COAL STRUCTURE: THE PROBLEM WITH MINERALS

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INTRODUCTION

Despite considerable effort to understand the chemical nature of the organic and inorganic portions of coal, and substantial advances in instrumentation and methodologies, much of coal's chemical nature remains intractable. This paper reviews methods and their limitations for the determination of specific minerals in coal, and presents results of efforts at Consolidation Coal Company to develop FTIR methods for routine coal mineralogy.

Mineral matter characterization has received considerable attention. Given and Yarzab (1) discussed the problems posed by mineral matter in various coal analyses. Furthermore, mineral matter complicates the chemical treatment of coal. It also has many adverse effects on commercial coal utilization. Coal consumers pay to ship mineral matter, to accommodate its impact on capital equipment and operations, and to dispose of the resultant ash. The impact of coal minerals on utilization motivated Consol's initial interest in mineralogy (2). The results reported here are from a second phase of the FTIR method development, in which extensive improvements were made to the methods.

EXPERIMENTAL

DESCRIPTION OF SAMPLES

Small Data Set. Low-temperature (plasma) ashes (LTAs) were obtained from ten diverse coal samples (Table 1), ranging in rank from lignite to Ivb. Infrared spectra were obtained of duplicate samples of each coal. A separate set of duplicates was generated for four of the coals.

Large Data Set. LTAs were analyzed by FTIR for 50 coals, ranging in rank from lignite to Ivb. These were a representative subset of duplicates of 95 unwashed and clean commercial coals from the eastern, midwestern and western U.S. and Alberta, Canada. The 50-coal set contained no duplicates, but different coal samples from the same mine were included.

Reference Minerals. The 42 reference minerals and the mineral classes used are listed in Table 2. Most of the minerals were obtained from Ward's Natural Science Establishment, Inc., Rochester, New York. Many of the silicate minerals were American Petroleum Institute (API) standard samples or their equivalents. Numbers given in the table (e.g., kaolinite 4) refer to the API standard designation.

METHODS

Coals ground to -60 mesh were low temperature (O_2 plasma) ashed for about 100-125 hours for bituminous coals and 200 hours for lower rank coals. Ashing containers were made of Pyrex or ceramic.

Mineral standards were hand crushed to -1/4 inch, then ground to a fine powder in a ball or Bleuler mill. The powder was aerodynamically classified, and the finest fraction was collected. This was accepted as a mineral standard if 90% or more by weight was 5 μm and smaller particles. Duplicate 13 mm KBr pellets were prepared and the spectra were weight-scaled by reported techniques (3,4). With one exception, all the mineral standard spectra were averages of spectra from duplicate pellets.

LTA samples were ground for 30 minutes in a Wig-L-Bug (15 mg LTA, 50 mg KBr and 500 mg acetone in an agate vial), dried and stored in a dessicator. 13 mm KBr pellets were made and resulting spectra were weight-scaled (3,4).

All spectra were run on a Nicolet 7199 FTIR spectrometer equipped with a wide-band MCT detector. A Nicolet least-squares analysis program (MCOMP) was modified extensively for efficient use with a large number of reference minerals. The reference mineral with the lowest negative concentration was omitted upon each iteration, until only non-negative results were obtained. Generally 12 to 18 minerals remained in the final calculation.

For PLS or PCR calculations, the spectra were transferred to a DEC VAX 11/750 computer. The PLS and PCR program with cross-validation was provided by David Haaland of Sandia National Laboratory (5).

RESULTS AND DISCUSSION

A CRITIQUE OF METHODS FOR COAL MINERALOGY

This survey of five major methods for coal mineralogy and their limitations includes only methods which can provide a "complete" mineral analysis. Methods of limited applicability, such as Mossbauer, are omitted.

