STUDY OF SULFUR BEHAVIOR AND REMOVAL DURING THERMAL DESULFURIZATION OF ILLINOIS COALS

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ABSTRACT

In this 3-year program, we investigated the thermal desulfurization of Illinois high-sulfur coal for the ultimate purpose of producing clean low-sulfur solid fuel. The two principal objectives were to optimize the conditions for sulfur removal and to analyze the behavior of sulfur during gas-phase desulfurization. We developed several unique methods to monitor the sulfur mobility during thermal desulfurization: stable sulfur isotope tracing (used to follow the types of sulfur during desulfurization), pH monitoring, and quadrupole mass spectrometer gas analysis (used to measure the relative rates of sulfur removal).

The thermal desulfurization processes studied were pyrolysis and post-pyrolysis treatments—most pyrolyses were carried out at 350° to 750°C under an atmosphere of nitrogen. From studying the behavior of the predominant forms of sulfur during pyrolysis, we determined that below 500°C the sulfur removed is almost entirely organic. Pyritic sulfur is not removed in any significant quantities until approximately 550°C and above. Other experiments show that pyrolyses carried out at or above 550°C produce the lowest sulfur content chars in the shortest time. During these studies a process was developed that is capable of converting nonmagnetic and weakly magnetic iron sulfides—the sulfides normally produced during pyrolysis—into a strongly magnetic iron sulfide that can potentially be removed by magnetic separation.

The post-pyrolysis desulfurization processes studied include partial oxidation and hydrodesulfurization. Post-pyrolysis oxidation experiments showed that partial oxidation must be carried out below 550°C to produce maximum sulfur removal with minimum carbon loss. Various hydrodesulfurization treatments were also studied to determine their effects on the rate and amount of sulfur removal from char. From coals that originally had 4 to 6 percent sulfur, hydrodesulfurization experiments using pure hydrogen produced low levels of sulfur—low enough to qualify as a compliance fuel. The effect of a small amount of hydrogen sulfide (H₂S) in the hydrogen flow was also investigated to simulate the effect of excess H₂S that occurs in large-scale systems during hydrodesulfurization in the absence of an H₂S scavenger. Post-hydrodesulfurization oxidation helped to overcome the problem of back reactions of H₂S with iron in the chars that occurred during hydrogen treatment.

The final phase of this research combined pyrolysis and post-pyrolysis desulfurization techniques to show the potential of gas-phase thermal desulfurization. Results indicate that pyrolysis with a trace of oxygen followed by magnetic separation of iron sulfides may be a process capable of producing relatively low-sulfur chars from coals with low organic sulfur and relatively high pyritic sulfur. For most Illinois coals with moderate to high organic sulfur, some type of post-pyrolysis treatment such as hydrodesulfurization will probably be necessary because organic sulfur is so difficult to remove. A promising desulfurization treatment is hydrodesulfurization plus post-hydrodesulfurization oxidation with 5 percent oxygen or with a trace of oxygen followed by magnetic separation.

INTRODUCTION

Much of the coal in the Illinois Basin is high-sulfur coal, greater than 3 percent total sulfur, which limits its use as a fuel source. A substantial portion of the coal desulfurization research at the Illinois State Geological Survey has been aimed at producing a clean low-sulfur solid fuel from Illinois high-sulfur coal. In this project our research efforts concentrated on pyrolysis and postpyrolysis desulfurization processes. Our principal objectives were to optimize conditions for maximum sulfur removal and to better understand the behavior of sulfur forms during pyrolysis and post-pyrolysis desulfurization. To achieve these objectives, we developed several unique techniques to monitor the mobility of sulfur during the thermal desulfurization processes studied: stable sulfur isotope tracing (to follow the types of sulfur during desulfurization), pH monitoring, and quadrupole mass spectrometer gas analysis (to measure the relative rates of sulfur removal).

Pyrolysis in an inert atmosphere removes a portion of organic and pyritic sulfur with the volatile gases (Kruse and Shimp, 1981). Elemental sulfur resulting from the decomposition of pyrite as well as hydrogen sulfide from any source can react with the organic matrix of the coal and remain in the char as organically bound sulfur (Given and Jones, 1966; Cleyle et al., 1984). Since the initial forms of sulfur undergo various reactions and can be converted to other forms during thermal treatment, the standard ASTM procedures for determining the forms of sulfur in coal may not be reliable when applied to chars.

In this project, we used naturally occurring differences in stable sulfur isotope compositions of pyritic and organic sulfur in coals to monitor the mobility of these two major forms of sulfur during thermal desulfurization treatment. The isotopic composition of either the sulfur in the volatiles or that remaining in the char will give the proportion of organic and pyritic sulfur removed or remaining, no matter what new chemical form each type of sulfur has taken. We also looked into the effects that different parameters—particle size, heating rate, soak time, and maximum pyrolysis temperature—have on the rate and amount of sulfur removed from coal.

After pyrolysis a significant amount of sulfur usually remains in the char, and many researchers have found that high-sulfur coals yield high-sulfur chars—thus further post-pyrolysis desulfurization treatments are usually considered necessary. We studied the removal of sulfur from char by partial oxidation and hydrodesulfurization because these gas-phase desulfurization treatments do not require subsequent washing, filtering, or dewatering steps. A review of recent literature on oxidation and hydrodesulfurization is given by Stephenson et al. (1985).

Generally, oxidation and hydrodesulfurization can significantly reduce the sulfur content of coals or chars. However, oxidation sometimes results in excessive carbon loss with only minor sulfur removal, depending on the oxygen concentration and temperature used. Hydrogen seems to be the most effective gas for desulfurization. Fleming, Smith, and Aquiro (1977) showed, on the laboratory scale, that hydrodesulfurization of char can produce a solid fuel product with a sulfur content lower than the EPA direct combustion standard of 1.2 lb SO_2 /MMBtu. However, hydrogen sulfide can react back with the iron formed from the reduction of iron sulfides in the char if the H₂S partial pressure becomes too high (Kor, 1977), resulting in little reduction in the inorganic sulfide sulfur content of the final char. We attempted to combine pyrolysis and post-pyrolysis processes in complementary ways to help minimize some major problems that can occur and to show the potential of gas-phase thermal desulfurization.

EXPERIMENTAL PROCEDURES

Detailed descriptions of the experimental apparatus and procedures are given in the appendix.

Apparatus for Pyrolysis and Post-Pyrolysis Treatment

Pyrolyses were carried out on 0.5- to 1-g size samples spread thinly in a quartz or ceramic boat. The experimental setup for the thin-bed pyrolysis system is very similar to that described in Frost, Auteri, and Ruch (1984) and Ruch, Chaven, and Kruse (1985). The pyrolysis apparatus consists of a bench-scale quartz tube reactor with two consecutive chambers. The first chamber is used for pyrolysis of coal samples at various temperatures under a nitrogen atmosphere, the second for combusting the volatile products to CO₂ and SO₂ with oxygen at 900°C. The sulfur dioxide formed by oxidation of the sulfur or sulfur compounds released during pyrolysis is trapped by hydrogen peroxide solution and then quantitatively measured as BaSO₄. The same pyrolysis apparatus was used for partial oxidation experiments. The N₂ flow was diluted with 4 to 5 percent O₂ by volume for post-pyrolysis oxidations.

A similar bench-scale system was set up for hydrotreating the chars at 800°C. The sulfur released as H_2S during hydrodesulfurization was trapped and precipitated as CdS and converted to Ag_2S using a dilute Ag_2NO_3 solution. The Ag_2S was then weighed to calculate the quantity of sulfur removed.

The maximum heating rate that could be achieved with the tube-type pyrolysis/oxidation system in the 400° to 550°C temperature range, at which 90 + percent of coal devolatilization occurs, was about 60°C/min. Therefore, a special pyrolysis/oxidation system was constructed to carry out pyrolyses with high heating rates. With the new system, heating rates of 100°C + /min in the 400° to 550°C temperature range could be obtained.

Monitoring Techniques

Stable sulfur isotope analysis was used to monitor the behavior of organic sulfur and pyritic sulfur individually during thermal treatment of coal. Coals with a natural difference between the ³⁴S/³²S ratios of the pyritic and organic sulfur were used for this work. If the isotopic composition of the pyritic and organic sulfur in a coal

is known, the relative proportions of pyritic and organic sulfur removed during a particular desulfurization procedure can be calculated by measuring the isotopic composition of either the sulfur removed or the sulfur remaining in desulfurized coal or char. The use of stable sulfur isotopes as a tracer in desulfurization studies is also described in Liu, Hackley, and Coleman (1987).

For the initial isotopic characterization of the predominant sulfur forms, the pyritic and organic sulfur were chemically separated from a coal sample. Pyritic sulfur was extracted by the reductive lithium aluminum hydride (LAH) method (Price and Shieh, 1979; Westgate and Anderson, 1982). The organic sulfur was collected by combusting the LAH-extracted coal in pure oxygen at 1350°C (modified ASTM D1377-82 procedures, Frost, Auteri, and Ruch, 1984). Both forms of sulfur were converted to SO₂ and analyzed on an isotope ratio mass spectrometer. The appendix provides details of the procedures, including the description of a quick screening method developed for locating isotopically appropriate coals and an explanation of stable sulfur isotope notation.

For stable isotope monitoring during thermal desulfurization experiments, the sulfur liberated and the sulfur remaining in the treated chars were quantitatively collected, converted to SO_2 , and analyzed isotopically on a Nuclide RMS 6-60 isotope ratio mass spectrometer. The relative proportions of organic and pyritic sulfur in the desulfurized products were then calculated. The excellent chemical and isotopic mass balances achieved on three different Illinois Herrin (No. 6) Coal samples prove the reliability of this novel stable isotope tracing method (table 1).

