

AUTOMATED ANALYTICAL SCANNING ELECTRON MICROSCOPY AND IMAGE ANALYSIS METHODS FOR CHARACTERIZING THE INORGANIC PHASES IN COAL AND COAL COMBUSTION PRODUCTS

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ABSTRACT

Particle-by-particle scanning electron microscopy (PBPSEM) and scanning electron microscopy point count (SEMP) are being developed and applied for characterizing the inorganic phases in coal and coal combustion products. PBPSEM sizes, identifies, and quantifies coal mineral constituents and the degree of mineral-coal association. SEMPC determines the chemical composition and abundance of inorganic phases in coal ashes and deposits. Both methods are automated to minimize operator bias and to facilitate the acquisition of a statistically significant number of analyses to fully characterize heterogeneous samples.

INTRODUCTION

This paper describes two analysis methods: particle-by-particle scanning electron microscopy (PBPSEM) and scanning electron microscopy point count (SEMP), being developed and applied at the Energy and Environmental Research Center (EERC) for characterizing the inorganic phases in coal, coal ashes, and deposits. Both methods employ an automated analytical scanning electron microscope (SEM) integrated with a digital image analysis system. This instrumentation is very useful for characterizing complex heterogeneous materials because it provides the capability to efficiently analyze a statistically significant number of individual microparticles for both compositional and morphological information.

In recent years, considerable attention has been focused on developing and applying image processing and analysis techniques for quantifying the association of mineral grains with the organic coal matrix (1-3). Most image processing and analysis systems provide algorithms for acquiring the required morphological data for such an analysis. These algorithms are based on the creation of binary images from an original gray-scale image. The binary transformation process requires operator intervention to select thresholds for segmenting the coal and mineral phases from the gray-scale image. Unfortunately, this process can be very time-consuming and involves subjective judgement by the operator to create binary images that accurately represent the original image. At the EERC, we have formulated an automatic threshold selection algorithm and incorporated it into an image analysis application program. The program completely automates image acquisition and processing, thus enhancing the objectivity of analysis results. The PBPSEM method integrates this automated image analysis capability with electron-probe microanalysis to measure various morphological and compositional parameters for individual mineral grains in coal. These data are compiled and classified according to

compositional criteria into various mineral/chemical categories using a modified version of the Particle Characterization (PARTCHAR) program (4). The program provides a complete statistical summary for all the mineral/chemical phases in a sample, including the proportion of each phase directly associated with coal.

The SEMPC method for chemically characterizing and classifying the crystalline and amorphous phases in coal ashes and deposits has been improved greatly since its initial development (5). The method involves performing quantitative electron-probe microanalysis on a statistically significant number of randomly selected points on a sample. The compositional analyses are compiled and then classified according to stoichiometric criteria into standard phase categories using a best-fit algorithm (6). Applications of the method are presented elsewhere (7, 8). Recent improvements discussed in this paper include an automation routine for randomly selecting discrete image areas and analysis points on the sample, the capability to store digital images with documented analysis locations, and a more efficient and comprehensive phase classification program.

DESCRIPTION OF THE PBPSEM METHOD

Sample Preparation and Instrumentation. Coals to be analyzed by PBPSEM are pulverized to a standard combustion grind (i.e., approximately 80% of the particles -200 mesh), mounted in carnauba wax (9), cross-sectioned, and polished using standard petrographic procedures. Samples are then sputter-coated with carbon to minimize electron-beam charging artifacts. A JEOL JSM-35 analytical SEM equipped with a NORAN Instruments (formally Tracor Northern, TN) Micro-Z ultrathin window x-ray detector, TN-5500 x-ray analyzer, TN-5600 stage automation system, TN-8500 image analyzer, and GW Electronics annular solid-state backscattered electron (BSE) detector is utilized for performing PBPSEM analyses.

Digital Image Acquisition, Processing, and Analysis. The automated analytical SEM, operating in the BSE imaging mode, is programmed to analyze preselected areas on the sample. The electron microbeam is rastered across the analysis areas to acquire a digital image at a spatial resolution of 512 pixels in both the line-scan (x-) and frame-scan (y-) directions. Frame averaging is employed to enhance image quality.

