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EVALUATION OF AN OPTICAL MICROSCOPE METHOD FOR COAL-PYRITE/MARCASITE DIFFERENTIATION

Topical Report

May 1980

Coal Preparation Division
Pittsburgh Mining Technology Center

U. S. Department of Energy
Assistant Secretary for Fossil Energy

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W. S. Sanner, Jr. and D. L. Meteney

REPORT DATE - MAY 1980

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EVALUATION OF AN OPTICAL MICROSCOPE METHOD FOR COAL-PYRITE/MARCASITE DIFFERENTIATION

by

W. S. Sanner, Jr.¹ and D. L. Meteney²

ABSTRACT

A reflected-polarized light microscope technique for coal marcasite-pyrite differentiation is detailed. Presence of the two minerals was verified by x-ray diffraction analysis. The optical technique produced marcasite content values that were consistently lower than those measured by x-ray diffraction. Although the optical technique produces data that are at best semi-quantitative, it can be used to approximate ($\pm 20\%$) marcasite concentration in coal without a heavy mineral concentration step.

INTRODUCTION

Interest in marcasite, usually the less common of the two FeS_2 minerals in coals, appears to be growing. Marcasite concentration may be a factor in performance variations seen during froth flotation desulfurization of coal. Also, it has been suggested that marcasite may provide a disproportionately large contribution to the acid mine drainage production of a given coal bed. Some recent regulatory requirements have galvanized interest in marcasite levels present in coal. A methodology is therefore needed to differentiate marcasite from its stoichiometric twin, pyrite, and to delineate its concentration in coal. X-ray diffractometry (XRD) and polarized reflected light microscopy are two common techniques that can be used.

This paper will specifically detail the optical microscope technique used by DOE's Coal Preparation Division to determine the marcasite content in coal. Although this technique may be common knowledge to the ore or opaque mineral microscopist, it is presented in this paper because it is likely that many coal microcharacterization investigators and coal laboratory analysts may not be aware of the details of this procedure. Our purpose is to disseminate the details of a polarized reflected light microscopic differentiation technique for the two FeS_2 minerals in coal in order to help meet the growing need for smaller laboratories to determine marcasite content in coal.

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The technique to be outlined in this paper can also be tailored to fit identification routines for other selected coal accessory minerals. This work can be performed with an ore microscope or a slightly modified petrographic microscope, a fact which may also be beneficial to the smaller, less well endowed laboratories involved in coal microcharacterization investigations or coal analysis.

Microscopic examination of coal pellets under crossed polarizers frequently reveals two apparently different FeS_2 forms. During continuous stage rotation, one form remains dark while the other alternates between shades of blue, green, dark gray or tan colors, and extinction (See Figure 1). Such anisotropic behavior of plane-polarized light reflected from a surface is characteristic of uniaxial and lower symmetry minerals. Since pyrite is isometric, it should be isotropic; marcasite is orthorhombic and therefore should display anisotropic reflectance characteristics to plane-polarized light (5, 3)³. Utilizing these principles, researchers at Pennsylvania State University (4), West Virginia Coal Research Bureau (2), and elsewhere (7) differentiate pyrite and marcasite in coal.

ACKNOWLEDGMENT

We thank Dr. Sidney S. Pollack both for his help in preparation of diffraction patterns for several ultra fine powders and his evaluation of the other XRD analyses.

EXPERIMENTAL DESIGN

Description of Microscope

A standard large research Leitz Orthoplan⁴ microscope equipped for polarized reflected light observation was used. The 10x eyepieces, one containing a whipple grid micrometer, were mounted in a binocular eyepiece housing with a slide-in rotatable analyzer. This was connected to a stand equipped with an interchangeable reflecting plate/berek prism vertical illuminator. A 20x oil immersion objective provided the best compromise between resolution and vividness of anisotropic tints. The light source was a quartz-halogen illuminator; however, a xenon lamp would also be satisfactory. Details of microscope construction and operation for opaque mineral identification are given in other publications (6, 1).

Sample Preparation

All 1-inch diameter pellets were prepared by epoxy binding representative 1200 micron by 0 stage ground material in a compression mold. After curing, each pellet was ejected and sawed in half, parallel to its base. The two basal surfaces of the pair were successively ground on discs surfaced with 320, 400, and 600 grit SiC paper, rough polished with 1 micron diamond abrasive on Texmet⁵ and final polished with 0.05 micron Al_2O_3 on a silk-covered bronze wheel. After coating with immersion oil, the specimens were ready for microscopic examination.

