation is needed and utilizes vacuum to permeate the specimen with epoxy. Wet potting is used to prepare a polished section where the material has not been dried and therefore has not undergone any drying shrinkage. Wet potting is a three-step process where the pore solution is replaced with alcohol (200 proof ethanol), then the ethanol is replaced with a low-viscosity epoxy, and then the epoxy is cured. Cracks observed using this preparation may then be ascribed to physical or chemical processes acting upon the concrete, and not due to drying-related shrinkage [3]

A diamond blade slab or a wafering saw, lubricated using propylene glycol exposes a fresh surface that is smoothed by grinding using silicon carbide abrasive papers of 320, 400 and 600 grit. Polishing removes the damage imparted by the sawing and grinding operations using a sequence of successively finer particle size diamond polishing pastes from 9 μm to 0.25 μm, and a lap wheel.

A thin coating of carbon serves to dissipate excess charge from the specimen while exhibiting little effect on image contrast and little interference with elements of interest. Metal coatings such as gold or gold palladium are suitable for secondary imaging of topographic features. However, their x-ray lines interfere with elements of interest and their use decreases BE contrast.

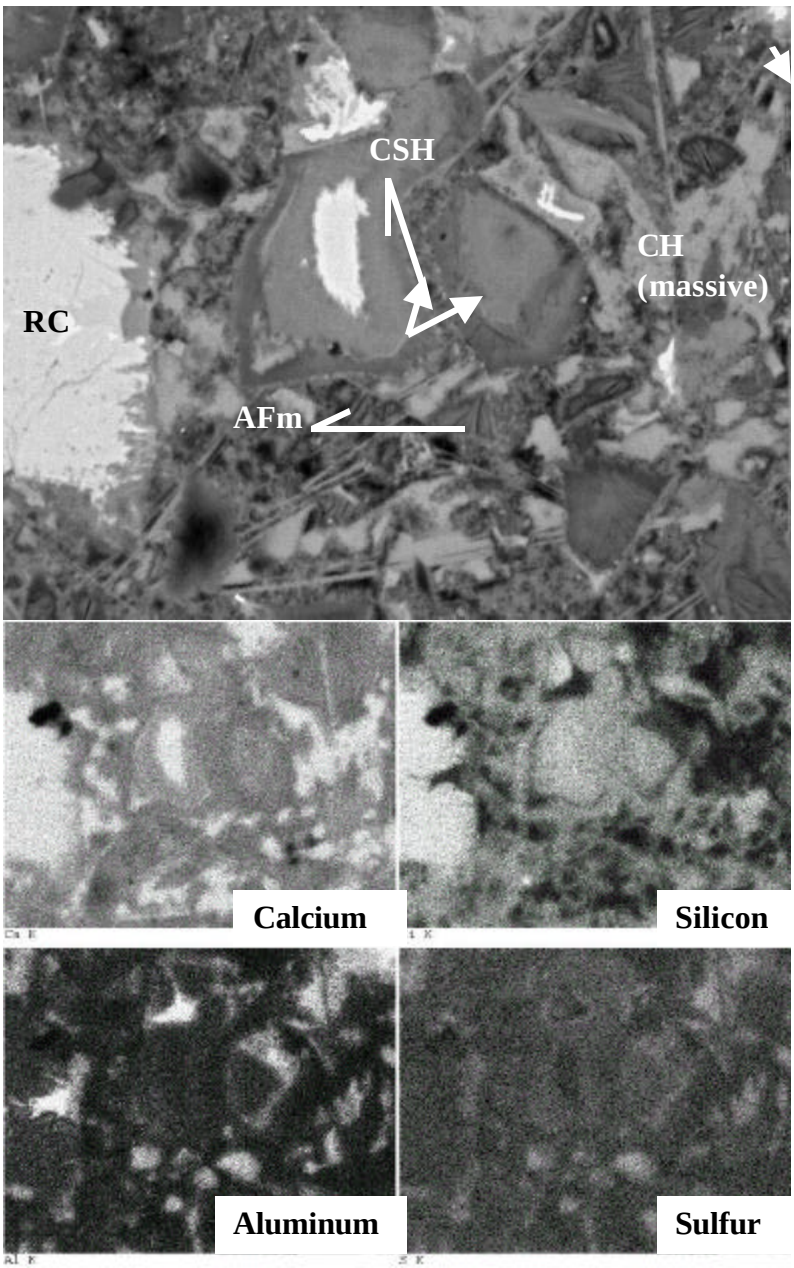

Figure 4. BE and X-ray imaging of a polished section of hardened portland cement paste. Residual cement (RC) appears brightest followed by calcium hydroxide (CH), calcium-silicate-hydrate (CSH), monosulfoaluminate (Afm), and other hydration products like ettringite and monosulfate. X-ray imaging acilitates distinction of the individual phases through examination of their constituent elements. Field width: 73 micrometers.

Quantifying microstructural features

The relationship between area fraction and volume fraction has been recognized for a long time, and was mathematically derived by Chayes [4] and explained by Galehouse [5] in the following way:

"In a randomly chosen area of a rock such as may be represented by a thin or polished section, the ratio of the area of a particular mineral to the area of all the minerals is a consistent estimate of the volume percent of the mineral in the rock. In simplified mathematical form, let

X = a particular mineral species in thin-section,
H = the thickness of the thin-section,
V = volume,
A = area.

Then the volume of X in the thin-section, V_x, equals $A_x \cdot h$ and the total volume, V, equals $A \cdot h$. Therefore:

$$\frac{V_x}{V} = \frac{A_x \times h}{A \times h} = \frac{A_x}{A} \qquad (1)$$

The problem of finding the volume percent of various minerals in a rock can therefore be reduced to finding the area percent of the mineral in a section."

