Specimen Preparation for Scanning Electron Microscopy

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SPECIMEN PREPARATION for SCANNING ELECTRON MICROSCOPY[1]

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Abstract

Microscopy plays an important role in the examination of cementitious materials. Optical and electron-optical techniques allow examination of microstructural details with sub-micrometer definition. The increased application of scanning electron microscopy in cement and concrete investigations has brought attention to differences in preparation techniques. The success of these investigations is, in part, influenced by the type and quality of specimen preparation. In particular, backscattered electron and X-ray imaging modes are influenced by the specimen surface characteristics, with the ideal surface being highly polished. Saw-cut surfaces that have not been epoxy-impregnated, nor polished, are not representative of the true microstructure, and are difficult to examine and interpret without bias. Sawing creates a series of fractures, which are enhanced with subsequent drying shrinkage. Particulate matter from the sawing is also deposited on the surface. These effects combine to present a surface that is not well suited for any type of microscopy and that is substantially different from the true concrete microstructure. Polished epoxy-impregnated surfaces are relatively simple to prepare and allow the researcher to avoid the above-mentioned difficulties. Claims that this procedure alters, or 'smears', the microstructure have not been substantiated. Procedures developed in our laboratory for preparation of polished sections of clinker, cements, and hardened portland cement concrete preparations are presented here.

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INTRODUCTION

Specimen preparation is important in any microscopical technique with proper preparation methods facilitating examination and interpretation of microstructural features. Improper preparation methods may obscure features, and even create artifacts that may be misinterpreted. Scanning electron microscope (SEM) analysis using backscattered electron and X-ray imaging requires a highly polished surface for optimum imaging. Rough-textured surfaces, such as those produced using only saw-cutting diminish the image quality by reducing contrast and loss of feature definition. Additionally, the lack of a polished specimen makes quantitative estimates arduous, as the surface is no longer planar. We have developed a series of preparation procedures in our laboratory that we feel provide simple, yet efficient specimen preparation, allowing clear definition of specimen features in SEM imaging [1,2].

SEM is used for a variety of projects under the National Institute of Standards and Technology (NIST) Building Materials Laboratory's Partnership for High Performance Concrete Program. We examine Portland cement clinker, cement powder, cement pastes, mortars, and hardened portland cement concrete [3,4,5,6]. Each of these preparations uses an epoxy resin to permeate the material's pore system or to encase powder particles. The specimens are then cut or ground to expose a fresh surface, and that surface is then polished using a series of successively finer grades of diamond paste. This polishing stage is necessary to remove cutting and grinding damage, and to expose an unaltered cross section of the material's microstructure.

Figures 1 and 2 show backscattered electron (BE) images of polished sections of portland cement particles and hardened portland cement paste. 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. The ferrite phase appears brightest in the cement image (Figure 1), followed by alite, belite, aluminate, and periclase. X-ray imaging facilitates identification of periclase, alkali sulfates, and calcium sulfates. Figure 2 shows that, for a 28-day hardened cement paste microstructure, demonstrates that polishing yields clear definition of the constituents: the black pore space filled with the cured epoxy; the bright grains of residual cement (C); the intermediate-gray calcium-silicate-hydrate (C-S-H); and somewhat brighter gray calcium hydroxide (CH).

In contrast, concrete that has been saw-cut using isopropyl alcohol as a cutting lubricant exhibits little constituent contrast and substantial cracking (Figure 3). The loss of contrast may be attributed to the roughness of the surface and the cracking to both the cutting and tearing action of the diamonds embedded in the saw blade, and drying shrinkage-related cracking of a damaged microstructure. A cross-section of this preparation, after epoxy impregnation and polishing, shows the extent of cracking resulting from the saw damage and drying shrinkage (Figure 4).

Epoxy impregnation of the pore system serves two purposes: A) it fills the voids and, upon curing, supports the microstructure serving to restrain it against shrinkage cracking, and B) it enhances contrast between the pores, hydration products, and cementitious material. With relatively high permeability materials or powders such as clinker or portland cement, an epoxy of low viscosity is necessary while for the less permeable cement pastes and concretes an ultra-low viscosity epoxy aids in rapid infiltration of the pore structure[2].

[2] Certain tradenames are used to more fully describe the procedure. In no case does this imply that these products are the best, nor the only, materials available for this purpose. Suitable epoxys include L.R. White, hard grade for ultra-low viscosity, and Epotek 301 for medium viscosity applications.

