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Standard Guide for
Examination of Hardened Concrete Using Scanning Electron Microscopy[1]

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1. Scope

1.1 This guide provides information for the examination of hardened concrete using scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX or EDS). Since the 1960s, SEM has been used for the examination of concrete and has proved to be an insightful tool for the microstructural analysis of concrete and its components. There are no standardized procedures for the SEM analysis of concrete. SEM supplements techniques of light microscopy, which are described in Practice C856, and, when applicable, techniques described in Practice C856 should be consulted for SEM analysis. For further study, see the bibliography at the end of this guide.

1.2 This guide is intended to provide a general introduction to the application of SEM/EDS analytical techniques for the examination and analysis of concrete. It is meant to be useful to engineers and scientists who want to study concrete and who are familiar with, but not expert in, the operation and application of SEM/EDS technology. The guide is not intended to provide explicit instructions concerning the operation of this technology or interpretation of information obtained through SEM/EDS.

1.3 It is critical that petrographer or operator or both be familiar with the SEM/EDX (EDS) equipment, specimen preparation procedures, and the use of other appropriate procedures for this purpose. This guide does not discuss data interpretation. Proper data interpretation is best done by individuals knowledgeable about the significance and limitations of SEM/EDX (EDS) and the materials being evaluated.

1.4 The SEM provides images that can range in scale from a low magnification (for example, 15×) to a high magnification (for example, 50 000× or greater) of concrete specimens such as fragments, polished surfaces, or powders. These images can provide information indicating compositional or topographical variations in the observed specimen. The EDX (EDS) system can be used to qualitatively or quantitatively determine the elemental composition of very small volumes intersecting the surface of the observed specimen (for example, 1-10 cubic microns) and those measured compositional determinations can be correlated with specific features observed in the SEM image. See Note 1.

NOTE 1—An electronic document consisting of electron micrographs and EDX (EDS) spectra illustrating the materials, reaction products, and phenomena discussed below is available at http://netfiles.uiuc.edu/dlange/www/CML/index.html.

1.5 Performance of SEM and EDX (EDS) analyses on hardened concrete specimens can, in some cases, present unique challenges not normally encountered with other materials analyzed using the same techniques.

1.6 This guide can be used to assist a concrete petrographer in performing or interpreting SEM and EDX (EDS) analyses in a manner that maximizes the usefulness of these techniques in conducting petrographic examinations of concrete and other cementitious materials, such as mortar and stucco. For a more in-depth, comprehensive tutorial on scanning electron microscopy or the petrographic examination of concrete and concrete-related materials, the reader is directed to the additional publications referenced in the bibliography section of this guide.

1.7 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with the use of electron microscopes, X-ray spectrometers, chemicals, and equipment used to prepare samples for electron microscopy. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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[1] This guide is under the jurisdiction of ASTM Committee C09 on Concrete and Concrete Aggregates and is the direct responsibility of Subcommittee C09.65 on Petrography.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

C125 Terminology Relating to Concrete and Concrete Aggregates

C294 Descriptive Nomenclature for Constituents of Concrete Aggregates

C295 Guide for Petrographic Examination of Aggregates for Concrete

C457 Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete

C856 Practice for Petrographic Examination of Hardened Concrete

C1356 Test Method for Quantitative Determination of Phases in Portland Cement Clinker by Microscopical Point-Count Procedure

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *BSE, n*—backscatter electrons; these are high-energy electrons emitted back from the specimen surface. Elements of higher atomic number will have stronger emissions and appear brighter.

3.1.2 *brightness, n*—the amount of energy used to produce an X-ray.

3.1.3 *charging, n*—the buildup of electrons on the specimen at the point where the beam impacts the sample. Charging can alter the normal contrast of the image (usually becomes brighter) and may deflect the beam. Coating the specimen with a thin layer of conductive material (such as gold or carbon) can minimize this effect.

3.1.4 *contrast, n*—the difference in intensity of the energy produced by varying elements when excited.

3.1.5 *dead-time, n*—the time of finite processing during which the circuit is "dead" and unable to accept a new pulse from the X-rays.

3.1.6 *EDX (EDS) (energy-dispersive X-ray spectroscopy), n*—the interaction of the electron beam with atoms in the sample produces characteristic X-rays having energies and wavelengths unique to atoms.

3.1.7 *live-time, n*—how the acquistion of X-ray data is timed when the rate of X-ray events between measurements are compared. Opposite of dead-time.

3.1.8 *K, L, or M peaks, n*—characteristic X-ray intensities detected for elements.

3.1.9 *raster, n*—to scan as when the beam from the filament sweeps back and forth over the sample

3.1.10 *SE, n*—secondary electrons; these are low-energy electrons emitted when the specimen is hit with the beam and associated with the topography of the same.

3.1.11 *SEM, n*—scanning electron microscope.

3.1.12 *stage, n*—platform upon which the specimen is placed within the vacuum chamber that can be remotely moved in various directions.

3.1.13 *working distance, n*—the distance between the detector and the sample. Each SEM will have an optimun distance in which X-rays can be collected for EDX (EDS).

3.1.14 *X-ray detector, n*—also known as EDX (EDS) system.

