

## 3.2 SEM Imaging

High-quality images for quantitative analysis can be obtained with the following SEM operating conditions:

1. 12 kV accelerating voltage,
2. 2 nA to 4 nA probe current, adjusted to keep a relatively high X-ray count rate with minimal dead time,
3. a scan rate of 5 min/frame for an image size of 1024 pixels  $\times$  768 pixels to minimize backscattered electron noise,
4. an accumulation of approximately 15 frames for a single field of view to improve the definition of the X-ray (XR) images, and
5. a magnification of 300 $\times$ , which provides a spatial resolution of approximately 1.0  $\mu\text{m}$ /pixel, which is typically on the order of the beam's interaction volume within the specimen.

These settings are a useful starting point to obtain high-quality images, and are judged to represent a balance between fast collection times, a match in resolution of BE images with X-ray map (XR) images, and instrument stability.

The local brightness in a backscattered electron (BE) image is proportional to the average atomic number,  $\bar{Z}$ , of the phase in that location, and the XR image reflects element spatial distribution over the same field of view. The backscatter coefficient,  $\eta$ , is a measure of the backscattered electron fraction and, following Goldstein *et al.* [26], is estimated using the mass fractions and  $\eta$  values for each constituent. Table 2 lists phases found in clinker and cement in descending order of their backscattered coefficient and gray intensity. Caution is necessary here because the brightness ranking may change depending upon chemistry variability due to impurities; the exact values are not as important as the general ranking of the phases in the table. The identification of the individual phases also includes supplemental information such as domain shape (*e.g.*, angular or rounded), position within the microstructure (*e.g.*, framework grain, matrix, dispersed phase), and bulk chemistry as described in Table 3.

The BE contrast between alite and belite is relatively strong, but that between belite and cubic tricalcium aluminate is generally too low to rely on contrast to distinguish them. For such phase pairs that have similar BE coefficients, or for phases that have BE coefficients too low to be resolved in the BE image, XR imaging is used to distinguish them based on their composition. For example, periclase and some alkali sulfates often appear black, like the epoxy-filled voids, because of the brightness and contrast settings necessary to make the other phases distinct. Combining the XR and BE images facilitates their discrimination much better than relying on either image alone. Information redundancies also occur that should be reduced or eliminated to improve the phase distinction. For example, the Ca and Si XR image, or a ratio of the two, may be considered for distinguishing the calcium silicate phases. The BE image, however, provides a much better distinction between the calcium silicates and is

Table 2: Cement phases, compositions, densities, average atomic number, and backscattered electron coefficient ranked according to relative SEM BE image brightness [27].

Phase	Composition	Notation	Density (kg m <sup>-3</sup> )	$\bar{Z}$	$\eta$
Ferrite	$\text{Ca}_2(\text{Al}_x\text{Fe}_{1-x})_2\text{O}_5$	$\text{C}_4\text{AF}$	3770	16.65	0.186
Free lime	$\text{CaO}$	$\text{C}$	3320	16.58	0.188
Alite	$\text{Ca}_3\text{SiO}_5$	$\text{C}_3\text{S}$	3130 to 3220	15.06	0.172
Belite	$\text{Ca}_2\text{SiO}_4$	$\text{C}_2\text{S}$	3280 to 3310	14.56	0.166
Arcanite	$\text{K}_2\text{SO}_4$	$\text{K}\bar{\text{S}}$	2670	14.41	0.165
Aluminate-c <sup>a</sup>	$\text{Ca}_3\text{Al}_2\text{O}_6$	$\text{C}_3\text{A}$	3040	14.34	0.164
Portlandite	$\text{Ca}(\text{OH})_2$	$\text{CH}$	2260	14.30	0.162
Aluminate-o <sup>b</sup>	$\text{Ca}_3\text{Al}_2\text{O}_6$	$\text{C}_3\text{A}$	2560	13.87	0.159
Aphthitalite	$\text{K}_3\text{Na}(\text{SO}_4)_2$	$\text{K}_3\text{N}_{0.5}\bar{\text{S}}_2$	2700	13.69	0.158
Syngenite	$\text{K}_2\text{Ca}(\text{SO}_4)2\text{H}_2\text{O}$	$\text{K}_2\text{C}\bar{\text{S}}\text{H}_2$	2600	13.60	0.156
Anhydrite	$\text{CaSO}_4$	$\text{C}\bar{\text{S}}$	2980	13.41	0.154
Bassanite	$2\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	$\text{C}\bar{\text{S}}\text{H}_{0.5}$	2700	13.03	0.149
Calcite	$\text{CaCO}_3$	$\text{C}\bar{\text{C}}$	2710	12.56	0.142
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{C}\bar{\text{S}}\text{H}_2$	2320	12.12	0.138
Thenardite	$\text{Na}_2\text{SO}_4$	$\text{N}\bar{\text{S}}$	2660	10.77	0.125
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	$\text{CM}\bar{\text{C}}_2$	2840	10.87	0.124
Periclase	$\text{MgO}$	$\text{M}$	3580	10.41	0.121