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

⁴Reference to trade names is made for identification only and does not imply endorsement by the Department of Energy.

⁵The AB Buehler LTD trademark for a hard, napless, textile surface which, in conjunction with diamond abrasive, produces a high cutting rate and low surface relief.

a.

b.

0°

c.

45°

d.

65°

FIGURE 1 - Photomicrograph of an FeS_2 particle in coal pellet, 320 x, oil immersion, a: polarized reflected light, b through d: pyrite remains gray through various stages angles with polars crossed, marcasite passes from gray through extinction to blue.

Optical Microscope Technique

The presence or absence of bireflection is an undisputed determinant used to differentiate pyrite from marcasite (5). This phenomenon is an observed light intensity change during stage rotation while the specimen is illuminated with plane polarized light (1). This intensity change can be very subtle and, if many grains need be identified, the task is painstaking.

A more rapid technique for microscopically differentiating the two iron disulfides utilizes crossed polarizers. Marcasite is strongly anisotropic, displaying intense blue, purple, green-yellow, and violet-gray anisotropic tints. According to at least one reference, pyrite will rarely show weak anisotropy with blue-green to orange-red colors, perhaps due to lattice strain caused by specimen preparation or lattice impurities (5). Such weak anisotropy has yet to be observed by the authors on coal or museum grade FeS_2 specimens. As a precaution, if one does encounter a weak anisotropy on an FeS_2 surface in coal, the analyzer should be removed from the optic path and the stage rotated to confirm bireflection. Pyrite in coal will not usually show the jet black extinction one might anticipate, but rather a uniform dark gray through all rotation angles. This may relate to internal reflection and/or the lack of precise isometric symmetry in single crystals of coal pyrite (8). Single crystals of hydrothermal pyrite show isometric symmetry and achieve total extinction (See Figure 2(a)).

ANALYTICAL PROCEDURE AND RESULTS

The optical data collection technique requires examination of approximately 350 microscope fields located on a 1-inch cylindrical specimen surface by stops on a one millimeter square-grid system provided by a mechanical stage. At each grid node, an eyepiece-mounted whipple micrometer was used to estimate the area subtended by marcasite within the field of view. Since the area of each field and the number of fields are known, the ratio of total marcasite area to total encountered field area is the area fraction of marcasite for those fields. This area fraction is proportional to the volume fraction of marcasite in the pellet.

XRD is usually performed on fine powders or single crystals; however, polished surface XRD examination was used in this case because it will provide a direct confirmation of marcasite quantity on the surface of each pellet which can be directly compared to the optical data. In this evaluation technique, an x-ray beam illuminates the polished surface of the specimen throughout the angular sweep of the diffractometer. One-to-one x-ray response ratios are assumed for pyrite and marcasite and thus the relative area under the charted response peaks should be proportional to the area fraction of the mineral with respect to the total crystalline material present on that surface. Again, as in the optical case, these area interrelationships can be assumed proportional to the relative volume interrelationships of phases within the cylindrical sample. Since direct comparison with the optical data is required, the surface XRD data must represent the total sample pellet, not just the crystalline material in the pellet. The average density, T , of the crystalline material within the pellet is computed by the formula

$$\sum_i d_i V_i = T, \quad (1)$$

where d_i and V_i are respectively the density and volume fraction of the i^{th} crystalline phase present in the sample. The volume fraction, x , of all crystalline material within the pellet can be calculated by the expression

$$T_x + 1.4(1-x) = D, \quad (2)$$

a.

b.

c.

FIGURE 2 - Museum grade FeS_2 particle mounts, reflected polarized light, 200 x, oil immersion, crossed polarizers.

a. pyrite at all stage orientations

b. marcasite at stage 0°

c. marcasite at stage 45°

where D equals the methanol displacement density of the pellet, and 1.4 gm/cc is the assumed density of the non-crystalline material, coal and epoxy, within the pellet. The variable x is then applied to convert the surface XRD data to a total sample basis.

For the conventional fine powder XRD technique, material was ground to pass 75 microns, analyzed, and marcasite x-ray response peaks were generated. A hydrothermal marcasite specimen was also ground in the same manner and combined with varying amounts of a mixture of silica and amorphous carbon selected to imitate the background x-ray response of coal. A standard x-ray response curve was generated by analyzing several synthesized samples and as a result, the area under a set of marcasite x-ray response peaks from an unknown sample can be directly related via standard response to weight percent marcasite in that sample.