4. Description of Equipment

4.1 The principles of the electron system of the scanning electron microscope, the interactions of the electron beam and the specimen under examination, and the detection systems used for the examination are based on concepts that need understanding if the resulting image and other analytical information obtained are to be best resolved and understood. An abbreviated discussion is provided here. A more comprehensive understanding can be obtained from texts devoted to this subject (**1**,**2**).[3]

4.1.1 *SEM Optics:*

4.1.1.1 An electron beam is generated in a column consisting of an electron gun and multiple electromagnetic lenses and apertures. The electron beam is generated by heating a filament so that it emits electrons. The most common filament for general SEM work is tungsten, but other filaments can be used for increased brightness. The electrons are accelerated towards the specimen by an applied potential and then focused by lenses and apertures. The energy of the electron beam influences resolution, image quality, and quantitative and qualitative X-ray microanalyses.

4.1.1.2 The electron beam is finely focused through electromagnetic lenses and apertures. A smaller beam size improves resolution, but decreases signal intensity.

4.1.1.3 Electron systems operate under vacuum. Specimens should be prepared to minimize alteration or damage when they are exposed to the vacuum (See 5.1.4). Variable pressure scanning electron microscopes, low vacuum scanning electron microscopes (LVSEM), and environmental scanning electron microscopes (ESEM) permit the examination of samples containing some moisture under low vacuum. The ESEM also allows analysis of organic materials. Even in an ESEM, however, some drying occurs.

4.1.2 *Signal Generation and Detection:*

4.1.2.1 The interaction of the electron beam with the sample generates several types of signals that can be utilized for imaging and X-ray microanalysis. The intensities of these signals are measured by detectors. The signals allow the examination and determination of properties such as surface topography, elemental composition, and spatial distribution of components. Signal intensities are generally used to provide an image on a screen.

4.1.2.2 The signals that are produced when the electron beam strikes the specimen surface are secondary electrons (SE), backscattered electrons (BSE), and X-rays.

4.1.2.3 To generate an image, the electron beam is moved repeatedly across the specimen to form a raster. The magnification is the ratio between the size of the raster and that of the screen image.

4.1.2.4 Images produced by secondary electrons are most commonly utilized for topographical imaging. The SE intensity depends mainly on the angles between the electron beam and

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[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

the specimen surface and between the specimen surface and the detector. The SE intensity is relatively insensitive to the specimen composition.

4.1.2.5 Images produced by backscattered electrons are often used for elemental contrast imaging. The BSE image is useful for identifying different chemical constituents in concrete. The BSE intensity depends on the average atomic number and density of each phase. The BSE intensity also depends on the angles between the electron beam and the specimen surface and between the specimen surface and the detector. Therefore, some BSE detectors can be manipulated to observe the sample topography.

4.1.2.6 The interaction of the electron beam with atoms in the sample produces characteristic X-rays having energies and wavelengths unique to atoms. Chemical analysis (or microanalysis) is performed using an X-ray spectrometer that measures the energies and intensities of the X-rays. The intensities of X-rays depend upon many factors, including electron beam currents and accelerating voltages, as well as chemical composition of the specimen interacting with the electron beam.

4.1.2.7 One important parameter for image quality is the working distance, the distance between specimen surface and the point where the electron beam exits the electron optics. Small working distances maximize BSE collection efficiency and improve the image resolution. Long working distances improve image depth of field for topographical images but decrease image resolution. The working distance generally must be within a predetermined range to perform X-ray microanalysis.

5. Materials and Features

5.1 Important microstructural features include the size and shape of individual constituents (including pores), the spatial relationships between these constituents (what constituents are touching or associated with each other), and the volume fraction of each constituent. Constituents are described in more detail by Taylor (**3**).

5.1.1 In order to study these microstructural features, it is necessary to recognize the individual phases which are usually recognized by their size, shape, association, backscatter intensity and elemental composition (See Note 1 for examples). These characteristics may sometimes be insufficient to conclusively identify a phase, or to differentiate between two phases, such as chert and quartz (See Terminology C125). In this case, other techniques must be used, such as XRD or polarizing light microscopy. Additional information can be found in Practice C856.

5.1.2 *Concrete*—Hardened concrete consists of aggregate, hydration products of pozzolanic and cementitious materials, residual cement particles, capillary pores and voids. Some concrete may also contain supplementary cementitious materials, organic, inorganic, and metallic fibers, and entrained air voids.

5.1.3 *Cement Paste*—The cement paste contains residual cement, frequently supplementary pozzolanic and cementitious materials, and various hydration products that together have a complex and porous microstructure. The paste is initially a mixture of individual grains of cementious materials and water, and may also contain chemical admixtures. Over time, hydration reactions consume the cement and produce various hydration products, some of which grow on the surface of cement grains, while progressively filling the initial water-filled space.

5.1.3.1 Residual portland cement particles appear dense and angular to subangular. Alite usually has at least one crystal face while belite is usually rounded and sometimes striated. In a BSE image, residual portland cement particles occur as relatively bright objects in a matrix of gray cement hydration products.