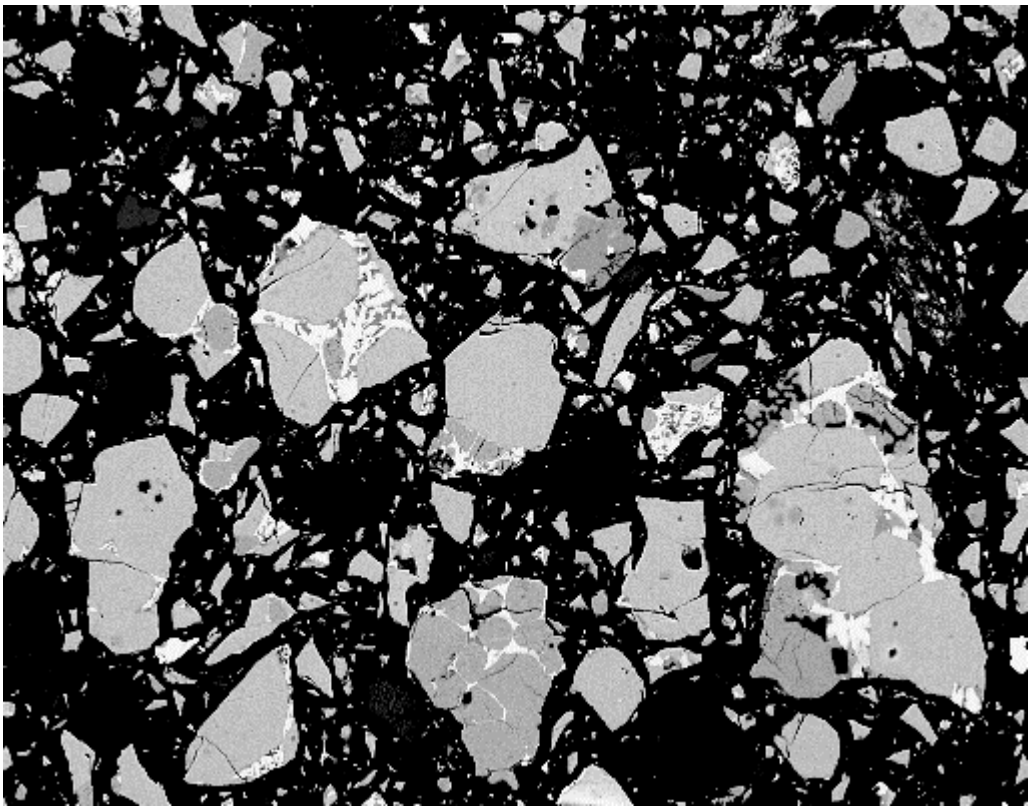


Figure 1. Polished section of Portland cement particles imaged using the backscattered electron signal clearly shows the constituent phases. Ferrite appears brightest followed by alite, belite, aluminate, alkali sulfates, and periclase. X-ray imaging facilitates distinction of the individual phases. Field width: 125 micrometers.

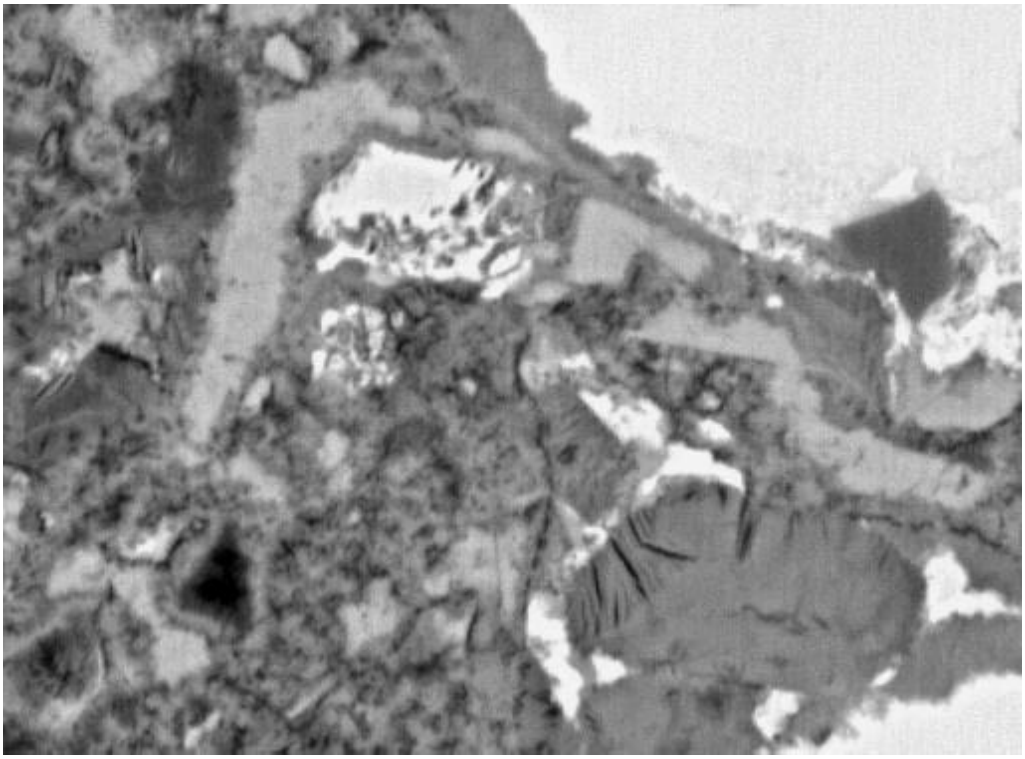


Figure 2. 28-day old hardened portland cement paste microstructure.
Image field width: 17 micrometers.