X-ray Diffraction. XRD is the most common method used for coal mineralogy (6,7,8). Its major advantage is the ability to unequivocally identify many minerals. The main disadvantages are: 1) reliance on reference minerals, 2) requires careful attention to sample preparation, and 3) low sensitivity to certain minerals (especially many clays) due to poor crystallinity and to particle orientation effects. Many laboratories analyze a separate concentrated clay fraction (less than 2 μm or 5 μm). However, sensitivity is still low and other limitations may arise: 1) the separated clay fraction may not be representative, and 2) the separation procedure can alter the sample. The original coal, instead of the LTA, can be analyzed by XRD. However, this is not satisfactory, since sensitivity is even lower. An extensive interlaboratory comparison of XRD results with Illinois 6 coal showed highly variable results (7). That study also included results from FTIR, SEM and other methods.

Infrared Spectroscopy. The use of IR (9,10,11,12) and FTIR (3,4) for coal mineralogy has been reported. Painter and coworkers (3) demonstrated that FTIR can provide a virtually complete analysis. Painter, Brown and Elliott (4), and others (9,10,11) discuss sample preparation, reference minerals, and data analysis. The advantages of IR are: 1) high sensitivity to molecular structure, 2) unequivocal identification of a number of minerals, 3) small sample size (a few milligrams), and 4) rapid analysis time (once LTA is available). Disadvantages include: 1) reliance on reference minerals, 2) requires careful attention to sample prepraration, and 3) limited selectivity (discrimination among similar minerals).

The problem with limited selectivity includes some of the minerals which are problems for XRD: illite, muscovite, smectites and mixed-layer clays. Poor crystallinity creates problems with both XRD and FTIR. The IR spectrum of an amorphous material lacks sharp distinguishing features but retains spectral intensity in the regions typical of its composition. The X-ray diffraction pattern shows low intensity relative to well-defined crystalline structures. The major problem for IR is selectivity: for XRD it is sensitivity. In an inter-laboratory FTIR comparison (7), two laboratories gave similar results for kaolinite, calcite, and illite, but substantially different results for montmorillonite and quartz.

Electron Beam/X-ray Spectroscopy. Several methods based on point count or automated image analysis (AIA) in scanning electron microscopy-energy dispersive X-ray have been reported (13-18). Point count analysis can determine mineralogy; AIA can also determine the size distribution of the minerals. These methods obtain a point-by-point or particle-by-particle elemental analysis. A mineral distribution and analysis is obtained by classifying each elemental composition into one of the mineral categories. Such methods have several advantages: 1) they can be automated, 2) the composite elemental composition can be checked against that of the bulk sample, 3) it is possible to run coal (not necessary to obtain LTA), and 4) they provide some information on statistical and perhaps spatial, size, or morphological distribution of the minerals. For these reasons, such methods have become more popular in recent years. The major disadvantages are: 1) the chemical information and thus the selectivity is limited, since it uses only elemental composition, 2) it relies on a suitable classification scheme for mineral categories, and 3) data collection can be time-consuming (especially for AIA), requiring many hours per sample.

Optical Microscopy. Optical microscopy is the traditional tool of geologists and petrographers for mineral identification and characterization (19). It has two main advantages: 1) positive identification of minerals can be achieved, and 2) information is obtained on mineral distribution and morphology. However, quantitation is difficult, and the analysis is time-consuming, requires highly trained technicians, and is not amenable to automation. Although in common use in petrographic studies, such methods have been displaced by XRD, IR, and SEM-EDS methods for mineralogical studies.

Thermal Techniques. Thermal techniques, especially differential thermal analysis (DTA) have been used for mineral identification (19) and for coal mineralogy (20). The advantages of thermal techniques are: 1) small sample size, 2) little sample preparation (applicable to whole coals), 3) potentially rapid analysis, and 4) information relevant to combustion behavior may be provided. The disadvantages are: 1) the chemical information is limited, resulting in a lack of selectivity due to overlapping curves for individual minerals, 2) identification/quantification depends on reference minerals (though perhaps less sensitive to such problems than XRD or IR), and 3) it is not developed for quantitative use. Interpretation of thermal data is difficult, but could be improved by appropriate software. Variations, such as using different gases to highlight or suppress features, have been used (20). Detection limits of less than 1 wt % to about 30 wt % were reported for different minerals.

