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SURFACE ELECTROCHEMICAL CONTROL FOR THE FINE COAL AND PYRITE
SEPARATION

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Introduction

This technical progress report covers the work completed from October 1, 1989 to December 31, 1989. The on-going work includes pyrite characterization, floatability evaluation, flotation selectivity between coal and pyrite, and the electrochemical properties of coal-pyrite and mineral-pyrite.

This report includes pyrite characterization to help explain surface electrochemical control for fine coal and pyrite separation. The research on floatability, selectivity and electrochemical characteristics will be presented in separated subsequent reports.

Pyrite characterization is divided into two parts:

Part I - Surface morphology and composition by SEM and EPMA

Part II- Qualitative FTIR study

Pyrite Characterization for Surface Electrochemical Control for Fine Coal and Pyrite Separation

PART I Surface Morphology and Composition by SEM and EPMA

ABSTRACT

Coarse-sized pyrites from both coal sources and mineral sources have been characterized using SEM (Scanning Electron Microscopy) and EPMA (Electron Probe Microanalysis). Discrete phases of Si- and Ca-containing minerals located at the periphery of pyrite particles are the major impurities in the pyrite samples. The SEM analysis indicates surface roughness in the pyrite particles varies depending on the extent of magnification and the sources from which they are formed. Mineral pyrites exhibit smooth surfaces and sharp edges on particles as large as 20 μm in size. Tiny globules of 1-2 μm size have grown on surfaces of small flaky coal pyrites. Deviation from the stoichiometric ratio of Fe/S in the pyrite composition has been detected on some of the Upper Freeport coal pyrite particles. The impurity minerals, surface roughness, pyrite composition and stoichiometric deviation will be taken as important factors in explaining and comparing the surface responses to the flotation processes and surface modifications.

INTRODUCTION

The sizes of the pyrite domains in the coal usually do not exceed 100 μm for occasions of massive occurrences found in cracks, cleats and fissures in the coal seams. The pyrite deposits in coals along the interstices of maceral and mineral aggregates through precipitation from percolated water during and after coalification stages. During size reduction of the coal, all minerals including pyrite as well as the coal are subjected to grinding actions and thus report to the fine fractions. It is not unreasonable to suggest that the coarse-sized pyrite is the major contributor of sulfur to the fine fractions while organic sulfur and locked pyrite are retained in the coarse fractions. This is because the coarse-sized coal pyrite, usually found as layered structures on the macroscopic scale, is fragile to external forces. Nevertheless, even when fully liberated, the coarse-sized coal pyrite may behave differently from that of ore sources during subsequent separation processes.

The characterization on the coal pyrite is still lacking in its ability to explain flotation behavior. The first approach of this study was to compare the composition and morphology of the coarse-sized coal pyrites with the mineral pyrite. The main reason is that, based on the geochemistry differences, the coarse-sized coal pyrite, although its size of limited size range and in need of further study, should not be treated in the same manner from the fine-sized coal pyrite. On the other hand, the mineral pyrite does not necessarily have the same composition and in many cases may not exhibit the same surface properties as the coarse coal-pyrite.

Coal pyrite has been divided into three groups according to their

separation potentials and cleaning difficulties [1]. Low values of specific gravity of the coal pyrite in the range of 3.2-4.7, in contrast to 5.0 from mineral sources, have been reported [1,2]. The rate of reaction of the coal pyrite is therefore expected to be different, especially in regard to the electrochemical modification processes.

EXPERIMENTAL

Pyrite Samples

Two pyrite samples from coal sources and another two samples from mineral sources were obtained for the preliminary characterization work. The samples were designated and described as follows:

- .PY-1: Sulfur ball pyrite from Pittsburgh #8 seam, PA coal. It was hand picked from coal fissures and then finely ground.
- .PY-2: Mineral pyrite from Colorado. It was also finely ground.
- .PY-3: Pyrite from Upper Freeport coal seam. It was received as agglomerates but crushed for examination.
- .PY-4: Mineral pyrite from Ward's Natural Science Establishment, Inc., finely ground.

No further purification steps were taken to preserve the originality of the samples. This is because the association of other minerals or carbonaceous materials with pyrite during its formation has been reported to be an important factor in the floatation process [3].