A modified version of NORAN Instruments Locked and Liberated image analysis program is used to locate particles and measure various morphological, phase correlation, and compositional parameters. Coal and mineral particles are delineated based on the atomic number contrast inherent in BSE imaging. An automatic threshold selection algorithm has been formulated to segment the coal and mineral phases from the gray-scale BSE image into separate binary images. The selection algorithm utilizes the image's gray-level histogram. Gray-level histograms of prepared coal samples are generally bimodal consisting of two peaks corresponding to the average brightness (i.e., mean atomic number) of mounting medium and coal, a valley that separates the peaks and represents the less heavily populated intermediate gray levels of coal particle edges, and an essentially featureless region corresponding to a large range in mineral gray level intensity as a result of compositional variation. In some coal samples, the mounting medium and coal peaks are poorly resolved, and the selection algorithm has difficulty in

locating the histogram valley separating the two peaks (Figure 1a). A median filter is applied to the image to create a more strongly bimodal histogram (Figure 1b). The filtered histogram facilitates the selection of thresholds by the method described in this section. The median filter was chosen because it suppresses digital image noise without significantly affecting particle edges or other image features (10). The automatic threshold selection algorithm searches for the mounting medium and coal peaks and then selects a threshold at the minimum intensity value in the histogram valley (Figure 1b). This method of threshold selection is referred to as the mode method or standard histogram method (11, 12). The threshold segments coal from the mounting medium. Another threshold is selected to segment the coal from minerals. The placement of this threshold involves a peak-modeling procedure to account for any asymmetry of the coal peak caused by the overlapping of coal and mineral gray levels. The procedure models the coal peak assuming a Gaussian distribution of gray levels and then establishes a threshold at the base of the modeled peak (Figure 1b). Thresholds are determined for each area of the sample analyzed. Automatic thresholding eliminates operator bias in the results and compensates for instrument drift.

After transforming the gray-scale image into coal and mineral phase binaries, the following morphological parameters are determined for each phase of a given particle using standard image analysis routines: minimum, maximum, and average cross-sectional diameter; area; and external perimeter. Two correlation parameters are also determined for each mineral phase: an indication of whether the mineral grain is included, attached, or excluded relative to the coal matrix; and the amount of mineral perimeter in contact with the coal or mounting medium. In addition to this morphological and phase correlation data, compositional information is obtained by acquiring an energy-dispersive x-ray (EDX) spectrum from each mineral grain's center. Spectral regions-of-interest (ROI) are defined to measure the characteristic x-ray emission intensities of twelve common, mineral-forming, major and minor elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe, and Ba). Relative intensities are calculated by dividing the net counts for each element by the total ROI counts for all elements. Morphological, phase correlation, and compositional data for approximately 3000 particles are collected at three magnifications to provide the spatial resolution necessary to analyze particles ranging widely in size. These data are transferred on-line to a personal computer where they are tabulated and stored to disk for subsequent reduction, report generation, and archival. The acquired BSE images with the locations of EDX analysis are stored to tape.

Data Reduction and Reporting. A modified version of the PARTCHAR data reduction program (4) classifies the mineral compositional analyses based on elemental relative intensities, relative-intensity ratios, and stoichiometric criteria into one of 33 mineral/chemical and mineral association categories. Analyses that do not conform to any of the specified criteria are termed unclassified. The program allocates the classified particles according to average diameter into six intervals so that the size distribution of mineral/chemical phases can be determined. A report is generated that summarizes the results in a series of tables containing information on the number, area, and proportions of mineral/chemical phases in their respective size intervals and according to their association with the coal matrix (i.e., included, attached, or excluded). Mineral weight percentages are calculated assuming that particle area is proportional to particle volume (13) and mineral densities are constants.

DESCRIPTION OF THE SEMPC METHOD

Sample Preparation and Instrumentation. Coal combustion products to be analyzed by SEMPC are mounted in epoxy resin, cross-sectioned, and polished; or dispersed ultrasonically and mounted on filter paper. Samples are sputter-coated with carbon prior to analysis. The SEMPC analysis is performed with a NORAN Instruments Automated Digital Electron Microscope (ADEM). The ADEM is a fully integrated analytical SEM and image analysis system equipped with a Z Max 30 diamond window EDX detector and LaB₆ gun. The ADEM has the capability to perform SEMPC analyses on multiple samples with unattended operation.

Digital Image Acquisition and Electron-Probe Microanalysis. The stage/electron-beam automation system is programmed to randomly select discrete locations on a representative area of the sample for digital imaging and quantitative electron-probe microanalysis. Specifically, the analyst specifies a rectangular analysis area on the sample. The number of analysis frames available in this area is calculated based on the magnification employed. An analysis frame is randomly selected, and a digital image is acquired. Brightness, contrast, and focusing adjustments are performed automatically by the instrument for each frame analyzed. A location grid is established on the image, and the electron beam is sent to an address on the grid to acquire an EDX spectrum for eight seconds. The x-ray count rate is monitored during the 8-second acquisition to exclude points that emit insufficient x-ray counts for complete chemical characterization. The count rate must exceed a predefined threshold value, typically 1000 counts/second, for the analysis to be accepted. If the count rate is less than the threshold value, the beam is moved to another location. However, if the point is acceptable, the acquisition continues for an additional 17 seconds. The spectrum is then transferred to another memory location for processing, while the next point is selected and analyzed. Elemental peaks are deconvoluted, and their net intensities are extracted from the spectrum using the filter-fit method (14). The x-ray intensity data are corrected for matrix effects, and concentrations are calculated using the ZAF correction procedure. Mineral standards are used to calibrate the procedure. A maximum of 18 elements may be included in the analysis. Quantitative analyses for typically 250 points per sample are collected and transferred on-line to a personal computer for reduction and archival purposes. The acquired digital images with documented analysis locations can be archived for additional analysis.