Methods were also developed for continuous monitoring of the sulfur removed during pyrolysis and postpyrolysis oxidation of coals. One method continuously measures the pH of a hydrogen peroxide solution used to trap the SO₂ produced in the bench-scale pyrolysis/ oxidation system. Because the solution pH is a direct function of the total amount of sulfur collected, a plot can be made showing the amount of sulfur evolved from the coal as a function of time. Differentiation of this curve provides information on sulfur removal rates.

For more accurate rate data, a quadrupole gas analyzer (QGA) was used during the later experiments to monitor the evolution of both sulfur and carbon during pyrolysis and post-pyrolysis desulfurization experiments. Also, other gaseous species present during the experiments can be monitored with the QGA. The QGA and temperature controller for the pyrolysis/desulfurization tube furnace are interfaced with an IBM PC computer, which collects gas composition and temperature data every 6 seconds during an experiment. Rate data can be calculated from the QGA data.

Standard X-ray diffraction methods were used to determine the changes in iron-sulfur mineral content and structure that occurred when a coal was pyrolyzed or treated by post-pyrolysis desulfurization. Pyrrhotite crystal structure and stoichiometry were determined by comparing the sample X-ray diffraction patterns with X-ray patterns prepared from standard pyrrhotite samples. The position of the major pyrrhotite X-ray diffraction peaks, located between 43.2° and 44° 20, was used to monitor the changes in pyrrhotite composition; the location of this major X-ray peak depends on the pyrrhotite crystal structure and stoichiometry (Smith et al., 1984).

Estimates of the relative order of abundance of minerals present after charring were made using the relative X-ray peak intensities. Although this method is not quantitative, it generally gives a fairly good estimate of the relative abundance of minerals present (Arnold, 1966; Brindley, 1980; Hughes, personal communication). No attempt was made to quantify the percentage of each sulfide or iron-related mineral present because of the many variables that control these peak intensities, such as sample purity, structural factors, particle size, and crystallinity. X-ray data were integrated with the other data collected in this study so that the reactions involved in coal desulfurization would be better understood.

Table	 Chemical analysis, sulfur isotopic composition, and
mass	balance calculations of Herrin (No. 6) Coal samples
used	in pyrolysis experiments

	C	oal samp	le
$\begin{tabular}{ c c c c c } \hline Coal sample & \hline Coal sample \\ \hline RK-B-3 & RK-A-4 \\ \hline \hline RK-B-3 & $	CR-B-4		
Chemical analysis (%)		·	
Moisture	9.0	9.6	11.5
Volatile material	41.5	37.5	46.1
Fixed carbon	49.2	41.9	46.6
High-temp ash	9.3	20.6	7.2
Sulfate sulfur	0.01	0.01	0.01
Pyritic sulfur	0.73	0.74	0.33
Organic sulfur	2.33	2.02	3.03
Total sulfur	3.07	2.77	3.37
Isotopic composition of sulfur	(‰)		
Pyritic sulfur	+25.4	+ 8.2	+8.5
Organic sulfur	- 2.9	- 5.1	- 5.7
Total sulfur	+3.9	- 1.4	- 4.2
Isotopic mass balance (%)			
Calculated values (total sulfur)	+ 3.8	- 1.5	-4.3

$$\delta^{34} S_{TS} = \frac{\chi_p (\delta^{34} S_p) + \chi_{or} (\delta^{34} S_{or})}{\chi_{TS}}$$

δ ³⁴ S ₇₅	isotopic composition of total sulfur
δ ³⁴ S _p , χ _p	isotopic composition and percent pyritic sulfur
$\delta^{34} S_{or}, \chi_{or}$	isotopic composition and percent organic sulfur
Χтѕ	percent total sulfur

Coal Samples

Bituminous Illinois Herrin (No. 6) Coal was used for this study. Many samples were collected by hand at freshly cut coal faces in underground mines. Chemical and isotopic analyses were performed as quickly as possible. Three coal samples, RK-B-3, RK-A-4, and CR-B-4, were selected for further study because of the large difference between the stable sulfur isotopic composition of the pyritic and organic sulfur. Another sample, RK-B-5, was used in some experiments because of its high pyrite content. In addition to the samples collected by hand, two Illinois Basin Coal Sample Program coals (IBC-101 and IBC-103) were also used in much of this project.

RESULTS AND DISCUSSION

Pyrolysis under N₂: Behavior of Organic and Pyritic Sulfur

The most abundant forms of sulfur in coal are organic and pyritic sulfur. Sulfur can also occur in coal to a lesser degree as sulfate, elemental sulfur, and other sulfide minerals. Some FeS_2 in Illinois coals exists as the polymorph marcasite, but for this paper all FeS_2 will be referred to as pyrite.

The chemical and isotopic analyses of three Herrin Coal samples used in the initial pyrolysis studies on the behavior of pyritic and organic sulfur are shown in table 1. Pyrolyses were carried out at temperatures ranging from 350° to 750°C. The isotopic results shown in table 2 indicate that most of the sulfur removed with the volatiles is organic. Pyritic sulfur is not observed in the volatilized gases until 550°C and above.

To study the release of organic and pyritic sulfur in more detail, a stepwise pyrolysis experiment was conducted on coal sample RK-B-3. The volatile sulfur was collected consecutively at three different temperature intervals (25°-350°C, 350°-500°C, and 500°-650°C); results are shown in table 3. Note the change in the isotopic value of the sulfur volatilized between 500° and 650°C compared with the two intervals below 500°C. This finding indicates that the pyritic sulfur does not occur in the volatile gases (in any significant quantity) until above 500°C, supporting the initial pyrolysis data. Figure 1 displays the type of sulfur removed during pyrolysis from all three coals (RK-B-3, RK-A-4, and CR-B-4).

Most of the removable organic sulfur is released at pyrolysis temperatures below approximately 550°C (fig. 1). Higher charring temperatures result primarily in removal of pyritic sulfur and additional volatile matter. These results suggest that relatively low-temperature charring should be used to remove organic sulfur, and less destructive procedures such as physical separation methods should be applied to remove pyritic sulfur.

The greatest variation in the data occurs in the percentage of pyritic sulfur released at the higher temperatures. The differences in pyritic sulfur removed are probably a result of the different proportions of disseminated (finely dispersed) and massive pyrite present in the coals. Sample RK-B-3 had a greater percentage of pyritic sulfur removed (28%) than did RK-A-4 and contained more massive pyrite. The third coal sample, CR-B-4, contained the least amount of pyrite (0.33%) and lost the lowest percentage of pyritic sulfur at 650°C. Furthermore, microscopic inspection showed that nearly all the pyrite in CR-B-4 is disseminated.

Even though the pyrite contents of the samples were significantly different, similar percentages of organic sulfur were removed from each of the three coals. The

Table 2 Amount and origin of sulfur removed by pyrolysis of three Illinois coal samples

Coal sampl e	Charring	Total culture	δ ³⁴ S of volatile	δ ³⁴ S of char	Origin c in volati	Origin of sulfur in volatiles (%)	
	temp (°C)	removed (%)	(‰)	(‰)	Organic	Pyritic	recovered (%)
RK-B-3	450	40	-2.9		100	0	_
	550	53	- 0.9	+7.7	93	7	100.7
	650	58.5	+0.0	+7.5	90	10	102.9
	650	58	+ 0.0	+ 7.5	90	10	101.2
	750	60	+ 0.1	+ 7.5	89	11	102.6
RK-A-4	350	13	- 5.1	_	100	0	_
	450	39	- 5.1	+ 1.5	100	0	97.4
	550	53	- 4.1	+ 1.1	93	7	91.0
	650	58	-3.6	+0.8	89	11	94.9
CR-B-4	350	18	- 5.7	_	100	0	101.8
	450	46	-5.7	- 3.5	100	0	98.8
	550	5 9	-5.3	3.1	97	3	101.2
	650	63	- 5.3	-2.9	97	3	100.1

Table 3 Amount and origin of sulfur in the volatile gases of the stepwise pyrolysis of RK-B-3 $(\delta^{34}S_{\text{pyrtlic}} = +25.4, \delta^{34}S_{\text{organic}} = -2.9)$

Temp	Ramp time	Soak	Sulfur	δ ³⁴ S of volatile sulfur	Origin c in volat	of sulfur tiles %	Sulfur col	lected %
(°C)	(min)	(min)	(‰)	(‰)	Organic	Pyritic	Organic	Pyritic
25-350	10	15	14.2	-2.7	>99	<1	18	<1
350-500	9	15	31.0	-2.5	98	2	39	2
500-650	10	15	10.0	+ 10.2	54	46	7	22

implication here is that pyrite content does not affect the percentage of organic sulfur released during pyrolysis. Additional pyrolysis experiments were conducted to assess the effect of pyrite content. A sample of RK-B-3 was pulverized to less than 230 mesh (<63 μ m). A split of the pulverized sample was subjected to lithium aluminum hydride extraction to remove pyrite. Another split of RK-B-3 was subjected to a 1.4-specific gravity float-sink separation. Table 4 shows isotopic compositions of the pyritic and organic sulfur in the float and sink fractions, and table 5 shows the results of



Figure 1 Organic and pyritic sulfur removal as a function of pyrolysis temperature for three coals

650°C pyrolyses of these samples. Note that the isotopic composition of the volatilized sulfur from the pyrite-free sample is identical to the isotopic composition of the sulfur remaining in the char of that sample; both are indicative of the original total organic sulfur. The percentage of organic sulfur removed by pyrolyzing the pyrite-free sample is essentially identical to the percentage removed when the pyrite was present. In addi-

tion, the percentage of organic sulfur removed from the float and sink samples are virtually the same. These findings confirm that the presence of pyrite has no significant effect on the removal of organic sulfur under the conditions used in this study.