General Comments on Mineralogical Methods. The lack of a measure of quantitative accuracy is a general problem with mineralogy. A major limitation for XRD and IR methods is the use of reference minerals, and the standards used are from geological sources other than the coal analyzed. This limitation

will be avoided by only physical separation of the coal minerals or by data analysis techniques (such as factor analysis) which do not require reference minerals. Many studies have reported successful quantitation of mineral mixtures. This is a necessary, but not sufficient, criterion for a good mineralogical analysis. The differences between mineral mixtures and authentic samples are considerable, and good performance on real samples is not guaranteed. The major limitations of SEM-EDS and related techniques are appropriate classification of the elemental data, and obtaining a statistically sufficient number of data points. For classification of data, factor analysis, cluster analysis, or related multivariate techniques appear to be suitable (21).

The IR methods have progressed from hand-drawn baselines and peak height or area for quantitation, to spectral subtraction, to least-squares methods. Least-squares analysis eliminates the reliance on single peaks for quantitation and the subjectivity of spectral subtraction. However, negative concentration coefficients are a problem with least-squares analysis, since they have no physical meaning. Negative components can be omitted according to some criterion and the least-squares process iterated until only positive concentration coefficients remain. However, this does not ensure that the least-squares solution is a global minimum.

Haaland and coworkers (5) discussed other problems with classical least-squares (CLS) and its performance relative to partial least-squares (PLS) and factor analysis (in the form of principal component regression). One of the disadvantages of CLS is that interferences from overlapping spectra are not handled well, and all the components in a sample must be included for a good analysis. For a material such as coal LTA, this is a significant limitation.

Factor analysis extracts information from the sample data set (e.g., IR spectra) and does not rely on reference minerals. However, because abstract factors have no physical meaning, reference minerals may be needed in target transformations or other procedures to extract mineralogical information. One valuable piece of information obtainable without the use of extraneous data is the number of components required to represent the data within experimental error. Reported applications of factor analysis to mineralogy by FTIR are few (12). However, one commercial laboratory is offering routine FTIR mineral analyses to the petroleum industry, based on related methods (22).

The next section of this paper describes the use of classical least-squares analysis of FTIR data to determine coal mineralogy. This is followed by promising preliminary results obtained using factor analysis techniques.

RESULTS USING CLASSICAL LEAST-SQUARES

Reproducibility. Mineralogical results from the ten-coal set (Table 3) are presented as ranges of values. In most cases, the reproducibility is good. Quartz, for example, shows consistently high reproducibility. However, illite, mixed-layer clays and montmorillonite in the first four coals show high variability. These minerals are similar in composition and spectral features. The variability in the FTIR results for these samples is related to variability in the spectral data. The set of ten duplicate spectra gave a pooled SD of 0.03 abs, while the separate set of four duplicate spectra gave a pooled SD of 0.08 abs. Results from the first four samples in the table included the poorer spectral data, while the results from the last six samples were obtained from the better spectra. The reproducibility for total clay content is good, even when vari-

ability in individual clay concentrations is high. Iron sulfides, oxides and sulfates also show some variability, particularly in the first and fourth samples.

Accuracy. Although there is no way to measure the accuracy of the FTIR mineralogical results, there are three areas in which it can be addressed (2,4). The first method is to compare pyrite results obtained by FTIR with the conventional ASTM determination. The agreement (Figure 1) is quite good over the range of 2.9 to 28.1 wt % pyrite in the LTAs from the ten coals. Similar results were obtained based on the 475-400 cm^{-1} region for a smaller sample set (2). The present results are based on the 1575-400 cm^{-1} range. The good agreement for the present data set is surprising, since the only spectral feature reported for pyrite in the mid-infrared is at ca. 415 cm^{-1}. In these spectra, the noise level is high near 400 cm^{-1}, and the identification of such a feature is not clear. It appears that the results are derived mainly from baseline curvature (resulting from the Christiansen effect). For all the iron sulfide minerals in the reference set, the baseline absorbance is near zero from ca. 1300 to 400 cm^{-1}, but from 1300 cm^{-1} to 4000 cm^{-1} it curves upward.