Three approaches in determining the area percent of a constituent in a polished section are; A) the Delesse method of tracing and weighing each phase group; B) the Rosiwal-Shand linear traverse method; and C) the Glagolev-Chayes point count method. BE images are amenable to image analysis, a procedure comparable to that of the Delesse approach, while the Glagolev-Chayes point count method is often simpler and potentially faster. As the name implies, this technique involves sampling the polished section using a grid of points, and identifying the phase falling underneath each point. Additional points are measured by moving the specimen to a new field of view and again counting the phases under the points. The point count method is relatively simple yet provides a reliable means to physically measure phase abundance.

Hofmänner [6] indicated three sources of error that must be considered in point counting:

a) random sample errors,
b) errors in identification by the observer, and
c) measurement errors.

Implicit in this procedure is that a representative sample be collected. The measurement error of the analysis is related to the total number of points counted, with the absolute error at the 96% confidence interval given by:

$$\delta = 2.0235 \times \sqrt{\frac{P \times (100 - P)}{N}} \qquad (2)$$

Where

δ = the absolute error in percent,
P = the percentage of points of a phase, and
N = the total of all points.

The total error becomes smaller as the number of points counted increases, decreasing the uncertainty of the measurement. If desired, the results may be expressed as mass percentages, calculated by multiplying the volume fractions by the specific gravity of the corresponding phase and normalizing the totals to 100%

Image Processing and Analysis: Another approach to quantifying phase abundance is through image processing and analysis. Often features of interest may be uniquely identified based upon the gray level of the SEM BE image or by some combination of BE gray level and combination of X-ray images. The gray-level histogram is a plot of the number of pixels in each gray level and is helpful in setting thresholds for the upper- and lower-bounds of gray for a specific phase. The image processing operations, utilizing arithmetical and logical operations on the BE and X-ray images, serve to isolate features of interest while the analysis operations perform a measurement on the isolated features.

In Figure 5, X-ray imaging serves to identify the occurrence and distribution of calcium hydroxide in a hardened cement paste. Processing manipulates the image sets to produce a binary image of CH distribution. Here, CH is identified through specification of regions of moderate BE and moderate calcium intensity. Regions of the images satisfying these criteria are shown in the

binary image. This image may then be analyzed to estimate area fraction, phase shape, and distribution.