5.1.3.2 Calcium-silicate-hydrate is the major hydration product of portland cement and is usually amorphous or very poorly crystalline. Its morphology varies depending on the calcium to silica ratio, water to cementitious materials ratio, curing conditions, degree of cement hydration, and chemical admixtures. At high magnifications, the morphology of calcium-silicate-hydrate varies from very fine fibrous growths, to sheet-like units, to irregular massive grains.

5.1.3.3 Portlandite (calcium hydroxide) is a major phase of cement hydration and occurs in variable sizes and shapes including platy hexagonal crystals and sheet-like masses, depending on the orientation. Calcium hydroxide is normally observed throughout the cement paste and sometimes develops along paste-aggregate interfaces. It also sometimes occurs as secondary deposits in voids and cracks.

5.1.3.4 Ettringite is a primary product of the reactions between calcium aluminates and the sulfate phases in cement. It has a characteristic acicular shape. Ettringite often also appears as a secondary deposit. Secondary deposits of ettringite are commonly found in voids and cracks. X-ray microanalysis is sometimes required for its identification. A compound that has similar morphology is thaumasite (See 5.1.7 on secondary deposits). These two compounds can be distinguished by elemental analysis. In polished sections (See 6.1) ettringite may sometimes appear microcrystalline and high magnification (for example, 50,000X) may be needed to see individual crystals. In some cases ettringite crystals may be too small to be identified.

5.1.3.5 Calcium monosulfoaluminate usually forms platy crystals. Elemental analysis (EDX or EDS) may be required for its identification.

5.1.4 *Aggregates*—Descriptive Nomenclature C294 and Guide C295 outlines methods and information relevant to the identification and classification of aggregates. Microstructural features of individual constituents within the aggregate can be studied using BSE images of polished specimens. The elemental compositions of aggregates can be determined using SEM with EDX (EDS) and sometimes the generic rock type (such as limestone, sandstone, dolomite, and granite) may be inferred. Microstructural properties such as the amount of each phase and crystal or particle size may be determined using semiquantitative BSE techniques. Cathodoluminesence and electron backscatter diffraction may be used to further understand composition, grain structure and crystallographic texture. Other information about aggregates that can be obtained includes porosity, surface contaminants, and inclusions.

5.1.4.1 Coarse and fine aggregate particles cannot be identified based on size. In cross sectioned samples, most particles are not intersected by the plane surface at their largest diameter so that some intersected coarse aggregate particles may appear to represent fine aggregate. Aside from size, fine aggregate can only be identified when the lithology and mineralogy are different from the coarse aggregate. The shape and surface texture of aggregate particles vary greatly depending on the mineralogy of the aggregate. The distribution of the aggregate and its potential effect on the durability of the concrete should be evaluated. Positive mineralogical identification can be done using methods such as optical microscopy (See Guide C295).

5.1.5 *Paste/Aggregate Interfacial Zone*—The paste-aggregate interfacial transition zone, which is typically about 50 µm thick, is an important area to examine because it affects some physical properties of concrete. The interfacial zone may account for increased porosity and may be enriched with ettringite and portlandite. Some pozzolanic admixtures greatly reduce the thickness and porosity of the interfacial zone. Secondary compounds such as alkali silica gel may be deposited in this area.

5.1.6 *Supplementary Cementitious Materials*—Supplementary cementitious materials, including natural pozzolans, ground granulated blast-furnace slag, silica fume, and fly ash, may be identified in concrete.

5.1.6.1 Fly ash usually contains a major amount of spheres of glasses, and to a lesser extent, irregularly shaped particles. Particle sizes are similar to those of portland cement. Fly ash contains different phases and the chemistry of individual particles can be quite variable.

5.1.6.2 Ground granulated blast-furnace slag particles occur as bright, angular particles in a BSE image. Hydration rims may be present when hydration is incomplete. It is sometimes difficult to conclusively differentiate between granulated blast furnace slag and residual portland cement particles.

5.1.6.3 Silica fume occurs as spherical particles that are at least an order of magnitude smaller than fly ash and portland cement particles, and it therefore may not be distinguishable in concrete. Densified (nodular) silica fume that has not been well-dispersed appears as agglomerates of various shapes and sizes, which may be detectable in SE or BSE images.

5.1.7 *Secondary Reaction Products*—The reaction products formed during normal hydration of cementitious materials are considered to be primary. Sometimes these primary products react with other constituents to form secondary products. The type, location, and amount of secondary deposits are important indicators of the condition of the concrete. Some primary cement hydration products, such as portlandite and ettringite, may also occur as secondary deposits. Possible secondary products in concrete are listed in Table 6 of Practice C 856. Caution must be used in evaluating secondary deposits because they can be artifacts of the sample preparation.

5.1.7.1 Alkali-silica gel is a product of alkali-silica reaction. The appearance of the gel varies depending on its composition and where it occurs. It can appear as foliated to massive or spongy and have a grainy texture. Alkali-silica gel always contains silicon plus varying combinations and concentrations of calcium, potassium, and sodium.

5.1.7.2 Thaumasite is a secondary deposit that may form during sulfate attack. It occurs as acicular crystals similar in morphology to ettringite. The identification of thaumasite is aided by elemental analysis and usually requires the use of petrographic microscopy and other techniques.