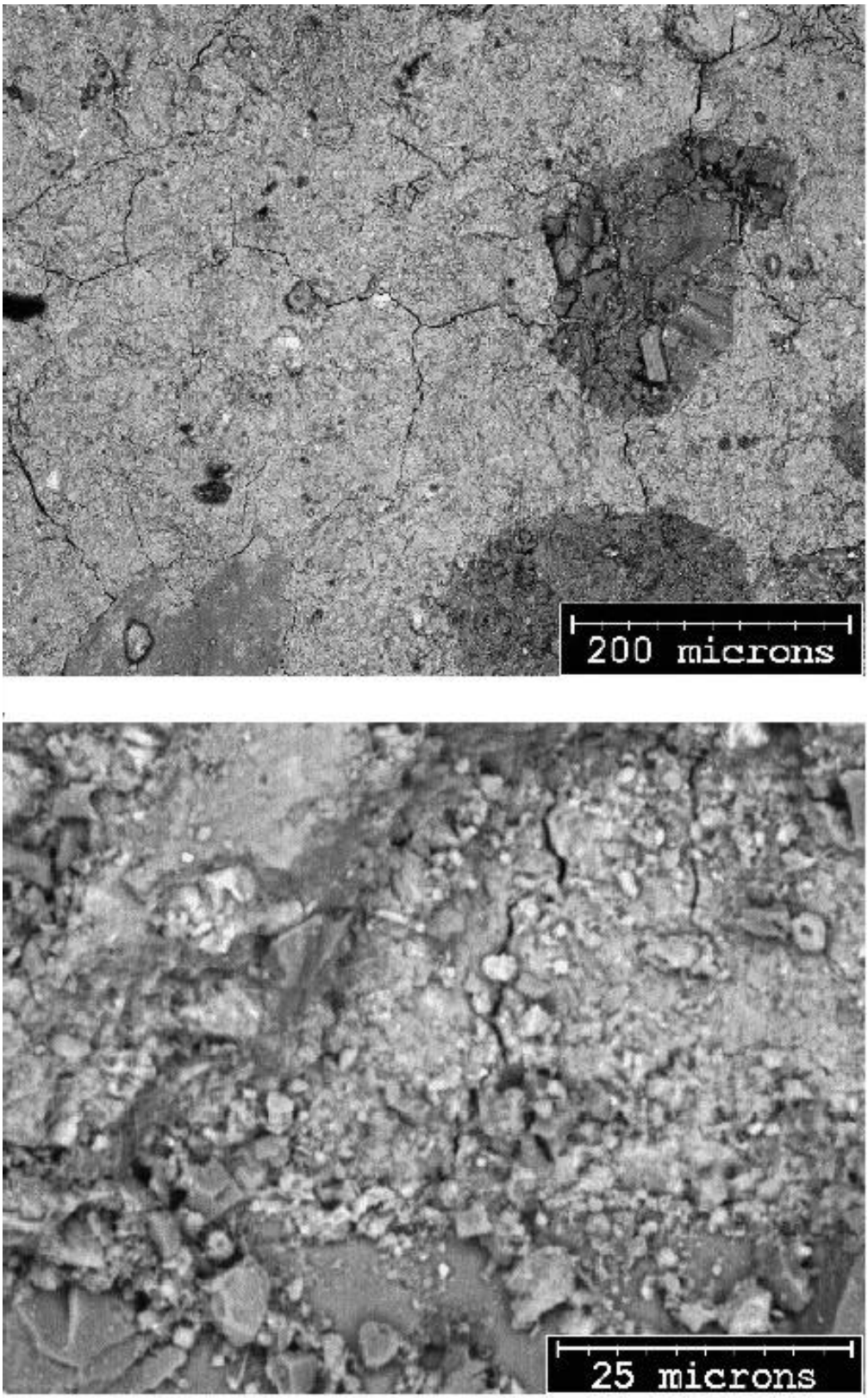
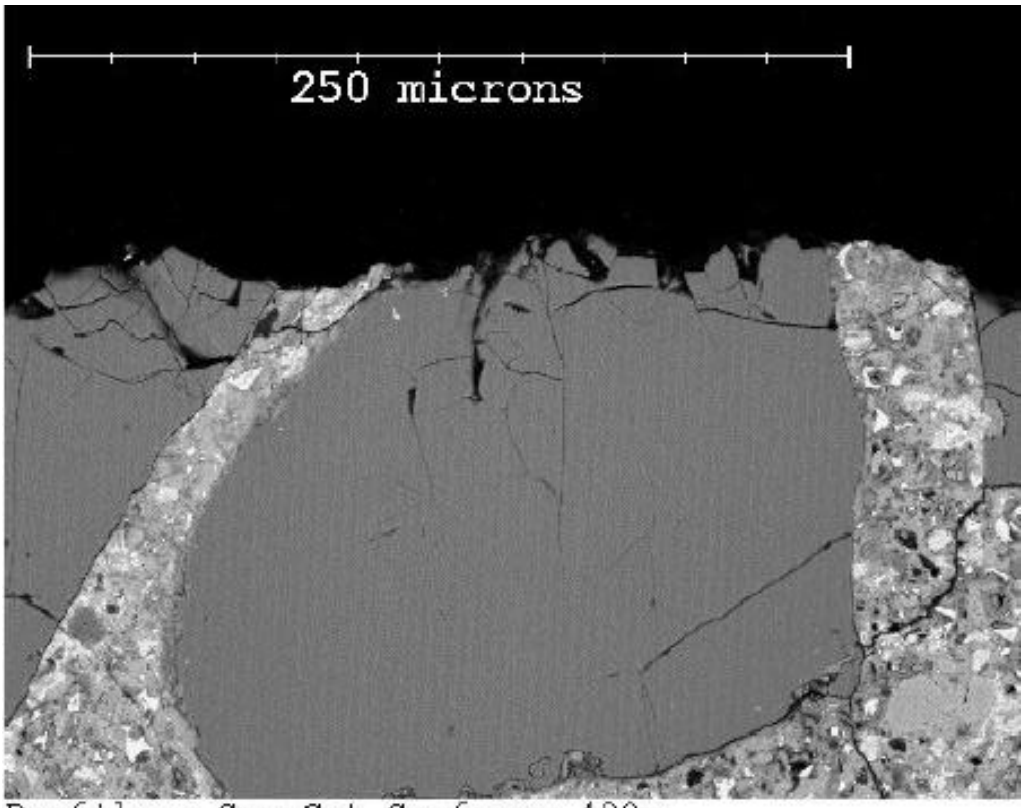
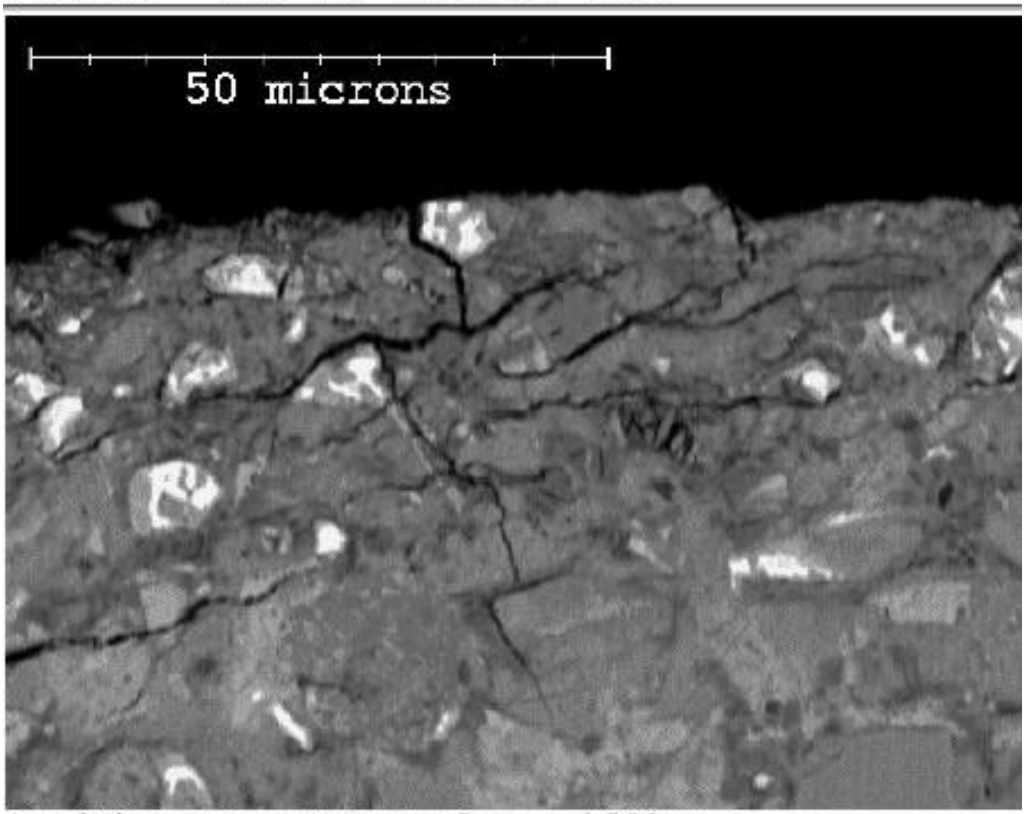


