

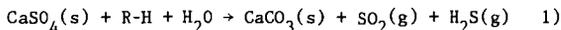
Using X-ray Methods to Evaluate the Combustion Sulfur Minerals  
and Graphitic Carbon in Coals and Ashes

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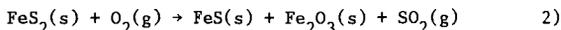
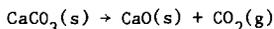
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INTRODUCTION

Coals are complex mixtures of vastly different materials whose combustion kinetics may well exhibit symbiotic effects. Although the sulfur oxide gases produced during the combustion of coals may have a variety of sources, they are frequently caused by the thermal degradation of inorganic minerals to produce "acid rain"; i.e.,



or



Since many of the minerals involved either as reactants or products in coal combustion produce well defined x-ray powder diffraction (XRPD) patterns, the fate of these minerals may be followed by measuring the XRPD patterns of combustion products.

Coal 1368P, a coal with an unusually high pyrite ( $\text{FeS}_2$ ) fraction, has been the subject materials in our investigations of the fate of the inorganic minerals during combustion. These studies include measuring the fate of pyrite and of graphitic carbon in coal 1368P under varying combustion conditions. The results discussed below were obtained by standard XRPD methods (1).

EXPERIMENTAL

The analysis of coal 1368P, as furnished by PSOC (2), is provided in Table I along with some specialized information which resulted from our x-ray analysis.

Table I. A Definition of Coal 1368P

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A. Rank:	high volatile bituminous A
B. Proximate Analysis:	
Ash:	16.7% (a)
Fixed Carbon:	40.0%
Volatile Matter:	37.1%
Moisture:	6.2%
C. Ultimate Analysis	
Carbon:	60.3%
Hydrogen:	4.4%
Nitrogen:	1.4%
Sulfur:	9.6% ( $\text{FeS}_2$ )
Oxygen:	1.3% ( $\text{SeO}_2$ )
D. Results of USM X-ray Measurements	
$\mu^*$ :	17.2 $\text{cm}^2/\text{g}$ by XRA
minerals in ash:	$\text{Fe}_2\text{O}_3$ and $\text{SiO}_2$ by XRPD
major elements:	Fe, S, and Si by XRF

(a) The ash weight is not necessarily the minerals fraction in the non-combusted coal.

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Each finely powdered sample of coal 1368P was combusted in a Lindberg Single Zone Furnace which approximates a stoker furnace. Each coal sample was weighed prior to and after combustion to determine its mass loss. Each partially combusted product was finely powdered and then loaded into our automated x-ray diffractometer. An x-ray powder diffraction pattern was obtained by measuring the counts accumulated in a ten second interval collected at increments of  $d2\theta = 0.05^\circ$ .

#### RESULTS AND DISCUSSION

The x-ray powder diffraction patterns of several partially combusted products from coal 1368P are shown in figure 1. These products were produced by one minute combustions with no air flow through the combustion chamber and at several different combustion temperatures. Key diffraction peaks characterizing quartz (Q), pyrite (P), hematite (H), and troilite (T) are indicated, as is the large, broad hump due to the amorphous material(s) in each sample.

**QUARTZ PEAK.** Previous results have shown that the  $3.343 \text{ \AA}$  peak of quartz is not measurably affected by the mild combustion conditions used in these experiments (3), so this peak has been used as a reference in the interpretation of each XRPD pattern. The increase in the intensity of the quartz peak indicates an increase in the abundance of quartz, which is due to the removal of the volatile and moisture fractions from the coal (4). Shown in Table II is the intensity of the quartz peak measured in the XRPD patterns shown in figure 1.

Table II. Absorption Corrected Intensity of the  $3.343 \text{ \AA}$  Quartz Peak Measured in the XRPD Patterns of the Combustion Products

Combustion Temperature	Peak Area
coal	2183
400	2545
600	2762
800	3326
1000	4072
1200	4017
1400	3809 (a)

(a) Thermal degradation may be beginning to occur at this temperature.

Comparison of the areas of the quartz peaks in the XRPD patterns may be used to calculate the loss of the volatile components during each partial combustion. Shown in Table III is the mass loss caused by each combustion protocol calculated from our XRPD analysis and compared to the mass loss measured by normal gravimetric methods. The excellent agreement indicates that the XRPD patterns are sufficiently accurate to use for the semi-quantitative analysis of the pyrite and of the graphitic carbon in the combustion products of coal 1368P.

Table III. Mass Loss Caused by Combusting coal 1368P for One Minute With Zero Air Flow

Combustion Temperature	Mass Loss	
	Gravimetric	Our XRPD
400	17.1%	16.6%
600	20.9%	21.0%
800	35.3%	34.4%
1000	44.8%	46.4%
1200	46.1%	45.6%

By using the ratio of the intensity 2.40 Å pyrite peak/intensity 3.34 Å quartz peak the pyrite abundance in each sample may be determined without the necessity of adding an "external standard" to each combustion sample. Using the graphitic maximum/quartz peak ratio allows a similar determination of the graphitic carbon retained in each combustion product. The uncertainty in each analysis is ±5%.

**PYRITE ANALYSIS.** Although several of the diffraction peaks characterizing FeS<sub>2</sub> are in themselves suitable for the analysis methods we have developed, the 2.40 Å peak is not, in these complicated XRPD patterns, overlapped by diffraction peaks due to other materials. For that reason the 2.40 Å peak has been used in the subsequent analyses as a measure of the weight fraction of pyrite in the combustion products. Shown in figure 2 are the ratios of the 2.40 Å pyrite peak intensity/3.34 Å quartz peak intensity in each combustion product for which both the air flow and the temperature were varied. From the measurement of the pyrite peak in each combustion product, the percent pyrite reacted may also be calculated (fig. 2). These data indicate that the thermal degradation of pyrite begins at T > 600°C, with all of the pyrite reacted at T = 1200°C.

**GRAPHITIC CARBON ANALYSIS.** Shown in figure 3 is the ratio of the area under the broad amorphous maximum which measures the graphitic carbon (5) to the quartz peak area in each mixture. Also shown is the percent graphitic carbon reacted for each of the combustion products. These data indicate that only a small portion of the graphitic carbon reacts, even under the most severe combustion conditions employed in these experiments.

#### CONCLUSIONS

By using quartz in a sample of the powdered coal as the "internal reference" and our XRPD ratio method, the fate of pyrite and of graphitic carbon in combustion processes may be determined. These XRPD data may be manipulated to minimize the ratio of reacted pyrite/reacted graphitic carbon by measuring the pyrite and graphitic carbon retained in each combustion product.

The same XRPD data may be used to determine the combustion conditions at which the volatile and moisture fractions of the coal are completely removed and to evaluate the quality of the combustion product for commercial usage.

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