Data Reduction and Reporting. An off-line program classifies each compositional analysis according to stoichiometric criteria into one of 56 standard phase categories using a best-fit algorithm (6). The program has the option to incorporate a maximum of 10 additional user-defined phase categories in the classification scheme. Analyses that do not conform to any of the specified criteria are termed unclassified. The program calculates the abundance of each phase in frequency percent and a normalized cumulative bulk composition for the sample on a weight percent oxide basis.

SEMPC analysis results, when combined with crystalline phase identifications obtained by x-ray powder diffraction (XRD), can be used to infer a composition for the vitreous (i.e., liquid) phase of a deposit. This inferred liquid phase composition can be used as input for a subroutine of the program to calculate base-acid ratio and viscosity (15).

Liquid phase chemistry and viscosity is important for understanding deposit strength and development (7).

Quality Control. Bulk analysis techniques are utilized to validate SEMPC analysis results. The SEMPC calculated bulk composition is compared to the bulk composition determined directly by EDX fluorescence analysis to assess whether the SEMPC analysis is strictly representative of the sample. In addition, XRD crystalline phase identifications are referred to for confirmation of SEMPC phase identifications. Comparisons of SEMPC analysis results to mineralogical and chemical data obtained by bulk analysis techniques are presented elsewhere (5).

DISCUSSION

Development of the PBPSEM method is in its infancy, and several refinements are required before it can be used routinely for characterizing coal mineralogy. The automatic threshold selection algorithm requires a bimodal gray-level histogram for segmenting the coal particles from the mounting medium. This requirement is violated when the area imaged on a sample consists of only coal or mounting medium. Currently, the analysis is performed at low magnifications, generally less than 500, to prevent such an occurrence. This practice, however, results in rather poor spatial resolution, thereby limiting the method to analyzing relatively large particles, generally greater than about three microns in average cross-sectional diameter. Other methods for automatic threshold selection are being investigated to negate this particle-size restriction. Another limitation of the method is the inability to distinguish and quantify mineral-mineral associations for agglomerated particles. This information is extremely important when considering inorganic transformations that occur during combustion. Additional development of the data reduction program is needed to present quantitative mineral-coal association results in formats appropriate for various applications, such as in the field of physical coal cleaning or ash modeling. Work also needs to be done to optimize and validate the method.

In contrast to the PBPSEM method, the SEMPC method is in a mature stage of development. Efforts are primarily focused on developing automated image analysis methods for utilizing the stored digital images to relate the morphology in the vicinity of an analysis point to chemical composition. Porosity and the recognition and quantification of neck-growth development between particles are measurements being investigated for assessing deposit strength.

CONCLUSION

The PBPSEM and SEMPC analysis methods have been developed to provide detailed morphological and compositional information on the inorganic phases in coal and coal combustion products. Developmental efforts are in progress to optimize the methods and assess their performance characteristics (i.e., limitations, repeatability, and reproducibility). Work will also continue to extract and quantify the wealth of information provided by these methods for various applications.

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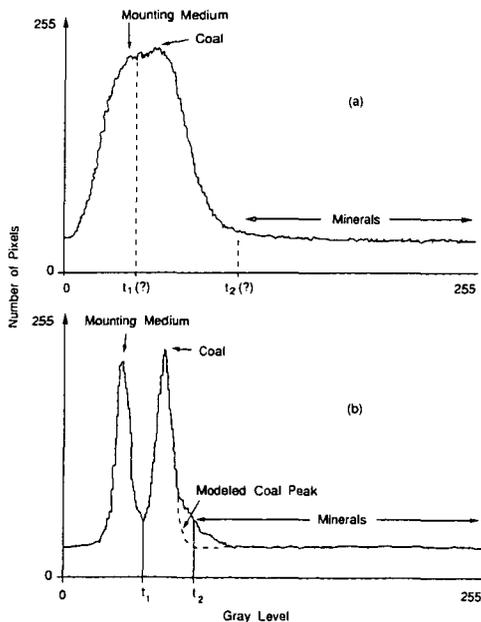


Figure 1. Grey-level histograms, (a) original histogram, the selection of thresholds segmenting mounting medium from coal (t_1) and coal from minerals (t_2) is arbitrary; (b) median filtered histogram (5×5 filter), mounting medium and coal peaks are resolved, thus facilitating automatic threshold selection by the method described in the text.