Scanning Electron Microscopy (SEM)

The powdered pyrite samples were examined with a Hitachi S-500 scanning electron microscope for the surface morphology comparison. The powders were scattered on top of epoxy resin hardened on aluminum stubs of 0.5-in. diameter

sizes and then sputtered with a thin layer of gold for conductive purpose to prevent electrical charge buildup. Images were selected at 2000, 3500, and 20000X magnifications and recorded with Polaroid 4 x 5 black-and-white instant photographic films (type 55). A Kevex S-5500 energy-dispersive X-ray (EDX) spectrometer was used to assist in the identification of the pyrite particles. It also provided a rough qualitative determination of the pyrite compositions. However, no elements of atomic number less than Na ($Z=11$) could be detected.

Electron Probe Microanalysis (EPMA)

Quantitative analyses of the pyrite compositions were performed with a Cameca SX-50 electron microprobe, facilitated with a image analysis system. The samples were embedded in epoxy resin of 1-in. diameter size and then polished to expose cross-sections of the sample particles. Conductive coatings of either aluminum or carbon were applied to the sample mounts. The area of detection limit was $1\ \mu\text{m}^2$, unless otherwise noted. Concentrations of the selected elements of interest were calibrated with standard minerals or metals prior to measurement. Characteristic X-ray signals of the elements were scanned and the X-ray element maps recorded. Secondary electron images were also recorded to locate the positions of the particles. All the digital mapping signals were stored on a PDP-11 computer and were later retrieved, processed and printed as hardcopies with a colorjet printer.

RESULTS AND DISCUSSION

Surface Morphology

Secondary electron photomicrographs obtained in SEM analyses are illustrated on Figure 1. The selection of the pyrite particles

presented was arbitrary. A summary of the photomicrograph descriptions for the samples examined is presented as Table 1. Here, emphasis should be placed on the surface morphology of the pyrite samples, since the EDX analysis provides only qualitative evidence of the pyrite compositions.

Although the description of surface morphology may vary according to the magnification during analysis, distinctive differences may still be observed. At 2000X magnification, surfaces of large pyrite particles (ca. 25 μm) from minerals sources (PY-2 and PY-4) are significantly smoother and show fewer deposits of tiny granules, compared with counterparts from coal sources (PY-1 and PY-3). The smooth surfaces and sharp edges are quite unique for the mineral pyrites. Observations at 3500X magnification indicate that the smooth surfaces are preserved even on smaller mineral pyrites of 5-25 μm sizes. Most of the sharp edges still prevail on the mineral pyrites while the medium-sized coal pyrites, whether spherical or granular, never exhibit smooth surfaces and sharp edges. When the tiny granules attached to coarser pyrite particles are examined at 20,000X magnification, the most interesting feature is the relative smoothness of the coal pyrite even though submicron-sized globules are apparent to a considerable extent. Although common features in surface morphology are found for both coal pyrites and mineral pyrites, minor differences can also be identified as indicated in Table 1. No framboids and cell fillings of the pyrites were observed for any of the pyrite samples. The surface morphology may be very important in explaining flotation reagents/particle interactions and bubble/particles attachment/stabilization.

No extensive porosity was observed for both coal pyrites and mineral pyrites. The higher BET surface areas of coal pyrites reported by Aplan and co-workers [1], have been attributed to surface roughness and porous grains. This suggests that the high porosity of coal pyrite results from the

Table 1. Sample Description of Scanning Electron Photomicrographs

Pyrite Sample: PY-1

Photomicrograph No.: 1

Description: coal pyrite from Pittsburgh #8 seam, Pa. coal at 2000X magnifications.

Major elements on the surface of the spherical particle (30 μm dia.) are (qualitatively) detected as: S (65%), Fe (26%), and Ca (9%). A typical Ca-riched granule (2.5 μm) has S (62%), Fe (20%), and Ca (18%).

Pyrite Sample: PY-1

Photomicrograph No.: 2

Description: coal pyrite from Pittsburgh #8 seam, Pa. coal at 3500X magnifications.

The small coal pyrite sphere (20 μm dia.) has a surface composition of S (59%), Fe (35%), and Ca (6%).

Pyrite Sample: PY-1

Photomicrograph No.: 3

Description: coal pyrite from Pittsburgh #8 seam, Pa. coal at 20000X magnifications.

A tiny granule (1.75 μm) shows S (60%), Fe (35%), and Ca (5%). The tiny granule looks flat and slab-like, without micron-sized porosity developed on its surface.

Pyrite Sample: PY-2

Photomicrograph No.: 4

Description: mineral pyrite from Colorado at 2000X magnifications.