In order to compare this weight percent and volume percent data, one system must be converted to the other to obtain a valid basis for comparison. First, the surface XRD and optical volume data must be rendered "epoxy-free". Since the pellets consist of an average 22 percent epoxy by volume, dividing raw volume percent by 0.78 will yield epoxy-free volume percent. Since the total weight of the sample equals the sum of the weights of all phases in the sample, then

$$\sum C_i d_i = C_T d_T \text{ and} \quad (3)$$

$$\sum C_i = C_T, \quad (4)$$

where C_T and d_T ⁶ are respectively the total sample volume and density, and C_i and d_i represent the same for the i^{th} phase constituting the sample. Weight percent, W_i , of any phase, i , in the sample is represented by the expression

$$W_i = \frac{C_i d_i}{C_T d_T} \quad (5)$$

Since the volume percent, V_i , of phase i in the sample is given by

$$V_i = \frac{C_i}{C_T}, \quad (6)$$

substituting equation 6 into 5 yields

$$W_i = V_i \frac{d_i}{d_T}. \quad (7)$$

This expression relates weight to volume percent as a function of phase and total sample densities, and it can be used to interpret either system in terms of the other.

Individual pellets of mineral specimen pyrite and marcasite were examined under reflected light with the polarizing microscope. The pyrite pellet was covered with isotropic mineral grains, and the marcasite pellet was covered with anisotropic

⁶ $d_T = D$, but d_T can be approximated by summing $d_i V_i$ for major phases present in the sample.

mineral grains (See Figure 2). XRD analysis confirmed that the latter specimen consisted of marcasite. No grains on the pyrite pellet showed any hint of anisotropy, strain generated or otherwise.

Pellets were prepared from anthracite coal collected near Nanticoke, Pennsylvania. This sample contained a maximum 0.6 percent total sulfur. FeS_2 particles, although sparsely distributed over the pellets surface, were either strongly anisotropic or isotropic. No curvilinear twin or crystal boundaries, or similar indicators of strain-generated anisotropy were found. Faulting and folding common to the Pennsylvania anthracite bearing strata could provide the necessary deformation to generate strain in pyrite; however, no evidence supporting strain-generated anisotropy was found in the FeS_2 in this sample. Since the Appalachian bituminous coal region was subjected to less regional tectonic activity than the anthracite-bearing strata of similar age, the probability is even more remote that anisotropy due to strain produced as a result of regional tectonism could develop in bituminous coal pyrite from that region.

Pellets were prepared from a sample of Middle Kittanning bituminous coal from Western Pennsylvania. This sample had approximately 4.2 weight percent pyritic sulfur, so ample FeS_2 was available on the polished surface. Utilizing the optical method, marcasite areas were accumulated for scans of the same pellet surface at 0° , 45° and 90° orientations. The resultant data is 0.20, 0.18, and 0.18 volume percent, respectively. If specific gravities of 1.24 and 1.60 are assumed for the epoxy and coal material, the D (see equation 2, page 6) value for this cylindrical sample is 1.52. The weight to volume percent conversion formula translates 0.2 volume percent to approximately 0.6 weight percent marcasite. Approximately 14 percent of the FeS_2 in this sample of Middle Kittanning coal is marcasite.

This coal was also examined by the surface XRD technique. Unfortunately the low level of marcasite in the Middle Kittanning sample and the problems with the coal carbon-generated background response barely permitted qualitative confirmation of marcasite within that coal sample.

The problems encountered detecting marcasite on the surface of the Middle Kittanning sample's coal pellet with XRD led to the use of a heavy mineral concentration technique. A 200-pound mixture of four individual high pyritic sulfur coals was ground to pass 1200 microns and then processed in a 2.9 specific gravity organic liquid. The resulting 13 pounds of sink fraction became the heavy mineral concentrate. A representative sample was extracted and six standard one-inch cylindrical pellets were prepared. Optical examination of the polished surfaces revealed abundant anisotropic FeS_2 material (See Figure 3).

The pellets were designated 1 through 6. All were analyzed by both previously described methods, surface XRD, and microscope particle-area accumulations. Volume percent marcasite was determined by each method and reported on an epoxy-free basis to represent the original nonformed sample. An additional fraction of the granular sample was subjected to fine powder XRD analysis, and the data was converted from weight to volume percent following the above described procedure. Results of the analyses are presented in table 1 on a volume-percent-of-the-original-sample basis. Table 2 displays the mean values, standard deviations, and error for the replications of the microscope and surface XRD techniques.

a. reflected polarized light, 200 x, oil immersion

b. same, but with polars crossed

FIGURE 3 - Photomicrograph of the surface of a heavy - mineral - concentrate pellet prepared from several coals.