Some authors suggest that sulfur forms in coal may be redistributed during pyrolysis (Cernic-Simic, 1962; Cleyle et al., 1984). Several experiments were conducted to determine if any redistribution of the sulfur forms could be detected by the inherent stable isotope tracing technique at 500°C and above. The coal with the largest isotopic difference between the pyritic and organic sulfur was pyrolyzed at 500°, 550°, and 650°C. The pyrolysis products were then pulverized to less than 230 mesh (63 µm), and the inorganic sulfur was chemically removed and collected. The remaining sulfur was extracted from the chemically treated char by the ASTM high-temperature combustion method. The isotopic compositions of each fraction of sulfur removed were measured to determine the proportions of organic and "pyritic"* sulfur present. The isotopic results indicate that a portion of the pyritic sulfur does get trapped by the organic matrix of the coal during pyrolysis. Approxi-

Tabie 4	Chen	nical analy	/sis	and isot	opic com	position of floa	ŧt
and sink	coal	fractions	of	RK-B-3	samples	(moisture-fre	θ
basis)							

Chemical	Float	Sink	δ S (‱)		
analysis	(%)	(%)	Float	Sink	
Volatile matter	41.3	31.3			
Fixed carbon	50.6	44.2			
High-temp ash	8.0	2 4.5			
Sulfate sulfur	0.01	0.01			
Pyritic sulfur	0.59	2.11	+ 25.9	+21.6	
Organic sulfur	2.55	1.76	- 2. 9	- 2.9	
Total sulfur	3.15	3.88	+ 3.9	+ 10.4	

*The term "pyritic" refers to the inorganic sulfide sulfur removed or remaining in a char even though pyrite begins to alter to pyrrhotite at approximately 500°C. "Pyritic" is used because much of the discussion is about the mobility of the two major forms of sulfur in coal (organic and pyritic) during thermal desulfurization. Distinctions are made between pyrite and pyrrhotite when appropriate.

Sample description	Pyritic sulfur in Sulfur		Organic	δ ³⁴ S	δ ³⁴ S	Origin of sulfur in volatiles (%)	
	coal (%)	removed (%)	removed (%)	sulfur	sulfur	Organic	Pyritic
Pyrite free	0	67.4	67	-2.9	-2.9	100	0
Normal coal	0.7	57.7	67	+0.4	+ 8.4	88	12
Sink	2.1	47.6	68	+ 5.7	+ 13.0	65	35
Sink (dup)	2.1	48.6	69	+5.7	+ 13.3	65	35
Float	0.6	57.1	67	- 1.7	+6.3	96	4

 Table 5
 Results of 650°C pyrolyses of samples of RK-B-3 containing significantly different pyrite concentrations

 ("pyrite free" and "normal coal" are <230 mesh)</td>

mately 6, 9, and 12 percent of the originally pyritic sulfur was incorporated into the organic matrix at pyrolysis temperatures of 500°, 550°, and 650°C, respectively. (For these results, we assume that the chemical extraction procedure used to dissolve the "pyritic" sulfur is approximately 95% efficient as determined by microscopic and Moessbauer analysis of extracted material.)

Effect of Various Parameters on Sulfur Removal

Considerable effort was directed toward determining the effect of process conditions—maximum temperature, heating time (soak time), heating rate, particle size, and coal types—on sulfur removal during pyrolysis of coals. The rate and amount of sulfur evolved during pyrolysis were determined by the pH monitoring method, and the total sulfur content of the chars was determined by a modified ASTM D1377-82 method.

About 90 pyrolysis tests were made using Illinois Basin Coal Sample Program coals (samples IBC-101 and IBC-103). Besides the very high ("flash") heating rate ($100^{\circ}C + /min$), heating rates of about 20°, 40°, and 60°C/min were used. The sulfide mineral content was determined by X-ray diffraction for the flash pyrolyses experiments and for pyrolyses that were heated at approximately 20°C/min. The porosity characteristics of selected nonflash and flash chars were determined from surface area measurements. The proximate analysis and sulfur forms from IBC-101 and IBC-103 are given in table 6.

The results of the various pyrolysis experiments are summarized in table 7 for IBC-101 and in table 8 for IBC-103; these data indicate that maximum pyrolysis temperature is the most important factor in determining the amount of sulfur evolved during pyrolysis. The importance of soak time is dependent upon the maximum charring temperature. As indicated by the char yield data, at 500°C maximum pyrolysis temperature, devolatilization of the coal is incomplete during heat up. However, at 600° and 700°C maximum pyrolysis temperature, devolatilization of the coal is virtually completed during heat up so that the soak time has minimal effect upon char sulfur content. The effect that soak time has at a pyrolysis temperature of 600°C upon char sulfur content is a result of incomplete thermal decomposition of pyrite to pyrrhotite as shown by the X-ray **Table 6** Chemical analyses of two particle sizes of Illinois

 Basin Coal Sample Program IBC-101 and IBC-103 (moisture-free basis)

Chemical	IBC	C-101	IBC-103		
analysis (%)	-20+35	-65+100	-20+35	-65+100	
Volatile matter	43.3	43.7	37.4	39.0	
Fixed carbon	46.9	46.7	53.7	53.1	
High-temp ash	9.7	9.6	8.9	7.9	
Sulfate sulfur	0.184	0.204	0.115	0.104	
Pyritic sulfur	1.08	1.04	0.94	0.92	
Organic sulfur	2.90	3.04	1.33	1.32	
Total sulfur	4.17	4.2 9	2.39	2.35	

diffraction data for pyrolyses conducted with IBC-101 (table 9).

Heating rate does not have a significant effect upon char sulfur content (tables 7 and 8). But heating rate does have a significant effect on the rate of sulfur evolution during pyrolysis (fig. 2). And as the heating rate increases, the temperature at which the maximum rate of sulfur evolution occurs also increases (fig. 2).

Figure 3 shows a selected series of plots of sulfur evolution rates and the effects of different maximum temperatures. In figure 3, experiment PH35, the coal was heated to 500°C and held at that temperature; for experiments PH34 and PH41, the coal was heated to 600° and 700°C, respectively. Note that in all three cases the maximum sulfur removal rate occurs at about 500°C. This peak probably results from the removal of organic sulfur; isotope monitoring indicates that most of the removable organic sulfur is released by the time a temperature of 500°C is reached. The identification of this peak as organic sulfur is further substantiated by the X-ray data (table 9), which show that only a small fraction of the pyrite has been converted to pyrrhotite at this temperature. On the basis of stable isotope data discussed earlier and X-ray diffraction data of these

	Heating	Mosh	Pyrolysis	Char	Char sulfur	Coal sulfur
Evneriment	(°C/min)	Rizo	time (min)	(%)	(%)	(%)
	(0/mm)	5120		(76)	(70)	(76)
PH81	20	- 20 + 35	500,0	75.6	3.29	40.3
PH100	20	-65+100	500,0	72.7	3.24	45.1
PH97	20	-20+35	500,18	70.4	3.01	49.2
PH62	20	- 65 + 100	500,18	67.6	3.15	50.4
PH70	20	- 20 + 35	600,0	68.8	2.82	53.5
PH52	20	- 65 + 100	600,0	66.5	2.99	53.7
PH69	20	- 20 + 35	600,18	66.1	2.86	54.7
PH58	20	- 65 + 100	600,18	65.0	2. 92	55.8
PH46	20	- 20 + 35	700,0	65.6	2.75	56.7
PH86	20	- 65 + 100	700,0	64.8	2.86	56.8
PH66	20	- 20 + 35	700,18	63.5	2.87	56.3
PH83	20	- 6 5 + 100	700,18	63.4	2. 9 4	56.6
PH130	40	- 20 + 35	550,18	67 <i>.</i> 5	2.80	54.7
PH82	40	- 20 + 35	600,0	68.5	3.24	46.8
PH54	40	- 65 + 100	600,0	66.4	2.95	54.3
PH61	40	- 20 + 35	600,18	66.2	2.86	54.6
PH64	40	- 65 + 100	600,18	64.2	3.06	54.2
PH80	60	- 20 + 35	500,18	69.4	3.13	47.9
PH98	60	- 65 + 100	500,18	68.4	3.18	49.3
PH57	60	- 20 + 35	600,0	67.8	2.81	54.3
PH94	60	- 65 + 100	600,0	67,1	3.12	51.2
PH79	60	-20+35	600,18	66.1	2.81	55.5
PH63	60	- 65 + 100	600,18	64.0	2.87	57.2
PH96	60	-20+35	700,0	65.1	2.65	58.6
PH89	60	- 65 + 100	700,0	64.1	2.88	57.0
PH67	60	- 20 + 35	700,18	63.1	2.77	58.1
PH65	60	- 65 + 100	700,18	62.1	2.82	59.2
1-5	200+	-20+35	500,0	78.1	3.46	32.5
1-6	200+	- 65 + 100	500,0	80.0	3.64	32.2
1-12	200+	-20 + 35	500,30	69.3	3.02	49.8
1-13	200+	- 65 + 100	500,30	69.8	3.21	49.7
1-2	200 +	-20+35	600,0	67.6	3.02	51.1
1-4	200 +	- 65 + 100	600,0	67.4	3.25	48.9
1-14	200+	- 20 + 35	600,10	64.9	2.98	53.6
1-15	200+	- 65 + 100	600,10	64.0	2.95	56.0
1-7	200+	- 20 + 35	600,30	63.8	2.78	57.5
1-8	200+	- 65 + 100	600,30	63.3	2.94	56.6
1-1	200+	-20+35	700,0	63.6	2.77	57.8
1-3	200 +	- 65 + 100	700,0	63.0	2.89	57.6
1-9	200+	-20 + 35	700,30	61.0	2.83	58.6
1-10	200+	-65 + 100	700,30	60.8	2.93	58.4