Figure 3. A sawn-surface preparation imparts substantial damage, leaving a rough surface and residual particulate matter. Poor imaging contrast and shadowing result and make BE and X-ray imaging difficult. Lack of epoxy to support the microstructure results in drying shrinkage-related cracking.



Profile - Saw Cut Surface, 400x



Profile - Saw Cut Surface, 1660x

Figure 4. An edge-on view of the sawn-surface preparation (epoxy-impregnated and polished) shows the surface damage imparted by the sawing action as well as the depth of drying shrinkage cracking resulting from drying a specimen without prior epoxy impregnation.

Materials for Sample Preparation

A list of equipment and materials necessary for preparation of polished specimens is given in Table 1. For some items, substitution may be possible if comparable supplies are available in the laboratory. The list is presented in order of use of the equipment or supplies.

Polished Powder Mounts of Portland Cement

Powder mounts are prepared by suspending cement powder in epoxy, curing the epoxy, cutting and polishing a surface of the powder / epoxy composite. The cement powder is mixed in about 5 g of epoxy, using enough cement to form a stiff ball. The cement / epoxy mixture is placed in a mold container and pressed to fill the base of the mold. The mixture is then consolidated in the sample mold by sharply tapping it on the laboratory bench top, and the epoxy is cured according to the manufacturer's guidelines. After curing, the specimen is removed from the mold, labeled and a fresh surface is exposed using a wafering saw or by grinding. Examples of this application may be found in references 1 and 2.

Table 1. Equipment and Supplies for Preparation of Polished Sections

Item	Purpose
Diamond blade slab saw	large-sized sample slabbing
Diamond blade wafering saw	cutting of thin (mm-sized) sections
Propylene glycol	diamond saw cutting lubricant
Alcohol: 200 proof ethanol	cutting lubricant, cleaning aid
Ultrasonic bath	specimen cleaning
Specimen jars and lids	for replacement steps
Potting epoxies (medium and low viscosity)	for powders and hardened pastes
Dye, blue or red, alcohol miscible	to estimate alcohol replacement depth
Refrigerator	epoxy storage
Vacuum chamber and pump	vacuum impregnation
Drying / curing oven	capable of at least 65 °C
Glass plate (400 x 400 mm)	smooth surface for grinding
Lapidary wheel (minimum 200 mm)	grinding and polishing
Mold cups	potting specimens
Aluminum foil (extra heavy duty)	for forming odd-sized specimen molds
Mold release	facilitates removal of specimen / epoxy
Metal trays to hold specimens	contains any leaking epoxy
Diamond pen	label engraving
Abrasive papers (silicon carbide)	coarse to fine grinding, 100 to 600 grit
Polishing cloths (low-relief)	6 μm and finer polishing
Diamond paste for polishing	6, 3, 1, 0.25 μm in non-aqueous suspension
Lint-free cloths	specimen handling and cleaning
Compressed air	specimen cleaning and drying
Vacuum dessiccators	specimen storage

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. Wet potting is used to prepare a polished section where the material has not been dried and therefore has not undergone any drying shrinkage. 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.