Less but still considerable amount of tiny granules are attached to and scattered on surfaces of the bulkier pyrite particles. Both the bulkier pyrite particle (25 μm) and the tiny granules (1-10 μm) have sharp edges and show fairly pure composition of S (67%) and Fe (33%). A pure pyrite would have S (53.4%) and Fe (46.6%) by weight. The large silicon-riched particle at upper left corner (20 μm dia.) has a composition of: Si (86%), S (7%), and Fe (7%). This indicates impurity on the mineral pyrite is mainly due to admixing with discrete mineral phases such as quartz or clay.

Pyrite Sample: PY-2

Photomicrograph No.: 5

Description: mineral pyrite from Colorado at 3500X magnifications.

Ore pyrite particles of various sizes (4-25 μm) show sharp edges and the surfaces are scattered with tiny pure pyrite granules.

Pyrite Sample: PY-2

Photomicrograph No.: 6

Description: mineral pyrite from Colorado at 20000X magnifications.

The tiny pure pyrite granule shows the surface is not as flat as those of "sulfur ball" coal pyrites (PY-1) but has been grown with (not by attachments) smaller globules (0.1-0.3 μm dia.) not observed on the coal pyrite tiny granules (cf. Photomicrograph No. 3).

Pyrite Sample: PY-3

Photomicrograph No.: 7

Description: coal pyrite from Upper Freeport seam, Oh. coal at 2000X magnifications.

Major elements on the surface of the particle (15 μm) at the left are S (52%) and Fe (48%). However, a granule at right side shows a higher content of Fe (78%). Surface composition with EDX analysis indicates elemental ratio of sulfur to iron varies significantly, occasionally with impurity from Si element (5-45%).

Pyrite Sample: PY-3

Photomicrograph No.: 8

Description: coal pyrite from Upper Freeport seam, Oh. coal at 3500X magnifications.

The coal pyrite particle (20 μm) has a surface composition of S (48%), Fe (50%), and Ca (2%).

Pyrite Sample: PY-3

Photomicrograph No.: 9

Description: coal pyrite from Upper Freeport seam, Oh. coal at 20000X magnifications.

A granule (3 μm) shows a surface composition of S (19%) and Fe (81%), indicating a high Fe content. No globules are observed on the surface and the granule does not look flat either (cf. Photomicrograph Nos. 3 and 6).

Pyrite Sample: PY-4

Photomicrograph No.: 10

Description: mineral pyrite from Ward's Natural Science Establishment, Inc. at 2000X magnifications.

Sharp edges appear on most large particles with attachments of smaller granules in several microns. The large particles have a high Fe content (ca. 85%).

Pyrite Sample: PY-4

Photomicrograph No.: 11

Description: mineral pyrite from Ward's Natural Science Establishment, Inc. at 3500X magnifications.

The granule at center has round edges while a group of granules has sharp edges. Surface composition of the sharp-edged granules is typically of S (53%) and Fe (47%).

Pyrite Sample: PY-4

Photomicrograph No.: 12

Description: mineral pyrite from Ward's Natural Science Establishment, Inc. at 20000X magnifications.

A cluster of attachments on a granule has S contents from 70-80%. Globules are grown on surfaces of these attachments, but in far less extent than in PY-2.

dissemination of fine pyrite grains incorporated during coal formation and is distinct in character from massive pyrite occurrences.

Pyrite Composition

Pure pyrite and marcasite have a stoichiometric compositions of 53.4% and 46.6% Fe by weight respectively. In the EDX analysis, during SEM examinations, qualitative variations in surface composition have been noted. With the wavelength dispersive X-ray (WDX) spectrometer equipment on the electron microprobe, quantitative analyses of the composition of the pyrites and impurity minerals may be readily determined. However, due to the lengthy operation of the equipment and the limit on the number of crystals used in the characteristic X-ray detection, five elements of interest, Si, Ca, Fe, S, and O, were chosen in most cases for X-ray counting. Within experimental errors, a total detection range between 99-101% of the element concentrations indicates satisfactory element selection. Detection of elements other than the selected ones listed above was accomplished with an EDX spectrometer which displays the whole X-ray spectrum starting from atomic number 6.