The second method for indicating accuracy is to examine the spectral residuals from the least-squares fits (Figure 2, Table 4). The worst case was the lignite (coal SL), the large misfit at ca. 1380 cm^{-1} being due to the omission from the reference minerals of nitrate, presumably produced in the low-temperature asher by fixation of organic nitrogen (23). The reproducibility of the 28 original spectra (pooled SD) was 0.05 abs, slightly higher than the pooled standard fit error of 0.04 abs (without the lignite). However, the ten original duplicate spectra gave a pooled standard deviation of only 0.03 abs, which is slightly lower than the fit errors for most of those samples. In general, the fit error approached the experimental error in the original data.

The third method for assessing accuracy is to calculate an elemental composition for each LTA's oxidized ash, based on the reference mineral compositions. Reasonably close agreement between the actual and calculated elemental compositions would substantiate (but not prove) the mineral analysis. The standard error of prediction (SEP) for CaO, Fe_2O_3, SiO_2 and Al_2O_3 (Table 4) ranged from 3.4 to 6.7 wt % for the various coals. The global SEP was 4.8 wt %. By major ash element, the SEP values were 2.8 for CaO, 5.6 for Fe_2O_3, 4.5 for SiO_2 and 5.8 for Al_2O_3. SEP values ranged from 0.3 to 5.7 wt % CaO, 2.3 to 10.3 wt % Fe_2O_3, 0.1 to 11.6 wt % SiO_2 and 3.0 to 5.6 wt % Al_2O_3. Inspection of the elemental results also show some bias. CaO values were usually low, Fe_2O_3 values were usually high, and Al_2O_3 values were always low. Calcite impurities may be present in some of the reference spectra, or something else may interfere with the calcite. The high Fe_2O_3 values, even though the pyrite values appear good, indicate that the determined iron oxides, sulfates, and/or siderite concentrations are too high. Somehow, certain iron minerals seem to be replacing or supressing the appropriate aluminosilicates in the analysis.

In the next section, the potential for factor analysis and related chemometric techniques for providing improvements in the determination of minerals in coal by FTIR are explored.

RESULTS USING PRINCIPAL COMPONENT REGRESSION (PCR)

PCR is a technique in which principal component analysis (one form of factor analysis) of the spectra is followed by regression of the factor scores to calibrate and predict an independently-measured quantity. Besides the spectral

data, these calculations require other data. An accurate mineral analysis of each sample could be used to obtain a calibration. Because this is not possible, one is limited to modeling and predicting other measurable properties such as ash combustion behavior. It is possible to by-pass the mineralogy altogether, and model the desired properties or behavior directly from the LTA spectra. Ash property data which are readily accessible are ASTM ash fusion temperatures (reducing and oxidizing conditions) and ash elemental composition. PLS and PCR are linear models, but are capable of modeling some non-linearities (5). Ash elemental concentrations should be linearly related to intensities of bands in the infrared spectra (under ideal circumstances). Thus, PLS and PCR are expected to do a good job in modeling ash composition. However, ash fusion temperatures are not expected to be linearly related to spectral features.

Infrared data in the 1575-400 cm^{-1} region (1218 points/spectrum) from LTAs from 50 coals (large data set) were used as input data to both PLS and PCR routines. This is the same spectral region used in the classical least-squares analysis of the small data set. Calibrations were developed for the eight ASTM ash fusion temperatures and the four major ash elements as oxides. The program uses PLS1 models, in which only one variable at a time is modeled. Cross-validation was used to select the optimum number of factors in the model. In this technique, a subset of the data (in this case five spectra) is omitted from the calibration, but predictions are made for it. The sum-of-squares residuals are computed from those samples left out. A new subset is then omitted, the first set is included in the new calibration, and additional residual errors are tallied. This process is repeated until predictions have been made and the errors summed for all 50 samples (in this case, 10 calibrations are made). This entire set of calculations is repeated once each time an additional factor is included in the model. The optimum number of factors is near the point at which the residual error reaches a minimum.