Dry specimen potting involves taking a sawn section or block of material and drying the specimen at low temperature (less than 65 °C). Removal of water is necessary as it can interfere with polymerization of the epoxy. The specimen is then placed in a container and surrounded by epoxy leaving a top surface exposed to the laboratory air, allowing the epoxy to be drawn into the microstructure by capillary suction. To speed the infiltration, the specimen may be completely immersed in epoxy, and a vacuum drawn to remove remaining air. Upon release of the vacuum, the epoxy is forced into the pore system. The epoxy is cured at low temperature (65 °C), and then is ready for the cutting and polishing.

Wet specimen potting is a three-step process where the pore solution is replaced with alcohol (200 proof ethanol), the ethanol is replaced with a low-viscosity epoxy, and then the epoxy is cured. The slab and wafering saws are lubricated with propylene glycol or isopropyl alcohol to keep the specimen from drying when cutting. The cut section is then placed in a lidded jar filled with 200 proof ethanol for the alcohol - pore solution replacement stage. The use of a companion specimen allows one to gauge the time necessary for the alcohol - pore solution replacement. This companion specimen is usually a remnant from the specimen after trimming. This specimen is placed in a jar filled with ethanol dyed a deep red or blue using any alcohol-miscible dye. By splitting or sawing the companion specimen after a period of time, the depth of replacement is seen by the depth of dye coloration. When this front is equal to half the section thickness, the pore solution in the section has been replaced by alcohol. The section is then placed in a container with the low-viscosity epoxy. The time necessary for epoxy replacement of the alcohol is at least equal to that required for the first replacement stage. In our laboratory we provide about 1.5 times the pore solution - alcohol replacement time for that of the epoxy - alcohol replacement. Implicit in this method is that the thinner the section, the shorter time is required for each stage. The specimen is placed in a mold with fresh epoxy, which is then cured at low temperatures according to the manufacturer's directions. The specimen is now ready for the cutting and polishing stages.

Cutting and Grinding

The cutting, grinding and polishing steps are common to all preparations to expose a fresh surface through cutting or grinding. Diamond blade slab or wafering saws, lubricated using propylene glycol, are suitable for exposing a fresh surface. This surface needs to be smoothed by grinding. Abrasive papers of 100, 220, 320, 400 and 600 (silicon carbide paper) used dry are also suitable for rapid removal of material by grinding. Using successively finer grades of abrasive paper removes damage produced by the earlier grit. After the 600 grit grind, the surface is smooth enough for polishing with the diamond pastes. Visual examination of the specimen allows one to identify when the abrasive has cut the entire surface. Grinding striations on the specimen surface indicate that grit has completely removed a layer of material. By alternating

grinding directions by 90 degrees one can insure that the entire surface has been ground. These operations damage the specimen surface necessitating a polishing step that is described next.

Polishing

Polishing removes the damage imparted by the sawing and grinding operations. This stage involves use of a sequence of successively finer particle size diamond polishing pastes ranging from 6 μm to 0.25 μm, and a lap wheel covered with a low-relief polishing cloth. This may be performed manually or, for greater sample throughput, using a semi-automated polisher.

Figures 5 and 6 illustrate the increased clarity of a clinker microstructure as the grinding damage is progressively removed with initial polishing stages using a 6 μm diamond paste. While illustrated using optical imaging, this improvement may be realized with any cementitous material for any microscopical method. Subsequent polishing stages of 3 μm, 1 μm, and 0.25 μm pastes remove fine scratches from the 6 μm polish, further improving constituent definition.

A comparison of the epoxy-impregnated, polished section BE images (Figure 7) with the saw-cut preparation (Figure 3) for the sections of the same concrete core illustrates the marked difference in feature clarity and artifacts. In Figure 3, the saw-cut surface exhibits cracking that resulted from drying shrinkage of a surface-damaged specimen. The surface, being rough and partly covered with particulate matter, exhibits little phase-related contrast. The image shows an aggregate at the base but, aside from the uniform hardened paste, no distinct hydration products. The epoxy-impregnated, polished specimen (Figure 7) shows microstructural feature clarity not seen in Figure 3. Here, the aggregate is not only clearly seen, but one can distinguish between silicious and carbonate aggregate by gray level. The residual cement grains appear bright and large voids within both the paste and aggregate are dark. In the higher-magnification image, the hardened cement paste / aggregate interfacial zone is shown. The residual cement grains are the brightest feature followed by calcium hydroxide, the carbonate aggregate, the C-S-H, and finally the black pores. The highly polished surface also aids in X-ray imaging. Figure 8 illustrates the use of X-ray imaging of a region shown in the BE image (top) to examine element spatial distribution. In this example, visual assessment of calcium, aluminum, and sulfur images allow one to locate monosulfate within the hardened cement paste. Referring back to the BE image shows the monosulfate as uniform-gray that is slightly darker than C-S-H, with a platy parting.

Summary

Proper specimen preparation is necessary for using the scanning electron microscope for the study of cementitous materials and hardened Portland cement concrete. Rough surfaces such as those prepared using only fracture, saw-cut, or rough-lapped preparations are not suitable. These preparations may actually create preparation-induced artifacts that are not representative of the microstructure, create a surface that is difficult to describe, and not being planar, are unsuitable for estimates of phase abundance. The backscattered electron and X-ray imaging modes are particularly sensitive to rough surfaces, which affect the definition of the constituents through loss of contrast and signal shadowing. Procedures for epoxy-impregnated, polished specimen preparations that have been refined in our laboratory over the past ten years are presented here for materials ranging from clinker and powdered cement to hardened Portland cement concrete.