Since the pyrite particles were embeded in epoxy resin containing both carbon and oxygen, an electron beam that overlaps the resin gives misleading results. This complicates efforts to evaluate surface composition and degree of oxidation manifested at the periphery of the cross-sectioned particles. However, X-ray mapping of the elements of interest, in which a maximum of four elements was chosen at a time, does allow visualization of surface composition and oxidation on a microscopic scale.

Table 2 summarizes the quantitative results of the composition analyses. Selection of sample particles was also arbitrary. Here, the stoichiometric atomic ratio of Fe/S in pyrite is used to represent deviation of

Table 2. Summary of Electron Probe Microanalysis (EPMA) Results 1.2

Samples:

- PY-1, sulfur ball pyrite from Pittsburgh #8 seam, Pa.coal. Hand-picked massive pyrite. Finely ground as received.
- PY-2, mineral pyrite from Colorado. Finely ground as received.
- PY-3, pyrite from Upper Freeport seam, Oh. coal. Agglomerates as received but crushed for examination.
- PY-4, mineral pyrite from Ward's Natural Science Establishment, Inc.

Run ID	Si %	Ca %	Fe %	S %	O % ³	% total Detected	% Undetected	Fe/S Atomic Ratio ⁴	Remarks
PY-1,1	0.039	0.375	45.531	52.223	2.041	100.209	-0.209	1:2.00	large particle, low magnification
PY-1,2	0.069	0.711	44.887	51.399	3.228	100.294	-0.294	1:1.99	another area of PY-1,1 particle, low magnification
PY-1,3	0.064	0.065	42.805	50.150	2.681	95.765	4.235	1:2.04	small particle, at 23557x
PY-1,4	0.075	0.059	43.563	48.004	4.772	96.473	3.527	1:1.92	small particle, low magnification
PY-1,5	0.071	0.058	45.306	51.636	2.723	99.794	0.206	1:1.99	same area as PY-1,4 particle, but at 25369x
PY-1,6	0.009	0.058	45.605	53.022	1.943	100.637	-0.637	1:2.03	large particle, high magnification
PY-2,1	0.046	0.000	45.560	52.384	1.610	99.600	0.400	1:2.00	large particle, high magnification
PY-2,2	0.060	0.008	45.893	52.575	1.319	99.855	0.145	1:2.00	large particle, high magnification
PY-3,1	0.064	0.104	0.389	1.380	5.374	7.311	92.689	1:6.18	cavity of inclusion (Al ₂ O ₃) in a large pyrite chunk
PY-3,2	0.183	0.000	44.075	50.385	2.754	97.397	2.603	1:1.99	large pyrite chunk outside of inclusion
PY-3,3	0.102	0.020	43.565	49.503	2.200	95.391	4.609	1:1.98	large particle, 10-µm beam size
PY-3,4	0.173	0.008	42.484	49.328	2.669	94.663	5.337	1:2.02	another area of PY-3,3, 10-µm beam size
PY-3,5	0.782	0.002	42.733	48.296	4.948	96.761	3.239	1:1.97	another area of PY-3,3, 10-µm beam size
PY-3,6	0.015	0.012	43.533	48.741	3.384	95.685	4.315	1:1.99	new particle, 10-µm beam size
PY-3,7	0.012	0.003	45.013	51.428	2.312	98.768	1.232	1:1.99	new particle, 10-µm beam size

Table 2. Summary of Electron Probe Microanalysis (EPMA) Results (continued)

Run ID	Si %	Ca %	Fe %	S %	O % ³	% total Detected	% Undetected	Fe/S Atomic Ratio ⁴	Remarks
PY-4,1	0.013	0.008	46.104	52.728	0.266	99.119	0.881	1:1.99	large particle, 10-μm beam size
PY-4,2	0.015	0.009	45.695	52.705	0.723	99.147	0.853	1:2.01	large particle, rough surface, 10-μm beam size
PY-4,3	1.353	0.000	3.077	0.293	0.000	4.722	95.278	1:0.17	large particle bright surface at 400x. Major elements are Cr and Co, 10-μm beam size
PY-4,4	1.241	0.000	2.969	0.335	0.000	4.545	95.455	1:0.20	same area as PY-4,3 but at 6823x, 10-μm beam size
PY-4,5	1.291	0.000	3.168	0.248	0.000	4.708	95.292	1:0.14	another area of PY-4,3 at 6823x, 10-μm beam size
PY-4,6	0.013	0.000	46.154	52.095	0.527	98.789	1.211	1:1.97	new particle, rough surface, 10-μm beam size
PY-4,7	0.622	0.000	69.890	0.142	0.000	70.654	29.346	1:0.35	bright particle riched in Fe and Cr, 10-μm beam size
PY-4,8	0.024	0.000	46.003	52.813	0.433	99.273	0.727	1:2.00	new particle, 10-μm beam size

Notes: 1. Crystals for elemental detection:

Si: TAP,

O: PCI,

Ca, S: PET, and

Fe: LiF.