Results from these preliminary modeling efforts with the large data set are shown in Table 5. These results were obtained with centering (x and y) and scaling (x) as a data pretreatment. Only PCR results are shown, even though the PLS calculations took less computing time and gave slightly better results. The PCR model is preferred because it provides some additional information on our original data set. Results are depicted graphically in Figures 3 and 4 for the best and worst calibrations, respectively. The main measure of the success of these models is the SEP. For ash fusion temperatures, the SEPs were in the range of 50 to 78°F. The fusion temperatures at oxidizing conditions generally gave slightly better results than those at reducing conditions. These values represent errors somewhat larger than ASTM repeatability and reproducibility limits. The largest single prediction error for these models was about 200°F. This is no larger than the spread in interlaboratory results seen in round robin analyses of standard samples. Furthermore, these results appear to be equivalent to the best predictions of ash fusion temperatures available from ash elemental compositions (24,25,26). Many of those models have incorporated ratios, squared terms and log terms to get better results. It appears that the PLS and PCR models work reasonably well for modeling non-linearities in this case.

The PCR results for CaO, Fe_2O_3 SiO_2 and Al_2O_3 are quite good, as anticipated. The SEPs for CaO and Fe_2O_3 of 1.7-1.8 wt % are higher than the ASTM reproducibility limits, but the results for SiO_2 and Al_2O_3 are within the ASTM limits for those elements. Note that all these errors are better than the value of 4.8

resulting from the mineralogical analysis. (However, the mineral analysis was not optimized to predict ash elementals.)

The calibrations obtained are valid over a significant range of each property. It is feasible to predict all these properties from the LTA from a small sample of coal, should that be desired. These results mainly show that the methods employed can model other ash properties which are more closely related to large-scale combustion behavior. This is one area where further study is desirable.

Although the software used was not a full-featured factor analysis program, portions of the printed output are useful in studying the spectral data set. The table below shows some information obtainable from PCR models (large data set) with 5, 10 and 13 factors. In this case, the "factors" are principal components derived entirely from the sample data set. PLS factors are not interpretable in the same manner.

No. of Factors	Prediction Residual Sum of Squares (Reconstruction of Original Data)	% of Total Spectral Variance of Data Set
5	89.9	93.5
10	28.1	98.0
13	11.5	99.2

An increase from 5 to 10 in the number of factors representing the original data results in a substantial reduction in the error. Because of the data pretreatment used, the spectral error cannot be directly compared to the experimental error determined from the data set. When five factors were used, two different lignite samples were flagged as possible outliers based on their spectral variances relative to the rest of the data set. With ten factors, one of the lignites was accommodated within the factor model (although ten factors may not have been required to accommodate it). With thirteen factors, both lignites were accommodated.

CONCLUSIONS

Experience in this laboratory has shown that even with careful attention to detail, determination of coal mineralogy by classical least-squares analysis of FTIR data may have several limitations. Factor analysis and related techniques have the potential to remove or lessen some of these limitations. Calibration models based on partial least-squares or principal component regression may allow prediction of useful properties or empirical behavior directly from FTIR spectra of low-temperature ashes. Wider application of these techniques to coal mineralogical studies is recommended.

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TABLE 1

DESCRIPTION OF COALS

Coals	Rank	Seam - Description
P1	hvAb	Pittsburgh - Underground, Clean Coal, Greene Co., PA
EH	hvAb	Elkhorn 3 - Underground, Unwashed, Breathitt Co., KY
I1	hvBb	Illinois 5,6 - Surface, Clean Coal, Jackson Co., IL
SL	Lig	Scranton - Surface, Mercer Co., ND
I2	hvBb	Illinois 6 - Underground, Clean Coal, Jefferson Co., IL
I3	hvBb	Illinois 6 - Surface, Clean Coal Perry Co., IL
P2	hvAb	Pittsburgh - Underground, Clean Coal, Marshall Co., WV
P3	hvAb	Pittsburgh - Underground, Clean Coal, Monongalia Co., WV
GE	hvAb	No. 2 Gas, Upper and Middle Eagle - Underground, Clean Coal, Raleigh Co., WV
PO	lvb	Pocahontas 3 - Underground, Clean Coal, Buchanan Co., VA