In Figures 6 and 7, the interfacial transition zone microstructure is assessed using SEM/BE imaging and image analysis. Four constituents are identified using the BE gray levels in Figure 6; residual cement being the brightest followed by calcium hydroxide, C-S-H gel, and pores showing as black. A gray-level histogram to the right of the image plots the number of image pixels across the gray scale. In Figure 7, the image is segmented into the four phases on the basis of gray level, and the constituents area fractions are estimated as a function of distance from the interface. This provides a graphical display of the changes in paste microstructure with distance. This plot is scaled to fit the image and is based upon single 10 µm-wide field estimates from the interface so no uncertainty values are available.

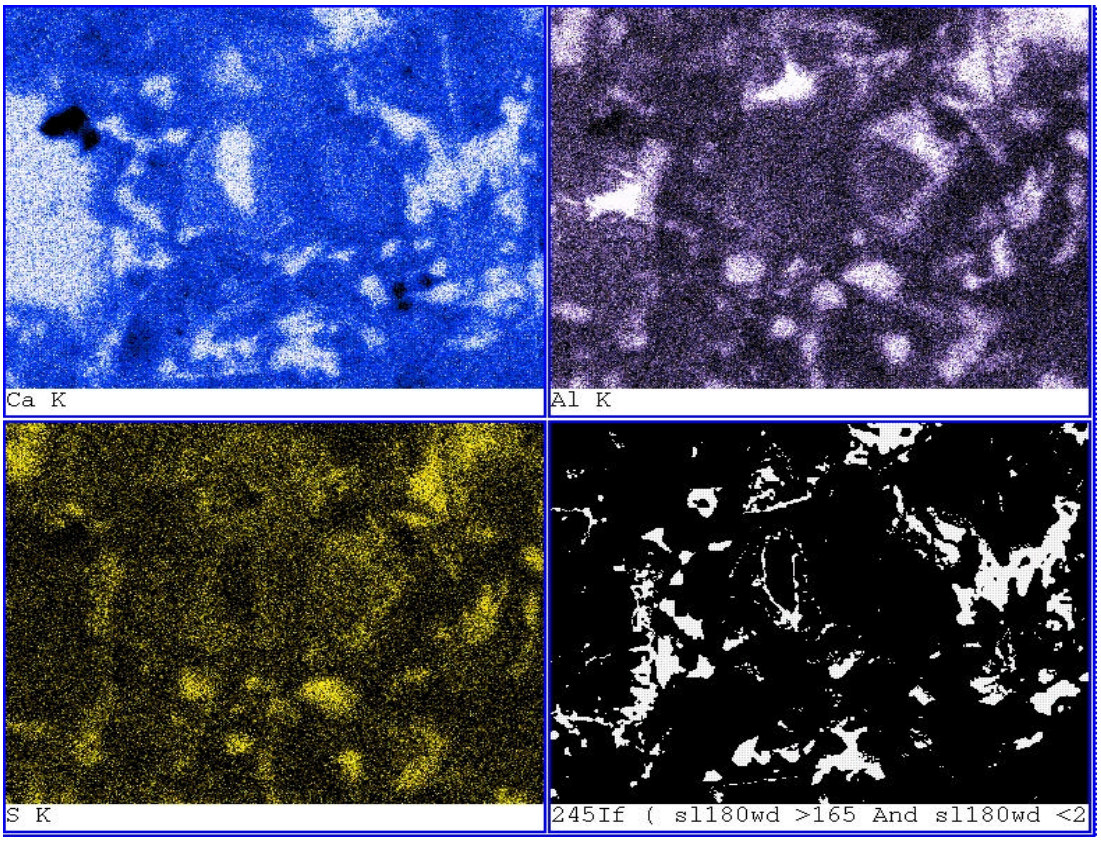

Figure 5. Image processing of BE and calcium X-ray images here highlights calcium hydroxide location. Analysis of the binary image of CH distribution (lower-right image) estimates 12% of the image field to be occupied by calcium hydroxide.