5.1.7.3 Secondary deposits such as gypsum and thenardite usually cannot be positively identified by morphology in the SEM. Elemental analysis is needed and identification may still be ambiguous when mixtures of phases are present. Petrographic microscopy or X-ray diffraction may be used to identify many deposits.

5.1.8 *Cracks and Voids*—Using the SEM, cracks and voids in aggregates and cement paste can be observed. The size, shape, and configuration of voids can also be observed and their volume estimated using image analysis techniques. The sample size, however, may be too small to meet the requirements of Test Method C457 and there are no standardized procedures for this using SEM. Caution must be used in evaluating the cause of cracks because they may be artifacts introduced during specimen preparation (drying), or formed due to dehydration of the sample during evacuation of the specimen chamber. Secondary reaction products may be observed in cracks and voids.

6. Specimen Preparation and Procedures

NOTE 2—Specimen preparation for scanning electron microscopy is discussed by Echlin (4).

6.1 *Specimens*—Various types of specimens (for example, fractured surfaces, sectioned or polished surfaces, thin sections, or powders) can be examined using SEM. For hardened concrete, it is often desirable to examine large specimens or a number of small specimens concurrently, and chambers are available that can accommodate specimen sizes up to 150 mm.

6.1.1 Guidelines for the selection of samples are given in Practice C856.

6.1.2 The examination of as-received surfaces is made more complex by carbonation and material adhering to surfaces. Contamination can occur during in-service use, specimen handling, or from debris produced during sample acquisition. Most contamination can be removed by careful cleaning.

6.2 *Visual Examination of As-Received Specimens*—Visual and stereo-optical inspections are important first steps and should be done before SEM analysis. Examination of as-received samples can help to characterize a variety of surface phenomena including efflorescence, pop-outs, carbonation, and cracking.

6.3 *Sample Drying*—Sample drying is needed for conventional high vacuum SEM examinations. Various drying techniques may be employed, such as air drying, oven drying, vacuum drying, freeze drying, and solvent exchange. The ESEM or LVSEM allows for analysis of samples that are not completely dry.

6.3.1 For oven drying, a maximum temperature of 105 ºC is often used to remove free water. However, drying at this temperature can have a destructive effect that includes dehydration of hydrous phases and micro cracking. Drying at about 40 ºC for a longer time minimizes these effects.

6.3.2 Freeze-drying reduces the amount of cracking caused by the removal of water. Specimens are placed in a mixture of solid CO_2 and methanol (-80 ºC) or liquid nitrogen. After freezing, specimens are transferred to a cooled chamber or freezer under vacuum where the frozen water sublimes.

6.3.3 Vacuum drying may take several days. To speed up the process, it can be carried out at an elevated temperature.

6.3.4 Solvent exchange is a relatively slow process that allows specimens to be impregnated with a polymer without any drying. Anhydrous ethanol is usually used as the solvent. The solvent may be removed using critical point drying or the solvent may be replaced by an epoxy or other polymer resin. After the resin-alcohol exchange is complete the resin can be cured either at some elevated temperature (for example, 40 °C) or at room temperature to avoid the effects that may be caused by heat. Some solvents may partially dehydrate phases including calcium silicate hydrate and ettringite, and alter crystallinity. For a more complete discussion, see Stutzman (5).

6.4 *Cleaning*—A pre-filtered non-aqueous solvent such as ethanol can be used to clean surfaces. The solvents used should be noted in any report.

6.5 *Fracture Surfaces*—Fracture surfaces may provide useful microstructural information. Breaking concrete, however, may produce cracks, so care should be taken in interpretations of cracks. Identification of materials in the cracks, such as alkali silica gel, ettringite, calcite, or calcium hydroxide, and the presence of polymers used to impregnate samples can help to determine if cracks are pre- or post-sampling.

6.5.1 Fracture surfaces can be created in the laboratory using standard ASTM strength testing equipment, or a hammer and chisel.

6.5.2 The fracture surface may be cleaned as described in 6.4. Unless it is concluded that the contamination will adversely influence the analysis, the best practice may be to leave the contamination and report it as such.

6.6 *Sectioning*—Section samples to reduce their size using a saw. If the specimen has fracture surfaces, they should be protected during sectioning. Non-aqueous cutting lubricants may be used to prevent dissolution during sectioning; these include propylene glycol (not ethylene glycol), ethanol, and isopropanol.

6.7 *Polishing*—Flat, polished specimens are required for quantitative X-ray microanalysis and for BSE imaging for compositional contrast. Because materials in concrete vary in hardness, special care is required in polishing. Too much polishing may produce undesirable relief and too little polishing may prevent microstructural details from being observed.

6.7.1 Sections 6.7.4 and 6.11 list equipment and techniques for lapping and polishing.

6.7.2 Procedures involved in preparing polished sections may include: *(a)* sectioning the sample to an appropriate size; *(b)* sample drying; *(c)* impregnation with a low viscosity epoxy, methyl methacrylate, or other suitable polymer; *(d)* trimming; *(e)* lapping to remove surface irregularities created during saw cutting; *(f)* polishing.