Table 7 Sulfur removal by pyrolysis of IBC-101

	·					
	Heating		Pyrolysis	Char	Char sulfur	Coal sulfur
	rate	Mesh	temp (°C),	yield	content	evolved
Experiment	(°C/min)	size	time (min)	(%)	(%)	(%)
PH101	20	- 20 + 35	500,0	78.2	1.83	40.1
PH73	20	- 65 + 100	500,0	78.0	1.99	34.0
PH84	20	-20+35	500,18	72.6	1.78	45.9
PH91	20	- 65 + 100	500,18	72.4	1.95	39.1
PH50	20	-20 + 35	600,0	70.6	1.82	46.2
PH51	20	- 65 + 100	600,0	70.7	1.79	46.1
PH59	20	-20 + 35	600,18	69.2	1.67	51.6
PH72	20	- 65 + 100	600,18	68.3	1.70	50.6
PH104	20	- 20 + 35	700,0	68.2	1.57	55.2
PH53	20	-65+100	700,0	68.3	1.62	52.9
PH78	20	- 20 + 35	700,18	67.0	1.59	55.4
PH74	20	- 65 + 100	700,18	66.8	1.60	54.5
PH55	40	- 20 + 35	600.0	71.8	1.86	44.1
PH71	40	- 65 + 100	600.0	70.7	1.76	47.1
PH77	40	-20+35	600.18	69.5	1.78	48.2
PH60	40	-65 + 100	600,18	68.7	1.71	50.0
PH103	60	- 20 + 35	500 18	73.3	1.86	43.0
PH99	60	-65 ± 100	500 18	73.1	1.89	41.2
11100		00 1 100	000,10			
P H8 6	60	-20 + 35	600,0	71.8	1.91	42.6
PH95	60	- 65 + 100	600,0	71.0	1.91	42.3
PH75	60	- 20 + 35	600,18	69.1	1.64	52.6
PH87	60	- 65 + 100	600,18	68.7	1.66	51.5
PH48	60	-20+35	700.0	68.8	1.67	51.9
PH93	60	- 65 + 100	700,0	68.1	1.68	51.3
PH85	60	- 20 + 35	700,18	66.7	1.68	53,1
PH90	60	- 65 + 100	700,18	67.1	1.64	53.2
3-3	200+	-20+35	500.0	85.2	2.02	28.0
3-6	200+	- 65 + 100	500.0	92.1	2.12	16.9
3-11	200+	-20+35	500.30	72.3	1.87	43.4
3-12	200+	-65+100	500,30	72.8	2.02	37.4
3-2	200 +	-20 ± 35	600.0	71 0	1.87	43.8
3-5	200+	-65 ± 100	600,0	70.8	194	41.5
3-14	200+	-20+35	600,0	69.0	1.68	51.5
3-13	200+	-65 ± 100	600,10	68.9	1.78	47.8
3-7	200+	-20+35	600 30	68.0	1.61	54.2
3-8	200+	- 65 + 100	600,30	67.9	1.69	51.1
2_1	200 -	_ 20 ± 25	700.0	68.2	1 67	52.3
3-1 2-4	200+	-20+35	700,0	67 4	1.07	52.3 53 A
3-4 3-10	200+	-00+100 -00±95	700,0 700 20	65.2	1.00	54 Q
3-0	200 -	-65 + 100	700,00	65.9	1 68	53.0
0-0	EVV T		100,00	0.00		00.0

Table 8 Sulfur removal by pyrolysis of IBC-103

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					Su	Sulfur evolved (%)		X-ray d	X-ray diffraction data for chars		
Experiment	Mesh size	Charring temp (°C), time (min)	Char yield (%)	Char sulfur content (%)	Total	Before max rate	After max rate	Pyrite- peak area (counts)	Pyrrhotite- peak area (counts)	Pyrrhotite (mol% Fe)	
PH31A	- 20 + 35	500, 5	69.1	3.27	41.1	18.2	22.9	6.3	4.0	47.6	
PH33	-20+35	500, 5	69.4	3.12	42.0	19.5	22.5	6.0	2.0	48.2	
PH35	- 65 + 100	500, 5	68.3	3.34	41.2	18.7	22.5	6.0	3.0	47.6	
PH43	- 20 + 100	500, 18	68.4	3.20	40.7	18.0	22.7	6.0	5.5	48.2	
PH36	- 65 + 100	500, 30	66.5	3.22	43.0	18.4	24.6	5.0	6.0	47.4	
PH40	-20+100	600, 5	65.3	2.89	48.9	18.7	30.2	2.0	11.2	48.2	
PH39	- 20 + 35	600, 18	64.9	3.00	49.0	16.6	32.4	1.0	10.0	48.6	
PH45	- 20 + 100	600, 18	64.6	2.79	50.1	17.3	32.8	2.0	11.2	48.6	
PH41	- 65 + 100	600, 18	64.1	3.01	48.8	18.0	30.8		12.0	48.2	
PH42	- 20 + 100	600, 30	63.9	2.71	52.5	18.6	33.9	—	15.0	48.6	
PH32	- 20 + 35	700, 5	62.8	2.82	54.1	18.0	36.1	_	12.8	49.4	
PH34	- 65 + 100	700, 5	62.0	2.84	53.4	19.0	34.4		11.2	49.1	
PH44	- 20 + 100	700, 18	62.1	2.77	53.0	18.7	34.3		10.5	49.1	
PH38	- 20 + 35	700, 30	62.2	2.80	49.4	17.8	31.6		9.8	49.8	
PH37	- 65 + 100	700, 30	61.1	2.86	52.1	18.1	34.0	-	12.8	49.1	

Table 9 Effect of particle size, maximum pyrolysis temperature, and soak time on total sulfur removal and sulfide mineral content for IBC-101 (heating rate was 18.5°C/min)

Table 10 Effect of heating rate and particle size on char pore structure (IBC-101 and IBC-103)

	Heating		Char sur	face area	Char	Charsulfur	Coal sulfur evolved (%)
Experiment	rate (°C/min)	Mesh size	N ₂ (m²/g)	CO ₂ (m²/g)	yiəld (%)	content (%)	
IBC-101							
PH69	20	-20+35	22.8	342.3	66.1	2.86	54.7
PH61	40	-20+35	27.7	338.3	66.2	2.86	54.6
PH79	60	- 20 + 35	27.5	341.8	66.1	2.81	55.5
PH58	20	- 65 + 100	13.3	354.5	65.0	2. 92	55.8
PH64	40	-65 + 100	17.8	350.5	64.2	3.06	54.2
PH63	60	- 6 5 + 100	19.9	361.1	64.0	2.87	57.2
IBC-103							
PH59	20	-20+35	7.1	317.8	69.2	1.67	51.6
PH77	40	-20+35	11.2	311.8	69.5	1.78	48.2
PH76	60	- 20 + 35	10.8	300.4	69.1	1.83	47.1
PH72	20	- 65 + 100	5.4	317.8	68.3	1.70	50.6
PH60	40	-65+100	8.2	306.8	68.7	1.71	50.0
PH87	60	- 65 + 100	10.9	322.4	68.7	1.66	51.5

chars in figure 3, the second sulfur evolution peak for experiments PH34 and PH41 is probably a result of the thermal decomposition of pyrite. The X-ray diffraction data indicate that at 600° and 700°C, most or all of the pyrite in the sample has been converted to pyrrhotite (table 9).



Figure 2 Effect of heating rate on sulfur evolution rate during pyrolysis of -20+35 mesh particles of IBC-101

Tables 7 and 8 show the effect of two particle sizes on the quantity of sulfur removed during pyrolysis. Most chars produced from -20+35 mesh coal particles have slightly lower sulfur contents than those produced from -65+100 mesh coal particles. The effect of particle size was investigated by more experiments using IBC-101 coal and a constant heating rate of 18.5°C/min. The time involved in heating the samples until the maximum sulfur liberation rate occurred (about 500°C) was constant for all runs. Therefore, by comparing the amount of sulfur liberated before the maximum desulfurization rate (R_{max}) was achieved, the effect of particle size on desulfurization rate could be evaluated. The fractions of sulfur evolved before and after Rmax are shown in table 9. From a comparison of the "before R_{max}" percentages, particle size clearly had little or no effect on the amount of sulfur evolved.

The results of surface area measurements on a select group of chars, produced at 600°C from IBC-101 and IBC-103 coals, are given in table 10. Very small pores were present in all the chars; the CO₂ surface areas are much higher than the N₂ surface areas. In most cases, the N₂ surface areas for chars produced from a given particle size fraction increase as the heating rate increases. In most cases, chars with higher N₂ surface area are produced from the larger particle size fraction, indicating that greater expansion occurs with larger particles during pyrolysis.