2. Applied voltage: 20 kV; beam current: 20 nA.

3. High oxygen contents may arise from epoxy cold mounting resin, Al₂O₃ polishing compound, or O-containing minerals.

4. Stoichiometric Fe/S ratios: pyrite and marcasite: 1:2

stoichiometry. The data seem to be quite scattered but still provide useful information on particle composition of the pyrite samples examined. The X-ray elemental maps determined from separated experimental sessions are shown in Figure 2.

PY-1 The sample has an overall high Ca content, suggesting significant calcite contamination. In the Si X-ray map in Figure 2, dispersed micron-sized thin layers containing Si are located only at the periphery of the pyrite particles. This suggests the contamination results from surface layers of quartz or clay. Calcite may deposit in a similar way. The six quantitative measurements show the S/Fe ratios in a range of 1.92-2.04.

PY-2 With only two quantitative measurements, the sample shows quite pure pyrite compositions and has a low content of mineral impurities. The Si-containing minerals also are located at the periphery of the pyrite particles.

PY-3 Bulky sized Si-containing particles as large as 50 μm are observed locked at the edges of the sample particles. An oxygen X-ray map shows coincidence of the O-element with Si-containing particles. Evidence of sulfur deficiency is illustrated for a -150 μm particle in which the sulfur concentration diminishes along fissures and cracks and falls to a minimum at the center of the large particle. Si-containing minerals are not found in the cracks but are apparent at the inlets of the pyrite cracks. This suggests the sulfur depletion resulted from reactions which occurred prior to Si deposition in the mineralization process.

Either Fe or S deficiency in local areas of detection have been detected quantitatively. The S/Fe ratio of about 1 may indicate the existence of iron sulfide (FeS) or FeSO_4 from oxidation reactions of pyrite. Concentrations of pyrrhotite (Fe_5S_6 to $\text{Fe}_{16}\text{S}_{17}$), hematite (Fe_2O_3) and magnetite (Fe_3O_4) which form

PY-1: Sulfur Ball Pyrite from Pittsburgh No.8 Seam, Pa. Coal

(1). PY-1, area 1: 48 X 48 μm

Si X-Ray Map

Secondary Electron Image

Fe X-Ray Map

S X-Ray Map

Figure 2. EPMA X-Ray Elemental and Secondary Electron Maps

(2). PY-1, area 2: 128 X 128 μm

Fe X-Ray Map

S X-Ray Map

Figure 2. EPMA X-Ray Elemental and Secondary Electron Maps (continued)

PY-2: Mineral Pyrite from Colorado

(3). PY-2, area 1: 97 X 97 μ m

Si X-Ray Map

Secondary Electron Image

Fe X-Ray Map

S X-Ray Map

Figure 2. EPMA X-Ray Elemental and Secondary Electron Maps (continued)

(4). PY-2, area 2: 48 X 48 μm

Figure 2. EPMA X-Ray Elemental and Secondary Electron Maps (continued)

PY-3: Pyrite from Upper Freeport Seam, Oh. Coal

(5). PY-3, area 1: 256 X 256 μ m

Figure 2. EPMA X-Ray Elemental and Secondary Electron Maps (continued)

(6). PY-3, area 2: 512 X 512 μm

Figure 2. EPMA X-Ray Elemental and Secondary Electron Maps (continued)

(7). PY-3, area 3: 88 X 88 μm

Figure 2. EPMA X-Ray Elemental and Secondary Electron Maps (continued)

PY-4: Mineral Pyrite from Ward's Natural Science Establishment, Inc.

(8). PY-4, area 1: 97 X 97 μm

Secondary Electron Image

Fe X-Ray Map

S X-Ray Map

Figure 2. EPMA X-Ray Elemental and Secondary Electron Maps (continued)

(9). PY-4, area 2: 97 X 97 μm

Secondary Electron Image

Fe X-Ray Map

S X-Ray Map

Figure 2. EPMA X-Ray Elemental and Secondary Electron Maps (continued)

at high temperatures are less likely to contribute to the high Fe content.