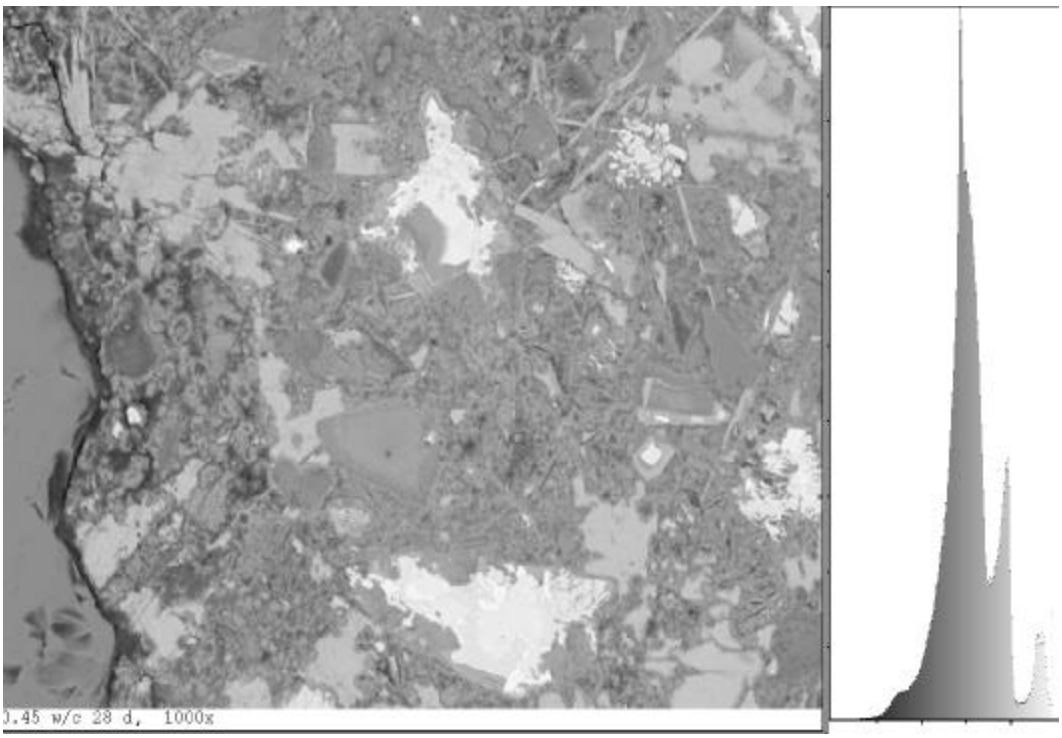

Figure 6. The paste / aggregate interfacial transition zone often shows increased porosity (dark) and calcium hydroxide, and less residual cement than the bulk cement paste. 150 μm field width.

Summary

The application of scanning electron microscopy enhances our ability to characterize cement and concrete microstructure, and will aid in evaluating the influences of supplementary cementing materials, evaluating concrete durability problems, and in the prediction of service life. SEM and X-ray imaging techniques allow imaging the complex microstructure of concrete with sub-micrometer definition. Careful specimen preparation is important as both BE and XR imaging require highly polished surfaces. Through combination of the information available in the backscattered electron and X-ray images, an accurate segmentation of the image into its constituent phases may be achieved. This allows measurement of those features using image analysis.