Significant differences are apparent between the physical and chemical characteristics of the two coal samples used for testing the effect of various parameters on the removal of sulfur during pyrolysis. For example, the organic sulfur content of IBC-101 is about 3 percent, whereas in IBC-103 it is about 1 percent. The



Figure 3 Rate of sulfur evolution during charring experiments PH34, PH41, and PH35 (table 9) (samples contained 3.04% organic sulfur and 1.04% pyritic sulfur)

volatile matter content of IBC-101 is about 4 percent higher than in IBC-103. In comparable pyrolysis experiments IBC-103 gives higher char yields and less evolution of sulfur than does IBC-101. In addition all chars from IBC-103 exhibit a much higher degree of agglomeration than do the chars produced under similar conditions from IBC-101. But even though the coals react differently under similar pyrolysis conditions, we found that for the parameters tested the relative effects on sulfur removal were similar for each coal.

Pyrolysis with a Trace of Oxygen

Normally when coal is heated above 500°C, pyrite (FeS₂) decomposes to nonmagnetic or weakly magnetic ic iron sulfides such as hexagonal pyrrhotites (Fe_{1-x}S) and troilite (FeS). Adding a trace amount of oxygen into

Experiment	% O ₂ in N ₂	Char yield (%)	Degree of magnetism*	Char mineral content†
RK-83B-5				
P-102	1.0	72.0	High	Hem, mag
P-123	0.5	71.1	High	Mag, hem, mono-pyrr
P-122	0.25	71.2	High	Mono-pyrr, (mag)
P-121	0.10	70.8	High	Mono-pyrr, (mag)
P-116	0.05	69.9	Moderate	Hex-pyrr, (mono-pyrr), (mag)
P-120	0.025	70.1	Slight	Həx-pyrr, (mono-pyrr)
P-117	0.0	69.5	Nonmagnetic	Hex-pyrr
IBC-103				
P-135	0.1	71.9	Moderate	Hex/mono-pyrr, (mag), (pyrite)

 Table 11
 Sulfide and iron oxide mineral content of chars produced from coals

 pyrolyzed 18 minutes at 550°C with various amounts of trace oxygen

* Degree of magnetism is an arbitrary estimate.

† Pyrr, pyrrhotite; mono, monoclinic; hex, hexagonal; mag, magnetite; hem, hematite; (), indicates trace amounts. Minerals are listed in order of estimated abundance based on peak intensities from X-ray diffraction patterns.

the nitrogen purging gas results in the formation of a significant amount of strongly magnetic, monoclinic pyrrhotite during pyrolysis. A guick and rather crude magnetic separation (by a hand magnet) made on a char produced at 550°C with a trace of oxygen showed that a significant amount of sulfur could be magnetically removed. The coal, RK-B-5, initially contained 3.8 percent total sulfur (see table 20 for proximate analysis), which was reduced to 2.5 percent sulfur when the coal (RK-B-5) was charred at 550°C with a trace of oxygen. After the crude magnetic separation, the sulfur content of the cleaned char was 1.2 percent. Although a significant amount of carbon material was also separated with the magnetic fraction of the char (about 48% total weight recovery), better magnetic separation techniques should significantly improve the separation vields.

Because of the potential for reducing the "pyritic" sulfur content of chars through conventional magnetic separation techniques, we further investigated the formation of magnetic pyrrhotite in chars. Efforts were directed toward studying parameters that affect the formation of magnetic pyrrhotite during pyrolysis: different amounts of trace oxygen used, pyrolysis temperature, and preoxidation. The mineralogical changes were monitored by X-ray diffraction.

The mineralogical results of several pyrolyses at 550°C using various trace amounts of oxygen are

shown in table 11. Adding 1.0 percent oxygen in the purging gas resulted in the formation primarily of magnetite and hematite. A small amount of monoclinic pyrrhotite was observed with 0.5 percent oxygen. The greatest formation of monoclinic pyrrhotite was observed when 0.25 and 0.1 percent oxygen were added to the purging gas. However, the char treated with 0.25 percent O₂ contained noticeably more magnetite than did char treated with 0.1 percent oxygen. The chars from runs with oxygen contents lower than 0.10 percent contained primarily hexagonal pyrrhotite with only a trace of monoclinic pyrrhotite. As observed previously, the 550°C pyrolysis under pure nitrogen contained only hexagonal pyrrhotite. To make certain that our results were not coal specific, a 550°C pyrolysis using 0.1 percent oxygen was performed on IBC-103; monoclinic pyrrhotite was also found to be present in the IBC-103 char.

A series of pyrolyses was run from 425° to 570°C to determine the sequence of sulfides that occur in the absence of oxygen. Table 12 shows the temperatures tested and the sulfide mineral contents of the resultant chars. Pyrite was the only sulfide mineral observed up to 500°C. This result differs from those of an initial experiment at 450°C in which a trace of monoclinic pyrrhotite was observed. However, Whiteway, Stuart, and Chan (1985) also observed some monoclinic pyrrhotite within the temperature range of 425°C to 500°C after pyrolyzing some Nova Scotia coals. Table 12 shows that at

Experiment	Pyrolysis temp (°C), time (min)	Char yield (%)	Degree of magnetism*	Sulfide minerals in char†
P-124	425, 18	82.5	Nonmagnetic	Pyrite
P-125	450, 18	76.0	Slight	Pyrite, (mag)
P-126	475, 18	74.1	Moderate	Pyrite, (mag)
P-127	500, 18	72.6	Moderate	Pyrite, hex-pyrr, (mono-pyrr), (mag)
P-128	525, 18	71.4	Moderate	Hex-pyrr, pyrite, (mono-pyrr), (mag)
P-130	550, 9	70.2	Slight	Hex-pyrr, (mono-pyrr) (pyrite)
P-129	570, 9	69.9	None to slight	Hex-pyrr

 Table 12
 Sulfide and iron oxide mineralogy of RK-B-5 chars produced by heating to various temperatures under pure nitrogen

* Degree of magnetism is an arbitrary estimate.

Pyrr, pyrrhotite; mono, monoclinic, hex, hexagonal; mag, magnetite, hem, hematite,
 (), indicates trace amounts. Minerals are listed in order of estimated abundance

based on peak intensities from X-ray diffraction patterns.

500° to 525°C a trace of monoclinic pyrrhotite was observed, but pyrite and hexagonal pyrrhotite were by far the most abundant sulfides. Perhaps a small amount of monoclinic pyrrhotite was formed due to the release of the inherent O_2 in the coal. At 570°C, only hexagonal pyrrhotite was observed in the char.

Another way to study the presence of magnetic minerals in chars after pyrolysis is to measure the magnetic susceptibility of the chars with a magnetometer. Magnetic susceptibility tests were completed on two sets of



Figure 4 Magnetic susceptibility measurements of chars prepared at various temperatures under pure N₂ and a 0.1% O_2/N_2 mixture for coal sample RK-B-5

chars from pyrolyses ranging from 425° to 600°C using RK-B-5 coal (fig. 4). The first set of pyrolyses was conducted under a pure nitrogen atmosphere, and the second with 0.1 percent oxygen (by volume) in the nitrogen flow. The magnetic susceptibility increases to a maximum as the pyrolysis temperature increases to 475°C under pure nitrogen. This finding corresponds well with the X-ray diffraction data, which showed the presence of magnetite and monoclinic pyrrhotite in chars heated up to 475°C (table 12). By 550°C the magnetic susceptibility had fallen more than one order of magnitude in the pyrolyses conducted under pure nitrogen.

The magnetic susceptibility of the chars heated under 0.1 percent oxygen also reached a maximum at about 475° to 500°C. However, the magnetic susceptibility did not drop much after 475°C but remained high for all the chars up to 600°C (fig. 4). X-ray diffraction data were collected on chars that were heated to 800°C and treated with H_2/H_2S gas. Some of these chars were cooled under pure nitrogen and others under 0.1 percent oxygen. The X-ray patterns show a shift in the subsequent iron sulfides from troilite to monoclinic pyrrhotite because of the trace of oxygen. Thus by using a trace of oxygen we were able to produce a ferromagnetic monoclinic pyrrhotite in many different chars over a wide temperature range.

From the sulfide studies of Taylor (1971) and Genkin (1971) and our own recent experiments on pyrrhotite in chars, we believe that the trace amount of oxygen added during pyrolysis drives the more iron-rich hexagonal pyrrhotite to the more iron-poor, magnetic, mono clinic pyrrhotite. Two experiments were performed to verify this hypothesis. The coal was heated to 550° and 650°C under nitrogen and the temperature held for 18 minutes. Previous X-ray data have shown that these

Experiment	Pyrołysis temp (°C), time (min)	Treatment	Char yield (%)	Degree of magnetism*	Char mineralogy†
Pure nitrogen			fm		
P-132	550, 30	Pure N₂ — 18 min 0.1% O ₂ — 12 min	69.6	Moderate to high	Hex-mono-pyrr, (mag)
P-133	650, 30	Pure N₂ - 18 min 0.1% O ₂ - 1 2 min	66.5	Moderate to high	Hex-pyrr, minor mono-pyrr
Preoxidation					
P-131	550, 18	5% O ₂ at 295°C 0.1% O ₂ at 550°C	76.0	Moderate to high	Hex-pyrr, minor mono-pyrr, (mag)

 Table 13
 Sulfide and iron oxide mineralogy of RK-B-5 chars treated with 0.1 percent oxygen after pure nitrogen treatment and preoxidation treatment

* Description of magnetism is an arbitrary estimate.

† Pyrr, pyrrhotite; mono, monoclinic; hex, hexagonal; mag, magnetite; hem, hematite; (), indicates trace amounts. Minerals are listed in order of estimated abundance based on peak intensitites from X-ray diffraction patterns.