TABLE 2

REFERENCE MINERALS

MAIN CLASSES

Kaolin - Kaolinite 4, 5, 6, Dickite 16, 27
Mica - Biotite, Phlogopite, Muscovite
Illite - Illite 36, Illite-Bearing Shale
Mixed-Layer Clays - Metabentonite 37, 42
Montmorillonite - 21, 22A, 22B, 24, 25, 26, 31
Feltspars - Albite, Anorthite, Orthoclase
Chlorite - Chlorite
Misc. AlSi - Attapulgite, Halloysite, Pyrophyllite 48
Quartz - Quartz, Agate
Fe sulfides - Marcasite, Commercial Pyrite, Mineral Pyrite, Pyhrrotite
Fe oxides - Goethite, Hematite, Magnetite
Fe sulfate - Difference spectrum weathered minus unweathered pyrite
Siderite - Siderite
Calcite - Calcite, Aragonite
Gypsum - Gypsum, Drierite
Dolomite - Dolomite

GROUPED CLASSES

Clays - Kaolin, Illite, M. L. Clays, Montmorillonite, Misc. AlSi
Other AlSi - Mica, Feldspar, Chlorite, Quartz
Sulfate - Fe Sulfate, Gypsum
Carbonate - Calcite, Siderite, Dolomite
Fe Altered - Oxides, Sulfate

In addition to spectra of the 42 minerals shown above, the least-squares components included 3 "spectra" representing 1) moisture in KBr blank (obtained by subtraction of 2 KBr blank spectra), 2) a constant baseline offset (1 abs from 4000 to 400 cm^{-1}), and 3) a sloping linear baseline (line from 1 abs at 4000 cm^{-1} to 0 abs at 400 cm^{-1}). Normalization of results used only the 42 mineral components, and disregarded these three components.