<sup>a</sup> cubic polymorph<sup>b</sup> orthorhombic polymorph

preferred because XR images have lower resolution and therefore appear grainier and noisier than the BE image. Further details and examples of how SEM images may be combined to render these phases distinct will be discussed in a later section.

### 3.3 X-Ray Microanalysis and Imaging

X-Rays are produced as a result of the interaction of the electron beam with the specimen, and they are typically displayed as a set of peaks with a continuous background. The energy-dispersive X-ray analyzer discriminates and counts emitted X-rays based upon their energy.

### 3.4 Image Processing

The next four sections briefly provide guidance for processing the experimentally obtained images and transforming them to a single phase segmented image suitable for quantitative stereological analysis. A more detailed procedure may be found in Stutzman *et al.* [20]

Table 3: Textural and chemical characteristics useful for distinguishing cement phases.

Phase	Identifying Characteristics
Free Lime	Bright BE, rounded crystals, sometimes clustered, strong Ca and no Fe
Ferrite	Bright BE, dendritic to prismatic matrix phase, high Ca, medium Fe and Al
Alite	Medium-high BE, euhedral to anhedral crystals, framework grain, strong Ca and Si, minor Mg and Al.
Belite	Medium BE, rounded crystals, framework grain, sometimes clustered, strong Ca and Si, minor Mg, Al, and weak S.
Aluminate	Medium BE, fine to lath-like crystals, matrix phase between ferrite crystals, Ca, Al, Mg, K, Fe and sometimes Na.
Arcanite	Medium BE, crystals dispersed along boundaries of matrix and framework grains, high K, S
Aphthitalite	Low BE, crystals dispersed along boundaries of matrix and framework grains, high K, Na, S
Syngenite	Low BE, K, S, Ca
Anhydrite	Ca, S, individual grain, may occur as perimeter phase on gypsum
Bassanite	Ca, S, individual grain, not typically resolvable from anhydrite or gypsum
Calcite	Ca, no S, K, or Na, individual grain, dark BE
Gypsum	Ca, S, no K, Na, individual grains
Thenardite	Low BE, crystals dispersed, typically along boundaries of matrix and framework grains, high Na, S
Dolomite	Ca, Mg, no Al or S, individual grain
Periclase	Low BE, Mg, O, equant to dendritic grains, clustered to dispersed

ImageJ<sup>6</sup> is used to preview the SEM BE and XR images and to interactively make some adjustments to the background and noise by improving the image quality. The original images are always retained and the *File→Save As* command is used to save a modified image. Appending the filename with an M to indicate the operation performed on the image indicates that it has been modified. By appending the filename with an operation code, the images will appear together in the directory, allowing for easy viewing of the available images. A TIFF file format is always selected to eliminate any image quality loss with subsequent processing operations.