6.7.3 *Impregnation*—Porous and friable materials like concrete should be impregnated with a hardenable material such as epoxy or other suitable polymers to stabilize the microstructure during sample preparation. Impregnation involves evacuating air and other gasses and filling cracks and pores with epoxy, all while the specimen is under a vacuum. A low viscosity epoxy is generally used. The hardened epoxy protects the sample from fracturing or plucking, and fills cracks and voids so that abrasive grit is not trapped.

6.7.3.1 Curing of the epoxy should be done as prescribed by the manufacturer. If curing at an elevated temperature is necessary, the temperature should not exceed 40 ºC. Some polymers contain chlorine, which may be detected during X-ray microanalysis. Shrinkage due to the vacuum applied during impregnation can cause additional cracking and other artifacts. 6.3.4 discusses a procedure where drying is not necessary.

6.7.3.2 It is important to evaluate the degree of polymer impregnation. This can be done with a stereomicroscope initially and as the specimen is ground or saw cut or both and new fresh surfaces are exposed.

6.7.4 *Lapping and Polishing*—Lapping and polishing are described in detail in Test Method C457.

6.7.4.1 Lapping of impregnated surface could be done either by using successively finer grit-sized metal or resin-bonded fixed abrasive discs attached to a horizontal rotary lapping wheel, or by spreading loose abrasive powder on the lapping wheel. After lapping, the specimen can be polished using micron or submicron compounds. Non-aqueous alcohol or oil-based lubricants should be used to avoid artifacts due to water.

6.7.4.2 The cloth used for polishing should be low in nap so as not to introduce undesirable relief.

6.7.4.3 After each lapping and polishing step, the specimen must be cleaned of all abrasive powder and polishing debris. Cleaning can be done using an ultrasonic bath with an alcohol medium.

6.7.4.4 It is important that the final specimen surface be clean and uniformly polished. It should be checked using reflective light microscopy.

6.7.4.5 Polished thin sections without a cover slip can also be examined in an SEM.

6.8 *Powder Samples*—Powders may be examined by SEM to determine size, shape, and elemental composition. Because X-ray results are affected by topography, powders should not be used for quantitative EDX (EDS) analysis.

6.8.1 Bulk samples can be crushed to provide powdered material. Crushing can be done using a mortar and pestle or a variety of mechanical equipment such as ball mills and vibratory mills. For concrete, softer paste can be separated from harder aggregate by crushing and sieving.

6.8.2 When mounting powder it is important to have every particle in electrical contact with the metal stub (see 6.9). Powders can be mounted using a variety of methods, including double-sided conductive tape, carbon or silver paint, or a grid manufactured for mounting transmission electron microscope specimens.

6.9 *Mounting*—For conventional high-vacuum SEM, it is necessary to mount specimens such that they are electrically grounded to avoid surface charging. Specimens are usually fixed to a metal stub using a conductive organic cement (for example, cement containing colloidal carbon or silver). The stub is then mounted in the SEM using a mechanical attachment designed for this purpose.

6.10 *Coating*—For conventional (high vacuum) SEM, it is necessary to electrically ground the specimen to avoid surface charging, which interferes with analysis. Grounding can be achieved by applying a conductive coating on the specimen surface. A variable pressure SEM, ESEM, or LVSEM dissipates the surface charge by having an elevated chamber pressure composed of ionized gases and so does not require sample grounding.

6.10.1 Surface coatings include carbon, gold, and palladium. Gold and palladium coatings are used because they are good conductors. For BSE and EDX (EDS) analysis, carbon coatings are usually used because they do not interfere with the compositional signal. Normally, gold and palladium are applied by sputtering, and carbon by evaporation.

6.11 *Accesssories*—The equipment and supplies required for specimen preparation of hardened concrete may vary depending on the type of examination. The following list includes accessories generally used:

6.11.1 Automatic or manual feed saw with a diamond-tipped cut-off blade large enough to make a full cut in one pass,

6.11.2 Cutting lubricant, preferably non-aqueous,

6.11.3 Horizontal metal lap large enough to process the specimen,

6.11.4 Polishing lap at least 20.3 cm in diameter and preferably of variable speed,

6.11.5 Oven, thermostatically controlled, for drying and curing samples,

6.11.6 Abrasive grits having a range of mesh sizes such as No. 100 (160 µm), No. 220 (68 µm), No. 320 (35 µm), No. 600 (14.5 µm), No. 800 (12 µm), and No. 1000 (9 µm),

6.11.7 Low nap polishing cloths and polishing compounds having grit sizes that may include 9 µm, 3 µm, 1 µm, and 0.25 µm,

6.11.8 Square glass plates approximately 300 to 450 mm in lateral size with a minimum thickness of 12.5 mm,

6.11.9 Vacuum impregnation jar and vacuum pump,

6.11.10 Metallographic microscope with vertical illuminator and low, medium, and high magnification objectives and appropriate eyepieces, and

6.11.11 Sputter coater or evaporator for coating specimen surfaces with gold, palladium, or carbon.

7. Quantitative Analysis

7.1 Quantitative analysis may be used to measure the volume fraction of constituents distinguished in the SEM. This analysis commonly uses BSE images in which constituents with different chemical composition are distinguished by their BSE intensity.