TABLE 3

FTIR MINERALOGICAL RESULTS

Mineral	P1 (a)		EH (a)		I1 (a)		SL (a)		I2		I3		P2		P3		GE		PO	
Class	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Kaolin	25.8	33.9	11.8	16.6	15.1	21.8	1.1	2.9	23.2	25.2	13.3	14.0	17.6	18.6	20.7	21.2	35.3	35.8	21.6	22.5
Mica	2.6	6.4	2.9	9.3	0.0	3.3	0.0	-	7.6	10.5	6.1	6.7	5.3	5.5	3.6	4.3	12.1	13.1	4.7	7.7
Illite	7.1	13.6	20.2	33.8	3.7	47.4	0.0	1.2**	20.8	25.1	9.4	10.8	5.3	5.5	10.0	10.4	8.0	9.9	16.6	17.0
Mixed Layer Clays	0.0	11.3*	6.2	16.6	0.0	15.8	0.0	-	0.0	-	0.0	-	0.0	-	0.0	-	0.0	-	0.0	-
Montmorillonite	4.2	13.4	3.4	5.9	0.0	26.0	15.5	20.4	5.0	9.4	13.5	13.8	11.7	11.8	4.9	5.9	4.9	5.9	3.1	3.8
Feldspar	0.0	3.8	0.0	1.3	0.0	-	0.0	13.5**	0.0	0.7	3.2	3.8	1.6	2.0	9.7	10.1	2.5	2.7	5.4	6.5
Chlorite	0.6	2.5	3.4	4.9	0.0	2.3	0.0	-	0.0	0.2	0.0	-	0.0	-	2.1	2.5	3.6	3.9	5.0	5.5
Misc. Clays	1.8	9.8	0.2	2.3	0.0	4.3**	0.0	2.7*	1.7	3.0	0.0	-	2.8	3.3	2.8	3.8	4.0	5.2	0.4	0.6
Quartz	7.7	13.8	12.5	13.6	11.0	14.6	15.5	20.9	14.1	14.8	14.2	14.2	8.1	8.1	4.9	6.0	12.2	12.9	6.5	7.1
Fe Sulfide	9.2	13.2	2.0	5.6	0.0	5.3	4.8	13.1	8.0	8.2	19.4	19.6	28.0	29.0	20.8	22.3	4.0	5.1	4.4	7.6
Fe Oxide	4.7	8.7	5.3	9.2	6.8	8.5	0.0	0.3*	5.5	7.3	4.9	5.6	2.9	3.0	4.8	5.7	7.7	8.3	8.8	10.4
Fe Sulfate	4.4	11.2	2.9	3.8	0.0	4.5	0.0	-	4.3	5.2	9.0	9.3	14.8	14.9	10.8	11.1	1.0	1.8	0.1	0.5
Siderite	0.0	-	1.5	2.4	0.0	-	2.4	5.8	0.0	-	3.7	4.0	0.0	-	0.6	1.1	0.0	-	6.3	6.6
Calcite	0.0	-	0.0	-	0.0	2.8*	0.0	-	0.0	-	0.0	1.6	0.0	-	0.0	-	0.0	-	9.0	9.4
Gypsum	0.0	-	0.0	0.5*	0.0	2.3**	34.4	49.2	0.0	-	0.0	-	0.0	-	0.0	-	0.0	-	1.1	1.6
Dolomite	0.0	-	0.0	-	0.0	-	0.0	-	0.0	-	0.0	-	0.0	-	0.0	0.1	0.0	-	0.0	0.3
Alternate Classes																				
Clays	54.0	60.0	55.3	59.7	67.7	71.5	19.6	24.9	56.4	57.0	36.9	37.9	37.7	38.9	39.4	40.4	53.7	55.4	42.8	42.9
Other Alumino Silicates	14.6	22.1	20.5	27.1	13.3	17.2	19.5	34.4	23.2	24.8	24.0	24.1	15.3	15.5	20.9	22.1	30.6	32.5	23.1	25.3
Sulfates	4.4	11.2	3.2	3.8	2.3	5.0	34.4	49.2	4.3	5.2	9.0	9.3	14.8	14.9	10.8	11.1	1.0	1.8	1.6	1.7
Carbonates	0.0	-	1.5	2.4	0.0	2.8*	2.4	5.8	0.0	-	4.0	5.3	0.0	-	0.7	1.1	0.0	-	15.5	16.0
Fe-Altered	9.3	20.0	8.2	12.4	7.5	13.0	0.0	0.3*	10.7	11.6	14.2	14.6	17.8	17.8	15.6	16.8	8.7	10.1	9.3	10.5

(a) Four samples run from each of these coals, two samples run from each of the remaining coals.

*One out of four samples gave a non-zero concentration.
**Two out of four samples gave a non-zero concentration.

TABLE 4

SPECTRAL FIT ERRORS AND ELEMENTAL PREDICTION ERRORS FROM FTIR MINERALOGY

Coal	Spectral Fit Error (1575-400 cm ^{1}), Std. Dev. in abs. Run 1	Run 2	Run 3	Run 4	SEP Oxide wt % of Ash
P1	0.028	0.027	0.038	0.041	4.4
EH	0.030	0.033	0.023	0.029	4.3
I1	0.026	0.026	0.029	0.031	4.7
SL	–	0.250	0.149	0.194	4.1
I2	0.033	0.028			5.2
I3	0.037	0.039			6.7
P2	0.040	0.040			4.4
P3	0.037	0.036			5.5
GE	0.038	0.037			3.4
PO	0.022	0.021			6.2