1. Read images individually or by drag-and-drop with ImageJ.
2. Tile images to arrange all on the monitor (*Window→Tile*)
3. Assign a gray lookup table (LUT) to each image (*Image→Lookup Table→Grays*)
4. Adjust each image's brightness and contrast to assess the noise associated with low element concentration or the background (image noise): *Image→Adjust→Brightness Contrast*
5. Subtract background noise with operation (*Process→Subtract*) using the preview check box in the Subtract operation window to interactively select the noise level. When acceptable, select OK.
6. Clean up any noise by filtering. The *Despeckle* and the *Remove Outliers* commands under *Process→Noise* can be applied to remove isolated pixels or small pixel groups. The median filter (*Process→Filters→Median*) or the *Thresholded Blur* will also work well to reduce image noise while retaining edge details. Apply any filtering lightly as edge blur may result in problems during the segmentation phase. Save the modified image using *File→Save As→TIFF*, appending the original file name with an "M" to indicate this file has been modified, so that the original is not over-written.
7. Use MultiSpec<sup>7</sup> to generate a segmented, indexed image where each pixel is uniquely assigned to the class it most likely belongs based upon a user-developed training set of data. An abbreviated set of steps, which will be detailed below include (a) reading image files, (b) linking files, (c) designating phase classes, (c) establishing training fields for each class, (d) selecting a classification algorithm, (e) evaluating the classification, (f) saving the project, and (g) saving the classified image as an indexed, segmented TIFF file. This image file will then be used for the image analysis for determining phase area fraction, phase mass fraction, and phase perimeter fraction. The resulting image and phase-related data are useful characteristics of the microstructure and for introduction into simulation models like VCCTL [28, 29] or THAMES [30].
8. In Multispec, read initial image as a multispectral type (*File→Open Image*), and check "multispectral type" box.

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<sup>6</sup><http://imagej.nih.gov/ij/>

<sup>7</sup><https://engineering.purdue.edu/biehl/MultiSpec/>

Under “Multispectral Display Specifications” accept the defaults with the exception of the “Enhancement” section, where you can opt to not change the image (the usual), clip it on the low and high end, or user selected clipping.

9. Link the set of X-ray images deemed useful in making a segmentation: *File*→*Open Image*. **Note:** This operation requires selecting “Link to active image window” from the drop-down box.

Select the X-ray images by clicking on them individually. Remember to select the modified ones (M). Use a standard image sequence so that the exact image source in the virtual linked files (BEI, Al, Mg, K, Na, S) can easily be recalled or write it down. They can be named later if necessary and excluded in the classification if desired. Click on the *Cancel* button to complete the linking.

10. Save the image set (*Processor*→*Reformat*→*Rectify Image*)

Use the window defaults (one could attempt to correct any displaced images here if needed), make sure the path is correct and provide a name, retaining the .LAN extension. Use the original file name to keep them together in a listing. If you do not include the extension, the file will be written without one and will not be recognized for future Read operations.

11. Open the .LAN image set for review, assigning classes and training fields, and classification (*File*→*Open Image*)

A window labeled “Multispectral Display Specifications” will appear, where color channels (R G B) can be assigned and the images enhanced by clipping or transformation. At NIST, enhancements are performed using ImageJ because Multispec seems to apply a single set of operations to each image. View the image using different channel/color combinations. The most useful are:

- BE, Mg, Al – alite, belite, aluminate, ferrite, periclase, lime, calcite, dolomite, voids
- BE, K, S – alkali sulfates, calcium sulfates

12. Establish training classes (*Processor*→*Statistics*)

Accept the defaults in the “Set Project Options” window by clicking *OK*.

In the new Project window you will see a Class Designation at the top. Enter the list of classes here by boxing in a region in the image for each, selecting “Add to List” and providing a name. The classes are listed based on this sequence and the ultimate index value used for VCCTL or THAMES, following this convention:

1 = alite	2 = belite	3 = aluminate	4 = ferrite
5 = periclase	6 = arcanite	7 = apthitalite	8 = void

Record the index designations for later use as some phases will be absent from some materials.

Subclasses can be created—for example, alkali sulfate could contain sub-classes arcanite (potassium sulfate) and apthitalite (potassium, sodium sulfate).

Add training classes then by selecting the class, boxing in more regions, and specifying “Add to List”. The more training pixels, the better the class characteristics are defined.