7.1.1 Quantitative image analysis has been performed to determine the percentage of the major constituents in Portland cement clinker and in concrete.

7.1.2 *Point Count Analysis*—The Glagolev-Chayes method, referred to as the point-count method, is widely used for quantitative mineralogical analysis and is the basis for the modified point-count method in Test Method C457. Details for sample preparation are given in Stutzman and Clifton (**6**), Test Method C1356, and Test Method C457.

7.1.2.1 The principal sources of uncertainty in the point counting method are random sample errors, and phase misidentification. The error becomes smaller as the number of points increases. A point count analysis can provide acceptable precision for phase abundance analysis at most concentration levels, providing the area of examination is sufficiently large to be representative of the linear distribution of each component in the sample. Minimum areas of examination for optical microscope analysis of concrete containing various sized aggregates are given in Test Method C457.

7.1.3 *Image Analysis*—In digital image analysis, an image is digitized into pixels (picture elements) that are assigned a gray level from 0 to 255 according to the signal intensity. As discussed in Section 3, BSE intensity depends on the average chemical composition of the specimen at the point of contact with the electron beam. Features are differentiated based on gray level, and most features comprise a range of gray values. It is possible to use selected materials to standardize gray levels. Once the suitable gray level range has been determined, area fractions with that gray level range are determined and expressed as volumetric percentages. Other properties that can be determined include number, size, shape, and spatial distribution.

7.1.3.1 Care must be taken in setting gray level thresholds for each feature such that all features of interest are included and unwanted features are excluded. It should be recognized that any changes to the microscope settings, such as beam current and working distance, affect gray level.

8. X-Ray Microanalysis

8.1 X-rays with characteristic energies (see Note 3) are produced when atoms are excited by the electron beam (see Note 4). The detector measures both energy and intensity. The X-ray energy depends on what chemical elements are producing the signal and the X-ray intensity depends (in part) on the proportion of that element in the portion of the specimen producing the signal.

NOTE 3—The energy and wavelength of all electromagnetic radiation, including X-rays, are related by two well-known equations:

$$v\lambda = c$$

and

$$E = hv$$

v = frequency,
λ = wavelength,
c = the speed of light (in a vacuum c = 3.00×10^{8} m/s),
E = energy, and
h = Planck's constant (h = 6.63×10^{-34} J-s).

Therefore X-rays with characteristic energies also have characteristic wavelengths.

NOTE 4—X-rays are also produced when atoms are excited by backscattered electrons and higher energy X-rays.

8.1.1 The X-ray detector measures either the energy or the wavelength. Energy dispersive X-ray (EDX or EDS) detectors are more common on SEMs and are therefore the focus of this section.

8.1.2 Plotting the intensity versus energy produces a spectrum with a series of characteristic peaks superimposed on a background. The X-ray signals can be used for: *(a)* qualitative analysis to determine which elements are present; *(b)* semi-quantitative analyses to identify chemical compounds; *(c)* quantitative analysis to determine what is the concentration of each element; and *(d)* mapping to image the distribution and relative concentrations of each element. Qualitative and quantitative analyses are affected greatly by instrument operating conditions and other factors. A full treatment of these factors can be found in textbooks **(1)** and is briefly discussed below.

8.1.3 *Instrumentation*—The EDX (EDS) detector (spectrometer) is placed near the specimen. The key active component in an EDX (EDS) spectrometer is a solid-state detector (typically a lithium-drifted silicon wafer) that measures the energy of each X-ray pulse that is absorbed by the detector. The detector can typically process thousands of individual X-rays per second and so provides nearly simultaneous analyses of all detectible elements present.

8.1.4 *Qualitative Analysis*—To perform a qualitative analysis, the measured spectrum is compared with a table of characteristic X-ray energies. A key to qualitative analysis is that all the characteristic peaks for each element (for example, K, L, or M peaks) must be present in their characteristic relative intensities. Qualitative analysis generally employs a process of elimination in which all characteristic peaks are sought for each potential element to confirm or reject its identification. Some peaks occur very near each other. For example, gold Mα X-ray lines may mask sulfur and phosphorus Kα emissions. Another key to qualitative analysis is that the accelerating voltage of the electron beam must be appreciably greater than the characteristic peak energy in order to excite that peak. Another key is that X-ray intensity depends in part on accelerating voltage and beam current. Smaller voltages and lower beam current diminish the intensity of each X-ray peak.

8.1.5 *Quantitative Analysis*—The intensity of X-rays depends on the concentration of the element in the sample. Mass concentration to a few tenths of a percent can be determined using an energy dispersive X-ray spectrometer. There are essentially two approaches for quantitative analysis. One uses standards to compare measured peak intensities for unknown and standard specimens under the same conditions and is commonly referred to as quantitative analysis. The other uses theoretical intensities and is commonly referred to as semi-quantitative analysis. The first approach is more time consuming while the second is quicker but more prone to errors.