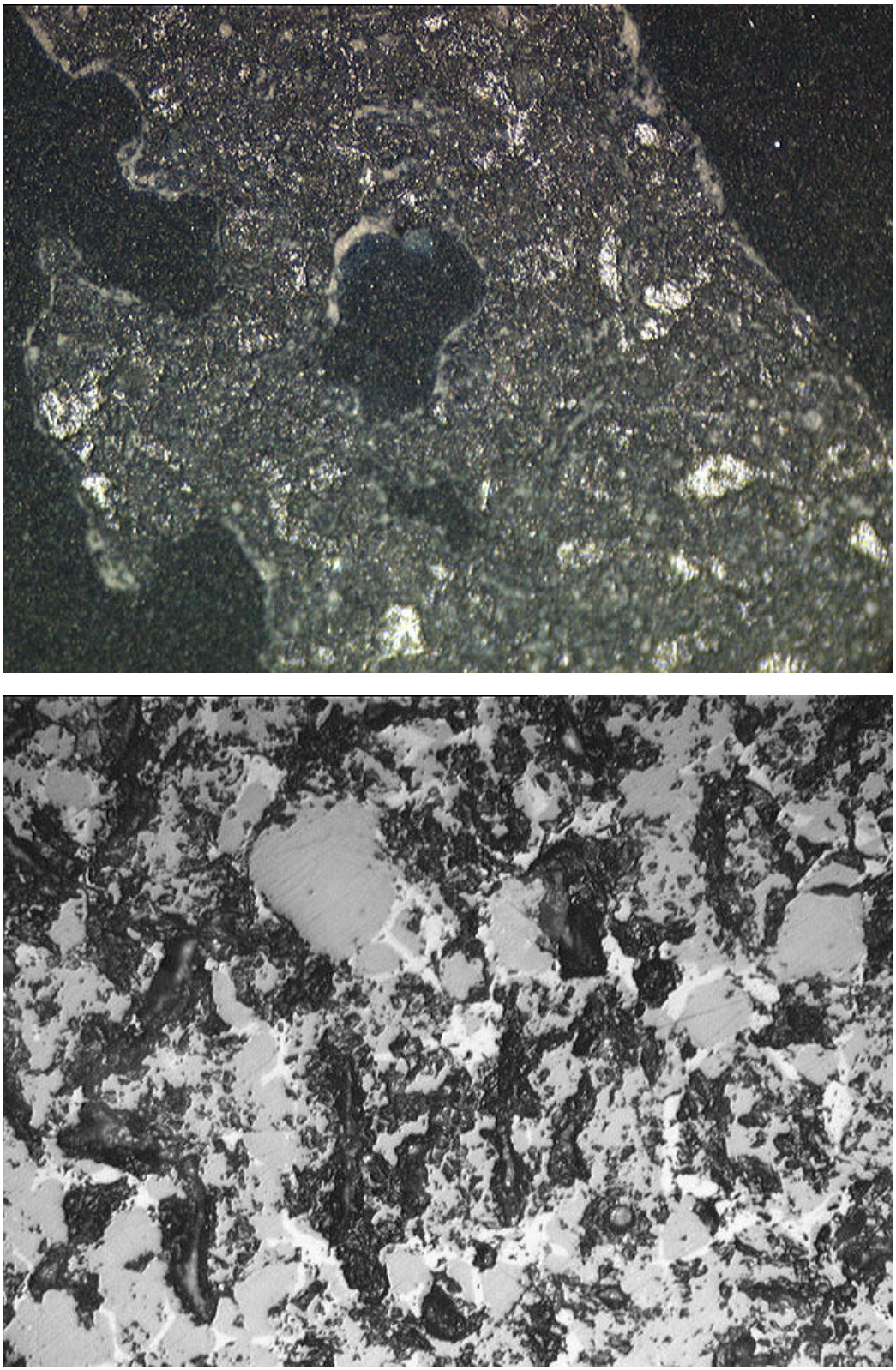


Figure 5. A clinker surface after saw-cutting and grinding using 600-grit silicon carbide (top image) exhibits no discernible microstructure due to the rough surface. Increased polishing time (bottom image) using 6 μm diamond paste progressively removes grinding and cutting damage pits and begins to reveal the underlying microstructural features.