In a separate optical microscopic examination, vitrinite maceral and non-maceral impurities were found. This is thought to be related in part to contamination during sample collection. No exinite and very little inertinite macerals were observed.

PY-4 Composition of the pyrite varies significantly. Elements such as Co or Cr seem to dominate in some bright particles (observed as a video image) that also have high Fe contents. Particles having rough surfaces show relatively pure pyrite compositions. X-ray maps of Si and Ca were not obtained due to poor signal resolution.

FUTURE STUDIES

The coarse-sized pyrite from coal sources and mineral sources exhibit distinctive features of surface morphology and bulk composition. The differences will be correlated with the pyrite behavior during flotation processing and with observed electrochemical modification. Collection of small-sized coal pyrite dispersed in coal particles, which is the major target in the investigation of advanced coal cleaning processes, is being planned. Pyrite particles reporting to both clean and refuse fractions will be characterized and compared.

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Part II- Qualitative FTIR Study

ABSTRACT

Pyrite samples were investigated using FTIR spectrometry to identify mineral contaminants in the samples. Quantitative evaluation was difficult because spectral peaks were complicated due to (1) weak band superposition, and (2) insufficient spectral information from the literature. Shifts in band positions also contributed to the difficulty of identification. However, minerals such as kaolinite, quartz, and calcite were found to be the major contaminating minerals in four samples from different sources. The relative abundances varied from sample to sample. Samples PY-3 and PY-4 seemed to have contamination of similar crystal structure evidenced by comparing the spectra below 400 cm^{-1} . Use of low temperature ashing is suggested as a means to investigate concentrated coal minerals in future studies.

INTRODUCTION

Fourier transform infrared spectrometry (FTIR) is a fast, powerful method among various techniques for the characterization of minerals. The peak positions manifested by bond vibrations are fingerprints of corresponding mineralogic structures. One disadvantage of the method is that the mineral identification can be severely limited by the superposition or overlapping of spectral bands of the constituents in the mineral sample. Complementary analyses such as X-ray diffraction (XRD), scanning electron microscopy with electron dispersive X-ray spectrometry (SEM-EDX), thermal analysis, chemical analysis or electron probe microanalysis (EPMA) are usually required to assist in mineralogical identification.

A multicomponent mixture of minerals may present a complex spectrum

which is difficult to resolve. For example, when the IR spectrum of a mixture of magnesite (MgCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), ankerite ($\text{Ca}(\text{Mg}, \text{Fe})(\text{CO}_3)_2$), and calcite (CaCO_3) is taken, the spectral bands are discouragingly complicated. This is due to small shifts in characteristic vibration bands and, as a result, superposition of the bands prevents clear resolution. In the cases of displacement of cations by heavier ones, the characteristic peaks will shift to lower frequencies (or wavenumbers) or longer wavelengths. Figure 1 illustrates the similarity in spectral bands for the above mentioned minerals and shows the small shifts of peak positions due to the displacement of heavier cations [1]. Although the method of difference spectrum has been introduced by successively subtracting the spectrum of each comprising mineral [2, 3], determination of most of the comprising minerals of high purities seems to be a prerequisite before such a method can be applied. In addition, a shift of a peak position will produce positive and negative components in the difference spectra, causing problems in the band identification.

Mineral impurities associated with the pyrite particles may play a role in determining the floatability of the pyrite. Locked silica materials have been reported to facilitate pyrite removal in coal flotation [4]. The massive pyrite samples characterized in this research project have silicates and calcites in close contact with the pyrite particles. Similar results have been reported in a previous study [5]. The limits of FTIR spectrometry applied to mineral identifications rest heavily on comparisons with spectra of known mineralogical structures.

Magnesite

Dolomite

Ankerite

Calcite

**Figure 1. Illustration of IR Spectral Similarity of Minerals:
(1) Magnesite, (2) Dolomite, (3) Ankerite and (4) Calcite**

EXPERIMENTAL

Pyrite Samples

Two pyrite samples from coal sources and another two samples from mineral sources were obtained for the preliminary characterization study. The samples were designated and described as follows:

PY-1: Sulfur ball pyrite from Pittsburgh #8 seam, Pa. coal. It was hand-picked from coal fissures and then finely ground.

PY-2: Mineral pyrite from Colorado. It was also finely ground.

PY-3: Pyrite from Upper Freeport seam, Oh. coal. It was received as agglomerates but crushed for examination. (How the sample was obtained still requires further checking.)