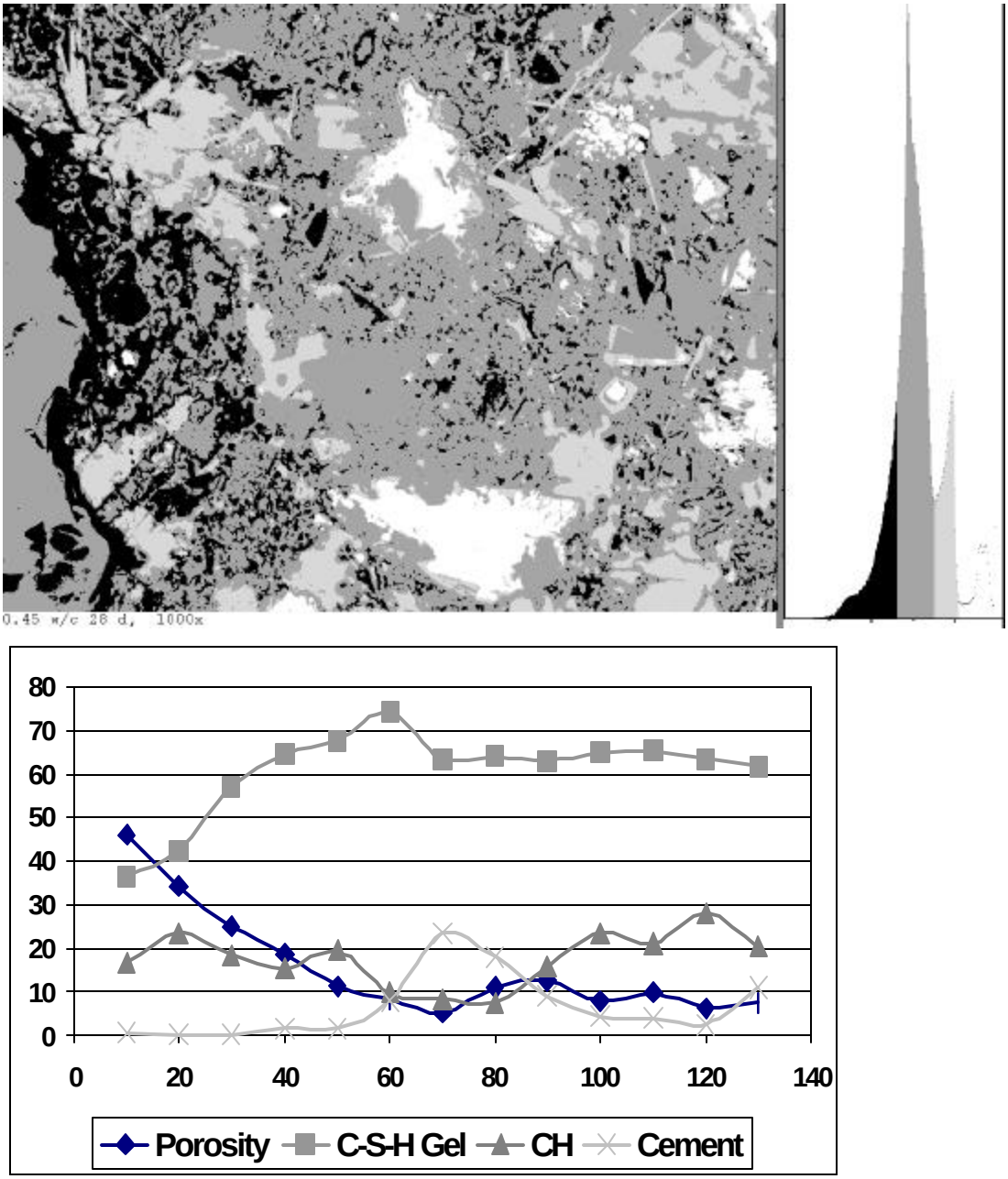

Figure 7. Thresholded backscattered electron image and gray-level histogram of interfacial transition zone allows identification and plot (to scale) of lateral distribution of porosity, C-S-H gel, calcium hydroxide, and residual cement: 150 µm field width.

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References

1. J. Golstein, D.E. Newbury, P. Echlin, D.C. Joy, C. Fiori, and E. Lifshin, Scanning Electron Microscopy and X-Ray Microanalysis, Plenum Press, New York, 1981, 673 pp.

2. P.E. Stutzman and J.R. Clifton, "Specimen Preparation for Scanning Electron Microscopy," in Proc. of the 21st Internat. Conf. On Cement Microscopy, L. Jany and A. Nisperos eds., pp. 10-22, 1999.

3. L. Struble and P.E. Stutzman "Epoxy impregnation of hardened cement for microstructural characterization," Journal of Materials Science Letters, 8, 632-634 (1989).

4. F. Chayes, Petrographic Modal Analysis, Wiley, New York, 1956.

5. J.S. Galehouse, "Point Counting", in Carver, R.E., Ed., Procedures in Sedimentary Petrology, Wiley, New York, 1971.

6. F. Hofmanner, Microstructure of Portland Cement Clinker, Holderbank Management and Consulting, 1973, 48 pp.