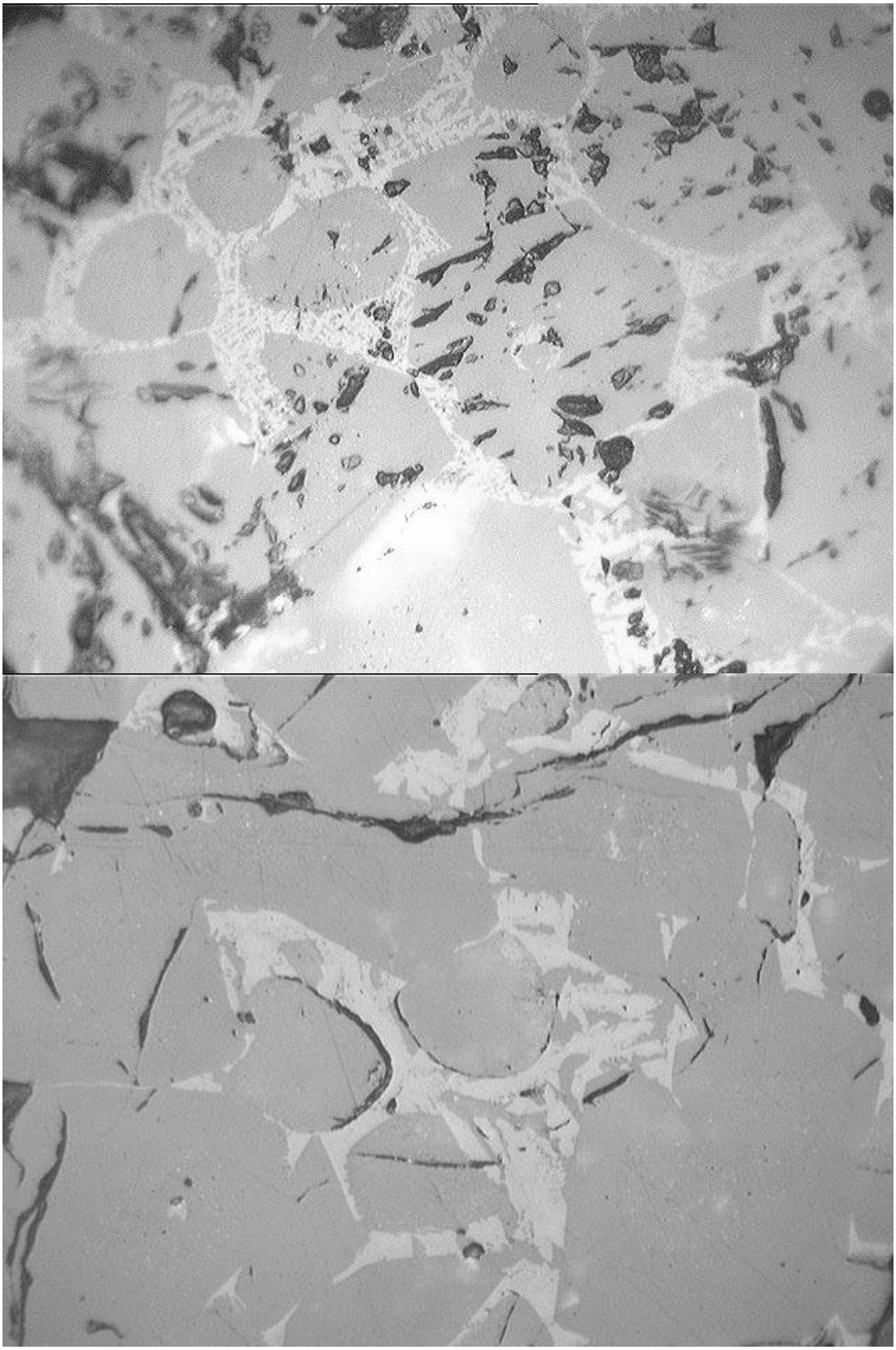


Figure 6. Continued polishing removes additional material of the damaged layer leaving fewer grinding pits as shown in the upper image. The lower image shows a specimen where all grinding pits have been removed and is now ready for the 3 micrometer and finer polishing steps to remove any fine scratches.