Charring		Sulfur removed (%)			Volatile loss	Origin of sulfur in volatiles (%)		Origin of sulfur remaining in char (%)	
Run	condition Total Org* Pyr* (wt%)	(wt%)	Org*	Pyr*	Org*	Pyr*			
Sink									
1	650°C	47.6	68	31	27.5	65	35	35	65
2	650°C	48.6	69	31	27.8	65	35	34	66
3a	450°C	24.5	50	3	—	93	7		—
ЗЬ	Part oxid	50.1	18	77	33.3	16	84	68	32
Float									
1	650°C	57.1	67	12	36.4	96	4	68	32
2a	450°C	37.4	46	0		100	0		_
2b	Part oxid	19.5	12	53	36.1	49	51	84	16

Table 14 Pyrolysis and post-pyrolysis partial oxidation experiments on sink and float coal fractions

* Values calculated from isotopic compositions.

conditions produce only hexagonal pyrrhotite. Monoclinic pyrrhotite was successfully produced at both temperatures with the addition of 0.1 percent oxygen for 12 minutes after the above conditions had been established (table 13).

To determine if preoxidation (used for deagglomeration purposes) would hinder the formation of monoclinic pyrrhotite, we ran a pyrolysis experiment in which we preoxidized the coal at 295°C with 5 percent oxygen and then used 0.1 percent oxygen at 550°C. Some magnetic pyrrhotite was successfully formed on the preoxidized char (table 13). All the pyrolyses up to this point had been carried out in our thin-bed bench-scale system using only 0.5 to 1.0 g of coal.

Through the cooperation of the ISGS Minerals Engineering Section, we were able to run one test of our parameters on a larger scale in a fluidized-bed system. Approximately 100 g of IBC-101 was run in the fluidizedbed system. The sample was preoxidized at 250°C with 5 percent oxygen for 15 minutes, then heated to 550°C and held for 20 minutes with 0.1 percent oxygen added to the purging gas. The initial results were very encouraging: X-ray diffraction showed that monoclinic pyrrhotite was present in the fluidized-bed char, although only a relatively small amount of the magnetic pyrrhotite was detected. The conditions that lead to the formation must be optimized. Preliminary data collected on the magnetic separation of the magnetic iron sulfide from the char indicate a need to improve the magnetic separation technique and equipment.

The work reported above suggests that for some coals, especially those with low to moderate organic sulfur contents, magnetic separation of sulfide minerals alone is potentially useful for producing low-sulfur chars.

Post-Pyrolysis Desulfurization

To produce clean low-sulfur solid fuel from most Illinois high-sulfur coals, post-pyrolysis desulfurization treatment is necessary. The two gas-phase post-pyrolysis treatments investigated were partial oxidation and hydrodesulfurization.

Partial oxidation To monitor the type of sulfur removed during post-pyrolysis partial oxidation, isotopically characterized coal samples were used in several partial oxidation experiments. In figure 5, an example of the results shows that pyritic sulfur is preferentially removed during partial oxidation. As already described, an Illinois Herrin Coal sample that had been previously well characterized isotopically was subjected to a float/ sink separation to provide a pyrite-rich and a pyrite-poor fraction (table 14). Table 14 compares the results of the pyrolysis and post-pyrolysis partial oxidation experiments on the sink and float fractions. As expected, the sink fraction showed a much greater sulfur loss during oxidation due to the preferential oxidation of the inorganic sulfide (pyrite and possibly a small amount of pyrrhotite). The much lower amount of pyritic sulfur removed during oxidation of the float fraction is probably a result of the pyrite in this fraction being primarily disseminated and thus not readily available for oxidation.



Figure 5 Proportions of original organic and pyritic sulfur remaining after charring and partial oxidation at 450°C

The effects of the following process conditions on sulfur removal during post-pyrolysis oxidation were studied: oxidation temperature, oxidation time, oxygen concentration, and the presence of water vapor in the oxidizing gas stream. The results are summarized in table 15 for IBC-101 and in table 16 for IBC-103. With IBC-101, the lowest sulfur content chars were produced

- Experiment	Oxidation conditions			Char	Char sulfur	Coal sulfur
	Temp (°C)	Time (min)	O ₂ Concn (%)	yield (%)	content (%)	evolved (%)
550°C/18 min						
PH130	_			67.5	2.80	54.7
PH132	450	15	1	66.7	2.70	56.8
PH131	450	5	5	67.1	2.46	60.4
PH129	450	15	5	61.7	2.30	56.0
600°C/18 min						
PH61		—		66.2	2.86	54.6
PH112	450	15	1	65.4	2.43	61.9
PH138	450	15	1*	65.4	2.39	62.5
PH114	450	5	5	65.8	2.33	63.2
PH110	450	15	5	60.5	2.25	67.4
PH136	450	15	5*	61.8	2.20	67.4
PH137	525	15	1*	64.3	2.47	61.9
PH109	525	10	3	62.6	2.44	63.4
PH115	525	10	5	60.3	2.37	65.7
PH135	525	15	5*	58.2	2.33	67.5
PH111	600	15	1	64.3	2.73	57.9
PH126	600	15	1*	61.9	2.54	62.3
PH113	600	5	5	63.1	2.62	60.4
PH133	600	15	5*	6.29	2.70	59.3

Table 15	Post-pyrolysis	oxidation	results fo	or IBC-101
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*in presence of water vapor.

	Oxidation conditions			Char	Charsulfur	Coal sulfur
Experiment	Temp (°C)	Time (min)	O ₂ concn (%)	yield (%)	content (%)	evolved (%)
PH77				69.5	1.78	48.2
PH121	450	15	1	69.1	1.43	58.7
PH123	450	15	1*	68.9	1.37	61.5
PH125	450	15	5	69.3	1.39	59.7
PH120	450	15	5	67.0	1.31	63.3
PH117	525	10	3	66.6	1.32	63.2
PH124	525	10	5	64.9	1.26	65.8
PH118	600	15	1	67.1	1.44	59.6
PH119	600	15	1*	66.3	1.45	59.8
PH122	600	5	5	6 6.6	1.42	60.4

Table 16 Post-pyrolysis oxidation results for IBC-103 (600°C, 18 min)

*In presence of water vapor.

by oxidation for 15 minutes at 450° C with a 5 percent O_2 gas stream. However, only a small reduction in char sulfur content is obtained at the expense of a significant reduction in char yield when the oxidation time is increased from 5 to 15 minutes. For pyrolysis of IBC-103, 525°C rather than 450°C appears to be the preferred oxidation temperature. However, chars from IBC-103 are highly agglomerated, suggesting that some carbon must be oxidized in order for some of the pyrite/pyrrhotite to be subjected to oxidation. The presence of water vapor in the oxygen stream has little effect on the sulfur content of an oxidized char.

Although the pH monitoring technique was only roughly quantitative in monitoring the sulfur evolution rates during the oxidation, results from it and the data in tables 15 and 16 do indicate that during the first few minutes of oxidation, the rate of sulfur oxidation is significantly higher than the rate of carbon oxidation.

For reasons explained in the appendix a guadrupole gas analyzer (QGA) was used to gain more accurate rate data. The QGA data collected during a pyrolysis experiment and a post-pyrolysis oxidation experiment are shown in figures 6 and 7, respectively. Data collected by the pH monitoring technique showed that for a heating rate of approximately 20°C/min, the maximum sulfur evolution rate occurred at 460° to 500°C. However, the QGA data (fig. 6) showed the maximum sulfur evolution occurred at about 435°C. We believe the latter temperature to be close to the true temperature for maximum sulfur evolution of Illinois coal during pyrolysis. The QGA data in figure 7 confirm pH monitoring results, which showed that during a 15-minute postpyrolysis oxidation at about 450°C, sulfur was preferentially oxidized during the first few minutes, after which carbon was preferentially oxidized.

Hydrodesulfurization Since hydrogen can be used in a gas-phase desulfurization process, the behavior of the organic and pyritic sulfur was investigated



Figure 6 Quadrupole gas analyzer (QGA) data collected during pyrolysis of IBC-101 (heating rate, approximately 20°C/ min)



Figure 7 QGA data comparing the evolution of SO_2 and CO_2 during char oxidation at 455°C of IBC-101, experiment QMS8 (table 19)

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using stable isotope analyses on untreated hydrodesulfurized chars, partially oxidized hydrodesulfurized chars, and acid-leached hydrodesulfurized chars. Since the hydrodesulfurization experiments were carried out at 800°C, the pyrite would have been completely converted to pyrrhotite. However, as mentioned earlier for the pyrolysis experiments, when discussing the isotopic results we refer to the inorganic sulfur as "pyritic" sulfur.

The isotopic data indicate that both organic and "pyritic" sulfur are removed during hydrogen treatment. However, the proportions of "pyritic" and organic sulfur remaining in the final products are guite different depending on whether the char has been acid leached or partially oxidized before hydrogen treatment (table 17). Most of the sulfur remaining in the acid-leached hydrodesulfurized chars is "pyritic" sulfur. In fact, in two of the three coals tested (RK-A-4 and CR-B-4) no organic sulfur remained in the acid-leached hydrodesulfurized chars. The sulfur remaining in the two chars that were oxidized before hydrodesulfurization (RK-B-3 #26 and RK-A-4 #18) was completely organic. Figure 8 displays the proportions of organic and "pyritic" sulfur remaining in the charred products after each type of treatment for the RK-B-3 coal.

We do not completely understand why most of the acid-leached hydrodesulfurized chars contained only "pyritic" sulfur and the partially oxidized hydrodesulfurized chars contained only organic sulfur (table 17). In the latter case, the fact that very little "pyritic" sulfur remains in the partially oxidized chars before hydrodesulfurization probably explains why only organic sulfur remains in the final char. However, for the acid-leached hydrodesulfurized chars, there is no obvious explanation why only "pyritic" sulfur remains in most of the final chars.