8.1.5.1 For both approaches, the first step is to determine the intensity ratio for each analyte by dividing the measured intensity of an unknown by the element intensity of a pure elemental standard. This is called the k-ratio and represents the first estimate of elemental concentration. For some assemblages, this ratio will be very near the true mass fraction for a given element and some analysts use this as the sole measure of element concentration. However, this value may be significantly different from the true mass fraction if inter-element effects are important. These effects include variances related to the target density (so-called Z effects), internal X-ray absorption (so-called A effects), and internal X-ray fluorescence or enhancement (so-called F effects). The second step in achieving a quantitative or semi-quantitative analysis is to correct the measured k-ratio for the above mentioned effects. Most commercially available EDX (EDS) systems have software to perform these corrections (called ZAF corrections). In many cases, the correction factors determined will be adequate to establish the true mass concentration within a 10 % relative accuracy (for example, 20 ± 1 %).

8.1.6 *Factors Affecting X-ray Intensities*—X-ray intensity is significantly affected by specimen topography and for that reason it is recommended that only flat, planar specimens be used for quantitative analysis. Other factors that affect the measured X-ray intensity include: the sample matrix, accelerating voltage, beam current, detector take-off angle, EDX (EDS) counting time, sample homogeneity, unseen phases below the surface and atomic number of the elements. Best results for quantitative microanalysis are obtained with the use of a polished surface, an analyte that is homogenous throughout the X-ray interaction volume, an analyte that does not degrade under the electron beam, and suitable reference standards. Some cement hydration products do not meet the requirements of homogeneity and beam stability. Advanced techniques have been developed to account for phase instability in some materials.

9. Keywords

9.1 analysis of concrete; EDX (EDS); energy-dispersive X-ray spectroscopy; microanalysis; microscopy; petrography; photomicrographs; scanning electron spectroscopy; SEM

APPENDIX

(Nonmandatory Information)

X1. SEM IMAGES

X1.1 The photomicrographs in Fig. X1.1 are supplied for illustrative purposes only. To the trained eye reaction gel can be seen filling some of the cracks.