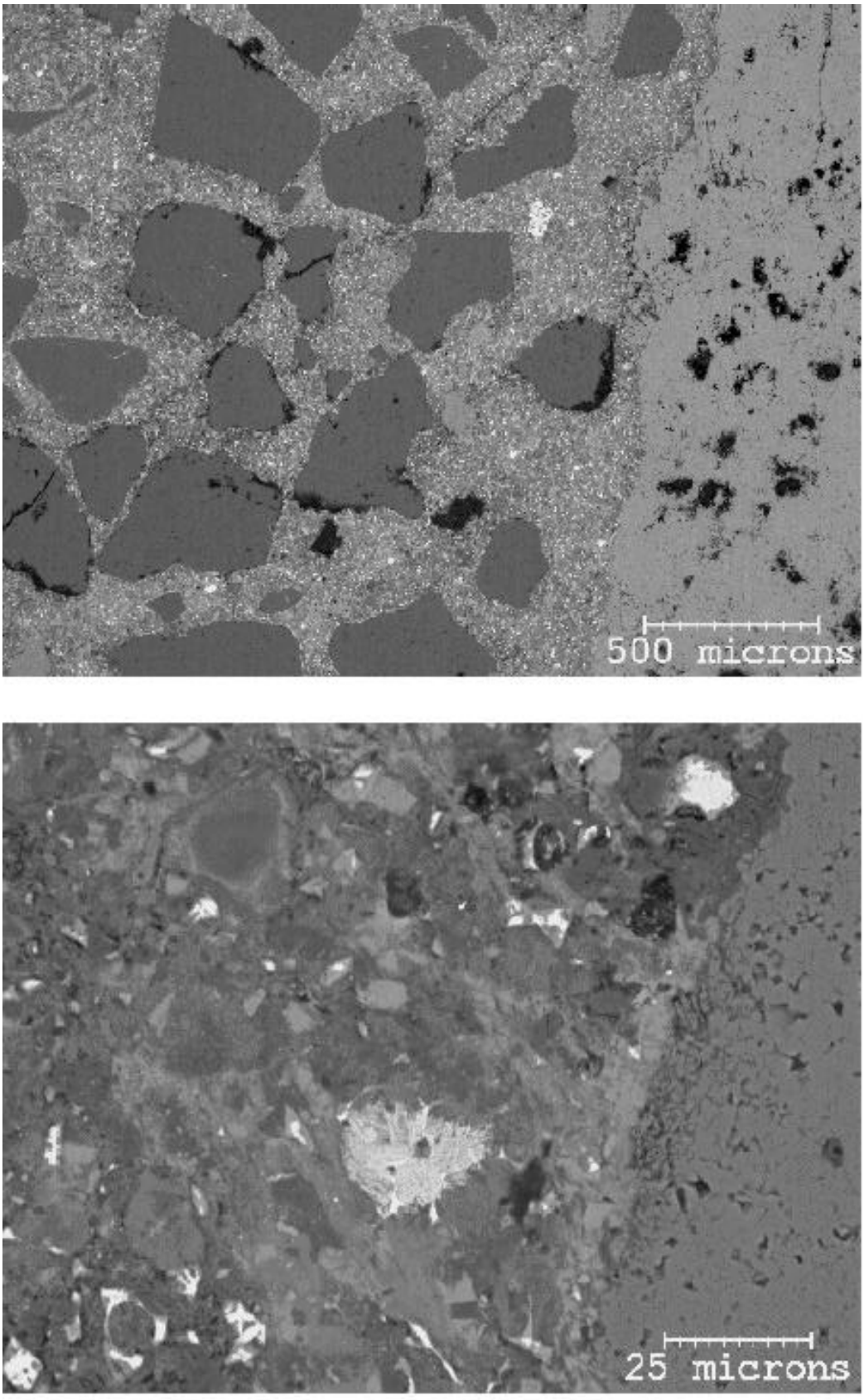


Figure 7. Epoxy-impregnated, polished section of concrete presents an optimum surface for backscattered electron and X-ray imaging.

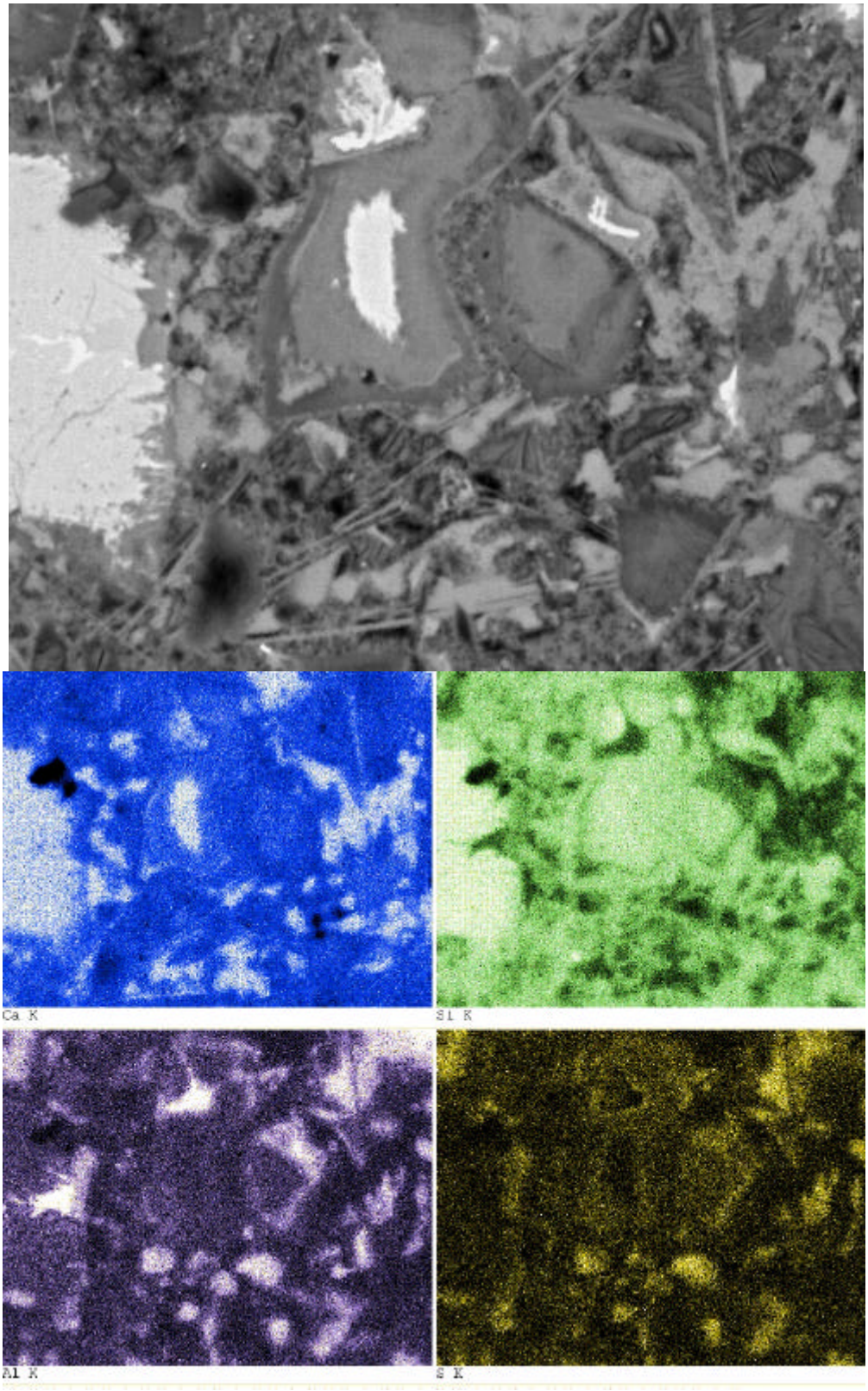


Figure 8. Backscattered electron (top) and X-ray (bottom) images of hardened cement paste show good definition of constituents. Regions of intermediate-intensity calcium (blue) and intermediate-intensity aluminum (purple), and high-intensity sulfur (yellow) define locations of monosulfoaluminate. Field width: 73 micrometers.

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