 Table 17
 Distribution of sulfur forms in hydrogen-treated chars after acid leaching and partial oxidation

		Sulfur in final char (%)						
Coal sample no.	Charring temp (°C)	Total remaining	Organic*	"Pyritic"*				
Acid-leached c	har							
RK-B-3 #13	450	7.5	41	59				
RK-B-3#16	650	3.3	35	65				
RK-A-4 #17	450	4.1	0	100				
RK-A-4 #19	550	4.0	0	100				
RK-A-4 #20	650	2.6	0	100				
CR-B-4 #21	450	4.1	0	100				
CR-B-4 #23	550	3.2	0	100				
CR-B-4 #24	650	2.0	0	100				
Oxidized char								
RK-B-3 #26	450	7.1	100	0				
RK-A-4 #18	450	10.0	100	0				

*Values calculated from isotopic composition.



Figure 8 Proportions of original organic and "pyritic" sulfur remaining in treated chars of RK-B-3 coal samples

Four hydrodesulfurizations, lasting 15, 30, 45, and 60 minutes, were made after 750°C pyrolyses to determine the type and amount of sulfur removed relative to the length of time for pure hydrogen treatment (table 18). The sulfur evolved during hydrogen treatment at 800°C is much more enriched in "pyritic" sulfur (44%) than the sulfur evolved during pyrolysis (14% "pyritic" sulfur). Figure 9 compares the desulfurization efficiency of 15- and 60-minute hydrodesulfurization. Pyrolysis plus hydrodesulfurization results in a significant removal of both organic and "pyritic" sulfur. The effect of hydrodesulfurization time can be seen more clearly in figure 10, which shows the amount and composition of sulfur removed by hydrodesulfurization and that remaining in the treated char. Of particular interest, sulfur removed by hydrodesulfurization was found to have a constant ratio of organic to "pyritic" sulfur with increasing hydrodesulfurization times. Much of the sulfur actually being removed by the hydrogen might have been primarily organically bound sulfur. Our earlier studies showed that during pyrolysis, some of the pyritic sulfur becomes bound into the organic structure and the amount of incorporation increases with temperature. The constant ratio of organic to "pyritic" sulfur observed during the different hydrodesulfurization times would be explained if the sulfur removed by the hydrogen is primarily organically bound sulfur, which includes both original organic sulfur and original "pyritic" sulfur,

Hydrodesulfurization rate data for a non-pretreated char, an acid-leached char, and a partially oxidized char are compared in figure 11. Obviously, acid leaching of the char (removal of iron) significantly increased its hydrodesulfurization rate. On the other hand, oxidation does not appear to have increased the initial rate of hydrodesulfurization, but because the rate did not diminish as much with time, oxidation did appear to reduce the time necessary for hydrodesulfurization to occur. This is addressed in more detail later when the relative rates of sulfur removal are discussed.

Table 18	Pyrolysis	and hydrode	sulfurization	results of	coal sample	RK-B-3
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Run no.	Temp (°C), soak time	Sulfur evolved (%)			Sulfur re	maining in	Sulfur	Char vield	
	(min)	Total	Org*	Pyr*	Total	Org*	"Pyr"*	in char (%)	(%)
Pyrolysis	 _								
197a	750, 5	60.2	86	14	39.8	63	37	1.88	64.4
196a	750, 5	58.9	86	14	41.1	63	37	1.94	64. 9
195a	750, 5	58.6	86	14	41.4	63	37	1.96	64.3
194a	750, 5	59.8	86	14	40.2	62	38	1.90	64.3
Hydrodesul	furization								
197b	800, 15	16.8	56	44	23.7	69	31	1.21	60.6
196b	800, 30	24.4	56	45	16.8	74	26	0.87	58.8
195b	800, 45	26.4	56	44	14.9	76	24	0.76	60.1
194b	800,60	27.1	57	43	12.9	77	23	0.68	59.6

*Values calculated from isotopic composition.



Figure 9 Sulfur removal by charring at 750°C for 5 minutes and hydrodesulfurization at 800°C for 15 and 60 minutes



Figure 10 Removal of organic and "pyritic" sulfur from char by hydrodesulfurization at 800°C for different lengths of time (percentage of sulfur evolved and remaining refers to amount of sulfur originally present in untreated coal). See table 18

Table 19 Separate pyrolysis and post-pyrolysis desulfurization experiments for IBC-101 (-20+100 mesh)

Experiment	Pyrolysis		Oxida	Oxidation		Ifurization	Oxidation			
	Temp (°C), time (min)	Calc char S content (%)	Temp (°C), time (min)	O ₂ concn (%)	Temp (°C), time (min)	H₂ concn (%)	Temp (°C), time (min)	O₂ concn (%)	Char sulfur content (%)	Approx net char yield (%)
QMS8	600, 18	2.79	455, 15	5	_				2.12	61.1
QMS6	600, 18	2.84	_	_	800, 60	100		_	0.82	58.3
QMS7*	600, 18	2.80	_		800, 60	100	_		0.48	51.9
QMS9	600, 18	2.82	455, 15	5	800, 60	100	—	_	0.76	58.5
QMS10	600, 18	2.89	—		800,60	100	455, 5	5	0.75	56.9

*Char was acid leached before post-pyrolysis desulfurization.

The experimental conditions and sulfur contents of the desulfurized chars are summarized in table 19. Acid leaching had the greatest effect on reducing the char sulfur content, whereas post-pyrolysis oxidation had only a small effect on char sulfur content. In a char desulfurization process, oxidation should probably be used after rather than before hydrodesulfurization. This idea was tested in experiment QMS10, which showed a small reduction in char sulfur content compared with the untreated char. However, the actual amount of sulfur evolved during post-hydrodesulfurization oxidation was quite small, so the differences in char sulfur contents may be within the limits of experimental error.

Combined Treatments for Thermal Desulfurization

Results presented in previous sections were obtained mainly from experiments designed to determine the optimum conditions for pyrolysis and various postpyrolysis char desulfurization treatments. Results presented in this section were obtained in a systematic study combining pyrolysis and post-pyrolysis treatments to show the potential of thermal desulfurization processes to produce low-sulfur chars from high-sulfur Illinois coals.

Four coals that differ in their pyritic and organic sulfur contents were used in this part of the project. The chemical analyses of the coals are given in table 20. With the exception of IBC-101, the coals are not necessarily representative of process coals. Coals CR-B-1, RK-B-4, and RK-B-5 were chosen because of their relatively high pyritic sulfur contents. The various combinations of desulfurization treatments investigated are listed in figure 12. The list begins with untreated pyrolysis and shows the various combinations of post-pyrolysis treatments tested, including partial oxidation (with 5 and $0.1\% O_2$), acid leaching (with dilute HCl), hydrodesulfurization, and magnetic separation of inorganic sulfides.

Analytical and mineralogical results The analytical results of the various treatments are summarized in table 21 (sulfur content and yield data) and the mineralogical results are summarized in table 22 (X-ray



Figure 11 800°C hydrodesulfurization rate data for experiments QMS6, QMS7, and QMS9 prepared for IBC-101 (table 19)

diffraction analyses). The yield data given in table 21 were calculated relative to the original coal. Acid leaching followed by hydrodesulfurization (treatment 5) always produces the lowest sulfur content chars, and thus is the treatment combination against which all other combinations should be compared. Data from the QGA concerning rates of sulfur removal are presented later.

As can be seen in table 21, hydrodesulfurization with pure H₂ (treatment 3) reduces the sulfur content of chars significantly compared with pyrolysis alone (treatment 1) and post-pyrolysis partial oxidation (treatment 2). To obtain similar results in an industrial-scale reactor, an H₂S scavenger would probably have to be mixed in with the char during hydrodesulfurization because of the excess H₂S present in the large-scale system. However, the sulfur-ladened scavenger would ultimately have to be removed from the char.

The combination of post-pyrolysis partial oxidation of chars followed by hydrodesulfurization (treatment 4)

Table 20 Chemical analyses of the four coals used in the combined gas-phase thermal treatment tests (moisture-free basis)

Chemical	Coal sample							
analysis (%)	CR-B-1	RK-B-4	RK-B-5	IBC-101				
Volatile matter	45.1	40.0	41.0	44.2				
Fixed carbon	47.5	41.6	45.9	45.9				
High-temp ash	7.4	18.4	13.1	9.8				
CaO	0.28	0.43	1.86	0.50				
Sulfate sulfur	0.067	0.022	0.044	0.158				
Pyritic sulfur	1.90	3.77	2.04	1.08				
Organic sulfur	3.01	2.38	1.74	2.77				
Total sulfur	4.97	6.17	3.83	4.01				



Figure 12 Various combinations of the thermal desulfurization treatments investigated