With SL, pooled std. dev. = 0.093
Without SL, pooled std. dev. = 0.041

TABLE 5

PRINCIPAL COMPONENT REGRESSION CALIBRATIONS FOR SELECTED ASH PROPERTIES

Type	No. of Factors	SEP	Magnitude of Max. Prediction Error	Range of Input Data Min. Value	Max. Value
Ash Fusion Temperature, °F					
RID	5	72.4	169.9	1918	2757
RST	5	77.9	153.5	1972	2808
RHT	5	65.9	201.8	2092	2958
RFT	5	56.2	157.6	2127	2968
OID	6	50.5	117.6	2115	2808
OST	5	60.4	149.8	2159	2858
OHT	5	54.0	163.8	2197	2881
OFT	2	61.1	148.1	2218	2769
Ash Element as Oxide, wt %					
SiO_2	10	1.38	2.81	29.15	56.45
Al_2O_3	13	0.74	1.33	9.12	27.34
Fe_2O_3	8	1.79	3.19	4.33	30.17
CaO	3	1.73	6.88	1.07	30.11

/Is

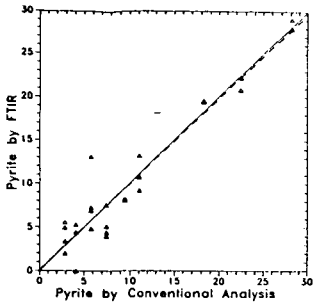

Figure 1. Comparison of FTIR and ASTM Results for Pyrite, wt % of LTA (Solid Line - Parity, Dotted Line - Least-Squares y = 0.985 x 0.098)

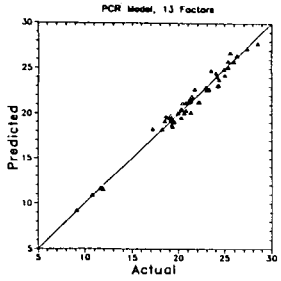

Figure 3. PCR Results for Al_2O_3 wt % of Oxidized Ash (Best Model of Ash Properties).

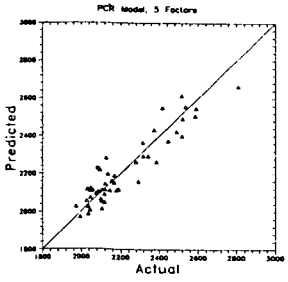

Figure 4. PCR Model Results for Ash Softening Temperature (Reducing), °F (Worst Model of Ash Properties).

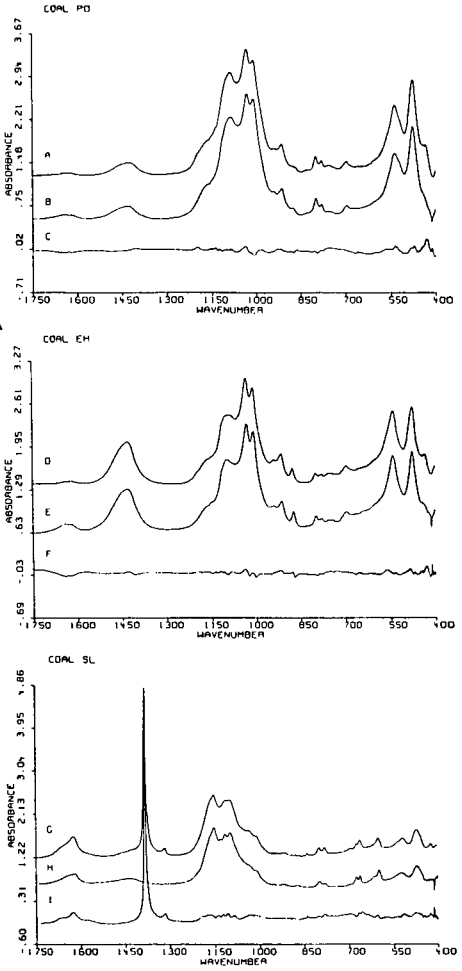

Figure 2. Spectral Residual for the Best (Coal PO), Typical (Coal EH) and Worst (Coal SL) Least-Squares Fits. Spectra Shown are Original LTA (A, D, G), Least-Squares Composite (B, E, H), and Difference (Original Minus Composite C, F, I).