PY-4: Mineral pyrite from Ward's Natural Science Establishment, Inc. Finely ground.

To preserve the originality of the samples, no further purification was performed.

Instrument and Sample Preparation

Preliminary X-ray diffraction analyses were not able to identify minerals present in minor concentrations or those having amorphous structures. It was thus decided to perform infra red analyses to see if special characteristic of minor minerals could be identified. A Digilab FTS-40 FTIR spectrometers was used for the study. The samples were studied in two modes: (1) diffusive reflectance mode for mid-infrared ($500\text{-}1500\text{ cm}^{-1}$) and (2) pellets in polyethylene for far-infrared ($100\text{-}500\text{ cm}^{-1}$) ranges. Different beam splitters were used for the two regions.

Grinding and mixing of the polyethylene and the pyrite samples in a Wig-

L-Bug was not fully successful due to the sticky polymeric nature of the polyethylene. The weight ratios of the mineral samples with polyethylene in the pellets therefore varied considerably.

RESULTS AND DISCUSSION

Figure 2 shows the FTIR spectra of the pyrite samples in the mid- and far-infrared regions. The absorption bands are quite complicated due to the existence of the contaminated pyrite and other minerals in low concentrations.

Illustrations of infrared spectral bands of selected minerals investigated by other researchers [2, 3, 6] are presented in Table 1. It is obvious that the band positions of the mineral standards are not in good agreement possibly due to the impurities in the samples tested. Mineral identifications in this work are primarily based on strong bands that are often used in Table 1.

Mineral Identifications

Table 2 lists tentative identifications of the minerals in the pyrite samples. Considering the shifts in peak positions of the main constituent, pyrite, it is apparent that the identifications may not be reliable for other minerals if the peak positions in Table 1 are to be used. For the cases of pyrites, the band shift may be as great as 10 cm^{-1} .

Far-infrared region The pyrite peaks for all the sample in the region are identified at 289-293, 347-349 and 415-417 cm^{-1} . These pyrite bands are strong due to their high concentrations in the samples except in the case of PY-4 which seems to be of lower concentration. The shapes and positions of the pyrite peaks in the samples seem to show evidences of their dissimilarity.

PY-1: Sulfur Ball Pyrite from Pittsburgh No.8 Seam, Pa. Coal

Figure 2. FTIR Spectra of Pyrite Samples in Mid- and Far-Infrared Regions

PY-2: Mineral Pyrite from Colorado

Figure 2. FTIR Spectra of Pyrite Samples in Mid- and Far-Infrared Regions (continued)

PY-3: Pyrite from Upper Freeport Seam, Oh. Coal

Figure 2. FTIR Spectra of Pyrite Samples in Mid- and Far-Infrared Regions (continued)

PY-4: Mineral Pyrite from Ward's Natural Science Establishment, Inc.

Figure 2. FTIR Spectra of Pyrite Samples in Mid- and Far-Infrared Regions (continued)

Table 1. IR Spectral Bands of Selected Minerals

A. 500-1500 cm^{-1} Range

Mineral	Wavenumber (cm^{-1}) ¹	Wavenumber (cm^{-1}) ²	Wavenumber (cm^{-1}) ³
Kaolinite	1108, 1025, 1000, 910, 782, 749, 690, 530	1095, 1026, 1002, 929, 908 , 782, 747, 689, 528	1035, 1010, (910), 535
α -Quartz	1160, 1065, 790, 770, 687, 500	1160, 1135, 1075, 790, 772, 688, 501	1080, 799, 779
Gypsum	1150, 1110, 1090, 1010, 660, 595	1155, 1132, 1106, 998, 660, 594	669, 603
Illite	1070, 1015, 920, 820, 750, 510		1025, 520
Sodium montmorillonite	1110, 1025, 915, 835, 790, 515		1050, 530
Calcite	1420, 871, 842, 710	1420, 869, 842, 707	1430, 872, 712
Dolomite	1435, 875, 730		882, 730
Siderite			872, 740

B. 80-500 cm^{-1} Range

Mineral	Wavenumber (cm^{-1}) ¹	Wavenumber (cm^{-1}) ²	Wavenumber (cm^{-1}) ³
Pyrite	411, 391, 340, 284	406, 391, 340, 284	~415
Kaolinite	460, 422, 360, 340, 268	460, 422, 405, 352, 338, 268	470, 278
α -Quartz	450, 388, 362, 256	465, 452, 388, 363 (360), 256	
Gypsum	450	445, 412, 298, 215	
Illite	460		
Sodium montmorillonite	460		
Calcite	310	337, 307, 217	
Dolomite	390, 355, 310		
Marcasite		422, 407, 396, 350, 321, 285	