Table 1. - Volume percent marcasite in heavy mineral concentrate pellets

Sample Type	Replicate Designation	Analytical Procedure		
		Microscope ¹	Surface XRD ¹	Fine Powder XRD
epoxy molded 1" cylindrical Pellets (1200 micron x 0 particles)	1.	6.4	9.9	
	2.	5.1	11.7	
	3.	5.1	11.8	
	4.	7.7	9.5	
	5.	7.7	16.5	
	6.	10.3	11.4	
Bulk	1.			19.9
Powder (75 micron x 0 particles)	2.			17.9

¹ Epoxy-free basis

Table 2. - Mean, standard deviation, and error analysis for each technique, volume percent

Statistic	Microscope	Surface XRD
Mean	7.1	11.8
Standard deviation	2.0	2.5
Error ¹	±2.1	±2.6

$$^1 \text{ Error} = \text{mean} \pm t_{\alpha} \times \frac{\text{standard deviation}}{\sqrt{\text{number of replications}}}$$

where t_{α} is taken from a t-distribution table at 0.95 confidence or probability.

DISCUSSION OF RESULTS

Museum grade FeS_2 specimens, prepared by exactly the same technique as the coal samples, yielded no optical evidence of strain generated anisotropy. All particles in the pyrite sample were isotropic; much less than 0.1 percent of the marcasite showed less-than-strong anisotropy. Since marcasite is an orthorhombic mineral, a specific crystallographic orientation between the two optic axes would have a single index of refraction; however, a plane polarized light wave reflected from this

surface would be elliptically polarized and therefore not extinguished by the analyzer (1). Thus this unique oriented anisotropic mineral section could not be confused with an isotropic mineral surface.

The gravimetric concentration procedure was necessitated by the inability of the surface XRD analysis to detect marcasite concentrations below one weight percent. No determination of the lower limits of detectability with powder XRD was made; however in the author's opinion, 0.5 weight percent would be a reasonable lower limit for marcasite detection in raw coal. Optical microscope and surface XRD techniques yielded results in the same range; however, powder XRD on the original material produced values somewhat higher than the other two methods. Error shown in table 2 for the microscope and surface XRD techniques is ± 2.1 and ± 2.6 volume percent respectively at the 95% confidence level. At best, data with error that large should be called semiquantitative and can only provide an estimate of marcasite content. Error in both surface XRD and the microscopic technique may be due to inhomogeneities in the cylindrical specimens. Error in the microscopic technique may also be attributed to an insufficient number of measured fields for each replicate sample. Sample replication of the powder analyses were of insufficient number for an error analysis.

The lowest mean marcasite value for the heavy mineral concentrate pellets was observed with the microscopic technique. Problems of pyrite-marcasite differentiation with polarized light microscopy that were discussed above would tend to overestimate marcasite content due to misclassification of pyrite as marcasite. However, the microscopic determination appears generally to underestimate marcasite content as compared to XRD techniques, suggesting that either marcasite is escaping detection or is being misclassified as pyrite. Only material with a flat polished surface will be detected and differentiated via polarized reflected light. It is probable that both interstitial material just below the epoxy surface and fine grains smaller than the optical resolution limit would be measured by XRD (See Figure 3). These particles cannot be discriminated by optical examination; hence one would optically measure less marcasite than is actually accessible to XRD analysis.

CONCLUSIONS

The optical evaluation technique is tedious and time consuming; however, marcasite concentration can be measured on a raw coal sample, a decided advantage over XRD techniques which require heavy liquid fractionation to concentrate mineral material prior to marcasite analysis. Although the error associated with the microscopic analysis is high, the data is in range with the surface XRD data. Large error common to both techniques may result from non-uniform distribution of marcasite within and between the sample pellets, a problem addressed by increasing the sampling area. The consistent underestimation of marcasite by the microscopic technique when compared to the surface XRD data may be a result of optical resolution limitations and increased penetration of the surface by X-rays.

If a laboratory requires only an approximation of marcasite concentration in raw coal, the microscope technique has some advantages. It can be brought on-line for less than half the cost of an XRD facility, and no heavy-liquid laboratory is required. Each analysis can be performed by a competent technician in a minimum one hour per each one-inch diameter surface. Smaller laboratories could use this procedure to maximum advantage.

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