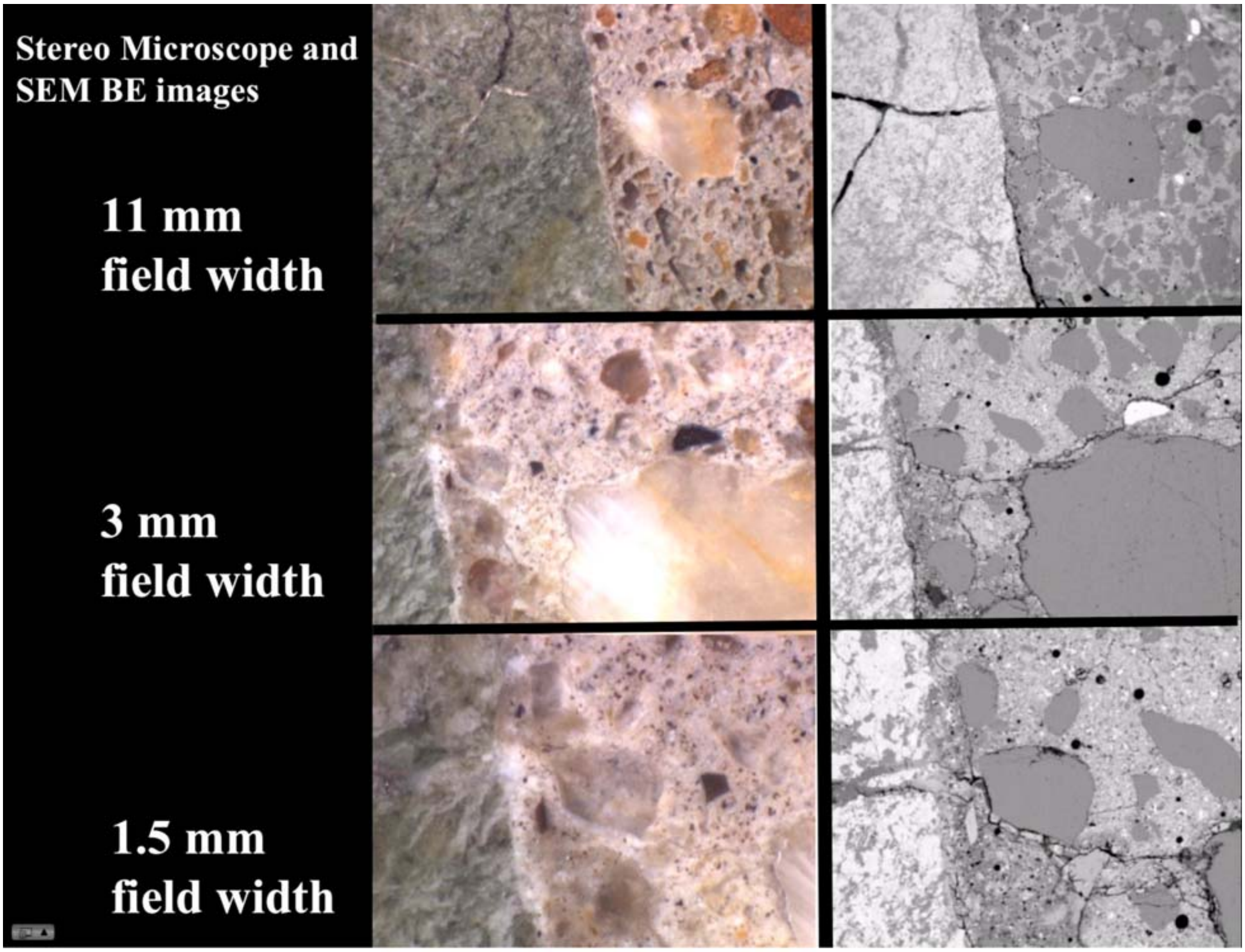

FIG. X1.1 SEM Images

REFERENCES

(1) Goldstein, J. I., Newbury, D. E., Echlin, P., Joy, Lyman, C., Sawyer, L., Michael, J., and Lifshin, E., *Scanning Electron Microscopy and X-Ray Microanalysis*, Kluwer Academic/Plenum Publishers, 3rd Ed., New York, NY, 2003.

(2) Postek, M. T., Howard, K. S., Johson, A. H., and McMichael, K. L., *Scanning Electron Microscopy—A Student's Handbook*, Ladd Research Industries, Inc., Williston, VT, 1980.

(3) Taylor, H. F. W., *Cement Chemistry*, 2nd Edition, Thomas Telford, London, UK, 1997.

(4) Echlin, P., *Handbook of Sample Preparation for Scanning Electron Microscopy and X-Ray Microanalysis*, Springer, New York, NY, 2009.

(5) Stutzman, P. E., "Applications of Scanning Electron Microscopy in Cement and Concrete Petrography," *Petrography of Cementitious Materials*, ASTM STP 1215, ASTM International, 1994, pp. 74–90.

(6) Stutzman, P. E., and Clifton, J. R., "Sample Preparation for Scanning Electron Microscopy," *Proceedings of the 21st International Conference on Cement Microscopy*, L. Jany and A. Nisperos, eds., ICMA, Duncanville TX, 1999 , pp. 10–22.

BIBLIOGRAPHY

(1) *Petrography of Cementitious Materials*, edited by DeHayes, S. M., Stark, D., ASTM STP 1215, ASTM International, 1994.

(2) John D. Verhoeven, "Scanning Electron Microscopy," *ASM Handbook*, Volume 10, Materials Characterization, ASM International, 2009, Online, Available: http://www.asmmaterials.info, 28 December 2009.

(3) Bonen, D., and Diamond, S., "Interpretation of Compositional Patterns Found by Quantitative Energy Dispersive X-Ray Analysis for Cement Paste Constituents," *Journal of the American Ceramic Society*, Vol 77 No. 7, 1994, pp. 1875–1882.

(4) Campbell D. H., *Microscopical Examination and Interpretation of Portland Cement and Clinker*, Second edition, Construction Technology Laboratories, Skokie, IL, 1999.

(5) Detwiler, R. J., Powers, L. J., Hjorth Jakobsen, U., Ahmed, W. U., Scrivener, K. L., and Kjellsen, K. O., "Preparing Specimens for Microscopy," *Concete International* , Vol 23, 2001, p. 50.

(6) Knudsen, T., and Thaulow, N., "Quantitative Microanalyses of Alkali-Silica Gel in Concrete," *Cement and Concrete Research*, Vol 5, 1975, pp. 443–454.

(7) Krinsley, D., Pye, K., Boggs, S., and Tovey, N.K., *Backscattered Scanning Electron Microscopy and Image Analysis of Sediments and Sedimentary Rocks*, Cambridge University Press, Cambridge, UK, 1998.

(8) Newbury , D. E., Joy, D. C., Echlin, P., Fiori, C. E., and Goldstein, J. I., *Advanced Scanning Electron Microscopy and X-Ray Microanalysis*, Springer, New York, NY, 1986.

(9) Reed, S. J. B., *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology*, Cambridge University Press, Cambridge, UK, 1996.

(10) Scrivener , K. L., "The Microstructure of Concrete," *Materials Science of Concrete I*, edited by J. Skalny, American Ceramic Society, Westerville, OH, 1989, pp. 127–161.

(11) St. John, D. A., Poole, A. B., and Sims, I., *Concrete Petrography*, Arnold, London, UK, 1998.

(12) Thaulow, N., Sahu, S., and Badger, S., "Identification of Phases in Cement and Concrete Using Backscattered Electron Imaging," *Proceedings of the 24th International Conference on Cement Microscopy*, ICMA, Metropolis, IL, 2002, pp. 214–223.

(13) Wang, Y. and Diamond, S., "An Approach to Quantitative Image Analysis for Cement Pastes," *Materials Research Society Symposium Proceedings*, Vol 370, 1995, pp. 23–32.

(14) Walker, H., Lane D.S., Stutzman, P., "Petrographic Methods of Examining Hardened Concrete: A Petrogrpahic Manual Revised 2004" VDOT, VTRC 04-R21, FHWA-HRT-04-150, 2006 , Chapter 14.

(15) Zhao, H. and Darwin, D., "Quantitative Backscattered Electron Analysis of Cement Paste," *Cement and Concrete Research*, Vol 22, 1992, pp. 695–706.