1. Data from reference [2] Jenkins, R. G. and Walker, P. L. Jr., "Analysis of Mineral Matter in Coal," in Analytical Methods for Coal and Coal Products, Karr, C. Jr., Ed.; Academic Press, New York, 1978, Vol. II, p. 265.
2. Data from reference [6] Estep, P. A., Kovach, J. J. and Karr, C. Jr., "Quantitative Infrared Multicomponent Determination of Minerals Occurring in Coal," Anal. Chem., (1968), **40**(2), 358. The wavenumbers in boldfaces were used in identification work.
3. Data from reference [3] Painter, P. C., Coleman, M. M., Jenkins, R. G., Whang, P. W. and Walker, P. I. Jr., "Fourier Transform Infrared Study of Mineral Matter in Coal. A Novel Method for Quantitative Mineralogical Analysis," Fuel, (1978), **57**, 337.

Table 2. Possible Minerals in Pyrite Samples

Sample	Mineral Identified	Band Position (cm ⁻¹)
PY-1	pyrite kaolinite α -quartz? calcite dolomite? illite? montmorillonite?	291-293, 347, 417 264, 527, (690), 750, 905, 1016-1028, 1098 253, (453), 501, (690), (799), 153 (214), 336, 712, 858-868, 1406-1413 (313), (347), (392), 735, 882, 1439 (453) (453)
PY-2	pyrite kaolinite α -quartz calcite? illite? montmorillonite?	291-293, 347, (392), 415 530, 747, (690), 1016-1042, 1098 263, 388, (453), (690), 791, 1159 (216), 306-313, (332), 709 (453) (453)
PY-3	pyrite kaolinite α -quartz calcite dolomite? illite? montmorillonite?	289, 349, 417 266, 462, 527, (689), 747, 901, 1014-1026, 1088 255, 386, (457), 501, (689), (800) (214), 303, 336, 710, 866, 1406-1420 (314), (349), (397), 735, 1437 (457) (457)
PY-4	pyrite kaolinite α -quartz calcite illite? montmorillonite?	289, 349-353, (397), 417 266, 461, 527-530, (689), 747, 901, 1022-1026, 1088-1092 255, 386, 455-457, 501, (689), (799) (214), 303, (314) 336, 712, 868, 1406-1413 (455-457) (455-457)

* Wavenumbers in boldfaces are those clearly identified in spectra; wavenumbers in parentheses are uncertain.

Peaks below 400 cm^{-1} are fairly well resolved for samples PY-3 and PY-4 but not for PY-1 and PY-2. Furthermore, these peak positions for PY-3 and PY-4 below 400 cm^{-1} are essentially identical. Spectral bands in PY-1 and PY-2, although being hindered by severe superposition, may indicate that the contaminated minerals are different. Band shifts are also possible due to some displaced lattice structures. Many spectral bands remain unsolved, mostly due to the lack of spectral information and unsatisfactory spectra obtained.

Mid-infrared region Judged from the relative intensities of the spectra, mineral contamination varies from sample to sample. Major identifiable minerals in the samples are kaolinite, calcite, and quartz. Sample PY-2 seems low in calcite but high in quartz. An unidentified mineral is present in PY-3 and PY-4 at $1230\text{-}1275\text{ cm}^{-1}$. PY-3 is high in calcite content. Relative mineral abundances are similar in PY-1 and PY-4. The concentrations of marcasite, dolomite, illite and montmorillonite are small.

CONCLUSION

The infrared spectra obtained in this study are very complicated and therefore limited. Minerals present in low concentrations are difficult to resolve. Although the method of difference spectra has been demonstrated successfully, the question of how to establish a reliable infrared spectral library of pure mineral standards is still pending. For minerals existing in coals, a technique such as low temperature ashing may be worthwhile to try to determine minerals of high concentrations, since surface structures of these minerals are also expected to be modified during the electrochemical reactions. Establishment of such a library may be required in the future if

the FTIR technique is to be used readily for mineral identifications. We propose to continue this work using the low temperature ashing technique to see if this technique shows more promise.

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