13. Classify (*Processor*→*Classify*)

Specify the “Minimum Euclidian Distance” algorithm as it works consistently well. Check the box “Write Classification Results” to Disk File and check the path, retaining the .GIS extension for this image.

Initial quality check is the percent re-assignment of the training set pixels and the quality of the class assignment seen in the .GIS image. The .GIS image is read into Multispec as a Multispectral type image and you will see the class assignments with distinct colors. The colors may be changed by double clicking on the class list followed by setting the color using the color picker.

14. Save the work as a Project

Even if not successful, you can go back and add training fields, delete fields, run alternate classification algorithms, and even exclude specific images to see if it can be improved.

15. Save the .GIS file as a TIFF file.

This preserves the color assignments for the phases and the index values. Do not save these in the .JPG format as the index values and colors will not be saved. A good practice is to append the file name with a MS suffix, to avoid overwriting the previous files.

16. Clean up any mis-assigned pixels using a surface blur filter that retains edge details.

The plugin “Thresholded Blur” works well for this by ignoring pixels that deviate from the mean and by allowing you to specify the kernel size (radius, start with 2 or 3), threshold (1 or 2 as this is an indexed image and the values differ by 1), softness (affects the edge blur) and strength (number of times to apply).

17. Read the TIFF file into ImageJ and write the ASCII Indexed file (*File*→*Save As*→*Text Image*).

This procedure produces an ASCII file with the phase index values. If needed, you can recall the .GIS file in Multispec or the \*MS.TIF file in ImageJ to see which index value corresponds to each phase.

### 3.5 Quantitative Image Analysis

The final result of phase segmentation is a 2D color image that identifies each pixel with an integer index associated with its assigned phase. Quantitative analysis can be performed on such an image to calculate, for example

1. the area fraction of each phase (on a total solids basis)
2. the perimeter fraction of each phase (on a total solid boundary length basis)
3. the spatial distribution of each phase, quantified, for example, by 2-point correlation functions
4. the possible percolation, or connectivity, of each phase in two dimensions

Many, if not all, of these operations can be performed by built-in functions, such as generating a histogram and list from the indexed image or augmenting ImageJ with Java plugins such as the correlation function. However, most of these plugins have been developed and optimized for image processing in other fields, especially biology, and are not well-documented or validated for use with clinker or cement microstructure images. As an alternative, NIST has developed a simple, fast computer program specifically for performing quantitative image analysis on clinker or cement microstructures. The program, called MicroChar [31], is available for Windows or Mac OS X computers, and performs all these calculations with minimal intervention by the user. Installation and use of MicroChar is described in Ref. [31].

## 4 Applications to Portland Cement Powders

This section demonstrates the use of the foregoing procedures to analyze three portland cement powders, which are designated as 3-70, 3-71, and 3-74.<sup>8</sup> Each of these cements was analyzed by XRD, both with and without selective chemical extractions, and by SEM/XMA.

### 4.1 X-ray Diffraction Results

X-ray powder diffraction analyses include triplicate scans of each sample treatment (bulk cement, KOSH residue, SAM residue) with sample re-packing for each scan. The replication provides multiple estimates of the phase composition for both the individual treatments and the averaged cement composition. A representative set of diffraction data for the three cements are shown in Fig. 6, Fig. 7, and Fig. 8. An initial comparison of the peak intensities between cements provides some insights on their relative compositions. The effects of concentrating specific phase groups is seen by the increased peak intensities in the extraction residue patterns as well as the improved clarity of the simpler residue mixtures.

For example, cements 3-70 and 3-74 have relatively high aluminate content and relatively low ferrite content compared to cement 3-71, looking at the diffraction peaks for these phases in the  $32^\circ$   $2\theta$  to  $36^\circ$   $2\theta$  region. A diffraction peak shows up in the SAM extraction residue for cements 3-70 and 3-74. Syngenite may form from a reaction between gypsum and one of the forms of potassium sulfate during storage of a cement [32]. It also may form during the

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<sup>8</sup>These designations reflect an internal material logging convention at NIST and have no other significance.