Coal	Total	1 Pyroly: (N ₂) char	sis	Oxid (5% ch	2 ation 0 ₂) ar ₂	3 Hydrodes (H ₂) char ₃	sulf	4 Oxida (5% hydroc cha	ation O ₂) Jesulf ar ₄	5 Acid lead (15% HC hydrodes char ₅	ch XI) sulf
sample	S	S	Yield	St	Yield†	S	Yield	S	Yield	S	Yield
CR-B-1	4.97	3.48	60.9	2.84	57. 9	0.71 0.78‡	57. 9	0.64	53.1	0.41	49.4
RK-B-4	6.17	4.33	64.4	2.99	61.2	0.79	61.2	0.60§	56.3	0.37 ± 0.04	52.8
RK-B-5	3.83	2.86	63.4	2.38	60.2	1.58 ± 0.07	60.2	1.24	55.8	0.30 ± 0.02	52.0
IBC-101	4.01	2.65±0.09	63.1 ± 0.23	2.20	60.9	0.88±0.05 1.05‡	60.9	0.70	55.1	0.42	52.1
					7 7	7		8	}	8	
Coal	Total	(H ₂ +0.44° 0x (5% char	% H ₂ S) (O ₂) 6	Hydru H ₂ + 0.4 ox (0.1 cha	44% H ₂ S) 1% O) ₂ ar _{M2}	Nonmagnetic fraction char ₇		Nonmagnetic fraction (N ₂ +0.1%O ₂) char ₇ char _{M1}		Nonmagnetic fraction char _e	
sample	s	S	Yield	S	Yield	S	Yield	S	Yield	S	Yield
CR-B-1	4.97	1.29	55.6	2.12	56.0	1.12	28.9	3.96	65.1	2.37	40.9
RK-B-4	6.17	1.36	59.2	3.93	60.1	1.27	16.4	5.29	69.7	2.03	44.6
RK-B-5	3.83	2.13 ± 0.08	56.6	2.91	57.1	1.24	31.9	3.11	67.4	1.20	48.1
IBC-101	4.01	1.16	56.7	1.88	57.7	1.25	26.4	3.00	67.5	2.14	52.2

Table 21 Sulfur concentration in chars and total char yields (by weight) after combined thermal desulfurization treatments (outlined in fig. 12)

* Values are given as percentages.

‡ 30-min hydrodesulfurization.

† Estimated values.

§ 7-min oxidation.

Table 22	Sulfide and associated iron minerals in chars after thermal desulfurization treatments (char subscripts, see fig. 12	2)*
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Coal sample	Coal	Char₁ (750°C) pyrolysis	Char ₅ acid leached H ₂	Char₄ O₂, H₂	Char₃ H₂	Char ₆ H ₂ + H ₂ S, 5% O ₂	$\begin{array}{c} Char_{HS} \\ H_2 + H_2 S \end{array}$	$\begin{array}{c} Char_{M2}\\ H_2 + H_2S,\\ 0.1\%O_2 \end{array}$
CR-B-1	FeS ₂ †	FeS	Fe(N) S(N)	Fe (CaS) (Fe₁₋ _× S)	Fe (Fe ₁₀ S ₁₁) (CaS)	Fe ₂ O ₃ Fe ₃ O4 Fe ₇ S ₆	Fe\$ (CaS)	Fe₇S₈ Fe_{1−x}S (Fe ₃ O ₄) (CaS)
RK-B-4	FeS ₂	FeS	Fe(N) S(N)	Fe (CaS) (Fe₁₋ _x S)	Fe (CaS)	Fe₂O₃ Fe₃O₄ CaS (Fe ₇ S ₈)	FeS (CaS)	Fe₁S8 Fe₁₋xS (Fe₃O₄) (CaS)
RK-B-5	Fe\$ ₂	—	Fe (N) S (N)	Fe CaS	CaS Fe	CaS Fe ₃ O ₄ Fe ₂ O ₃ (Fe _{1-x} S)	CaS FeS	CaS, Fe ₇ S ₈ Fe _{1-x} S) (Fe ₃ O ₄)
IBC-101	FeS ₂	FeS	Fe(N) S(N)	Fe (CaS) (Fe _{1-x} S)	Fe (CaS)		Fes (CaS)	Fe₁_S Fe₁_ xS (CaS) (Fe₃O₄)

Mineral content as determined by X-ray diffraction listed in order of estimated relative abundance: (N), none; (), trace;
 Fe, iron; S, sulfides; FeS, troilite; CaS, oldhamite; Fe_{1-x}S, hexagonal pyrrhotite; and Fe₇S₈, monoclinic pyrrhotite.

+ Bold type represents the most abundant sulfides or iron minerals present.

slightly reduces the sulfur content compared with chars produced by hydrodesulfurization and pyrolysis alone (treatment 3). Although not apparent from table 21, postpyrolysis oxidation also reduces the time required to reach a certain char sulfur content by hydrodesulfurization, especially for chars produced from high pyrite content coals. Most of the hydrogen treatments were carried out for 60 minutes; however, two hydrogen treatments for CR-B-1 and IBC-101, run for only 30 minutes, removed almost as much sulfur as did the 60-minute hydrogen treatment times. Additional considerations of the time factor will be presented with the discussion of relative rates of sulfur removal.

The combination of treatments 6 and 7, in which char hydrodesulfurization was carried out with the H_2/H_2S mixture, was included to simulate a large-scale system where excess H_2S could cause back reactions with iron in the char (assuming no H_2S scavenger is added to the system). We used 0.44 percent H_2S , a concentration above the 0.2 percent level, at which the back reaction of H_2S with iron becomes important (Stephenson et al., 1985). The chars treated with the H_2 + 0.44 percent H_2S were then subjected to oxidation by either 5 or 0.1 percent O_2 . For the 0.1 percent O_2 , the conversion of iron sulfides present after hydrodesulfurization to a magnetic form of pyrrhotite was investigated using X-ray diffraction.

The sulfur contents of chars treated with H_2 + 0.44 percent H₂S mixture were not determined, but should be close to the sulfur contents of the chars treated with H₂ + 0.44 percent H₂S mixture followed by the slight oxidation using the N_2 + 0.1 percent O₂ mixture (table 21, treatment 7). According to QGA results, very little sulfur is actually lost during slight oxidation with 0.1 percent O2. Obviously, the chars produced using the simulated excess H₂S would have to undergo a post-hydrodesulfurization treatment. Post-hydrodesulfurization oxidation helps to overcome the problem of H₂S back reactions with iron in the chars. On the basis of the char sulfur contents, except for the RK-B-5 char, very little difference is apparent between post-hydrodesulfurization oxidation with 5 percent O2 and with 0.1 percent O₂ plus a magnetic separation. The net process yield data included in table 21 would favor oxidation with 5 percent O₂ as the post-hydrodesulfurization treatment. However, oxidation with 0.1 percent O₂ plus magnetic separation is potentially useful if the yield of the nonmagnetic fraction can be significantly increased. A process including a magnetic separation step would be advantageous because it could produce chars with significantly lower ash contents.



Figure 13 Sulfur and carbon evolution versus pyrolysis temperature for four different coals (rate data were collected on the QGA)

Closer inspection of table 21 shows that hydrodesulfurization of chars produced from RK-B-5 does not reduce the char sulfur content nearly as much as the chars produced from the other coals. This observation is readily explained by the calcium contents (table 20) and the X-ray diffraction data (table 22). During hydrodesulfurization, a significant amount of CaS (oldhamite) forms. A char containing 1.0 percent CaO, could retain 0.57 percent sulfur as CaS (100% conversion). According to Nankervis and Furlong (1980), CaS is quite resistant to oxidation below 850°C. Because CaS sulfur cannot be removed by a post-hydrodesulfurization oxidation step at 450°C, CaS sulfur could contribute to sulfur emissions during combustion of the chars. Therefore, unless chars are subjected to acid leaching or some other treatment to remove calcium before hydrodesulfurization, coals with high calcium contents are poor candidates for use in thermal desulfurization processes.

One of the simplest coal desulfurization treatments tested is pyrolysis in the presence of a trace (0.1 percent) of oxygen to produce chars containing magnetic iron sulfides (no. 8, fig. 12). But the sulfur contents of the chars, except those from RK-B-5, are relatively high compared with the hydrogen treatments and the overall yields of the nonmagnetic fractions are poor (table 21). Although magnetic separation techniques may prove to be applicable for removing iron sulfides from chars, they cannot be expected to significantly reduce the organic sulfur content of chars. Therefore, coals such as CR-B-1, RK-B-4, and IBC-101 probably cannot be adequately desulfurized by the process, unless their chars are subjected to further desulfurization treatment after magnetic separation.

Relative rates of sulfur removal When the systematic study of the combined thermal desulfurization treatments diagrammed in figure 12 was initiated, we planned to use the QGA monitoring system to obtain quantitative sulfur rate data for most of the steps in the processes for inclusion in this report. Although several factors prevented the conversion of the QGA data to quantitative rate data, the QGA data did provide relevant information about the various desulfurization steps.

The QGA data in figure 13 show that the maximum total devolatilization as measured by the carbon evolution rate occurs at essentially the same temperature as does the maximum organic sulfur devolatilization rate. The second peak on the sulfur evolution curves is readily assigned to the thermal decomposition of pyrite on the basis of the absence of a corresponding CO_2 peak and X-ray diffraction and stable isotope data from earlier experiments.

Hydrodesulfurization QGA data for the four coals are shown in figures 14 through 17. In each figure, the shapes of sulfur-evolution curves obtained during hydrodesulfurization of an untreated char, an oxidized char, and an acid-leached char are compared. With the exception of RK-B-5, the curves obtained from the untreated and partially oxidized chars in figures 14 to 17 indicate that post-pyrolysis oxidation significantly reduces the time required for hydrodesulfurization. Data in table 21 show that post-pyrolysis oxidation does result in a small reduction of the sulfur content of chars hydrodesulfurized for one hour (treatment 4). Oxidation of chars removes primarily "pyritic" sulfur, and thus the removal of "pyritic" sulfur results in the reduction in time required for hydrodesulfurization of the oxidized chars. Acid leaching of chars heated to 750°C removes most of the iron, calcium, and inorganic sulfide sulfur from the chars. Thus, only organically bound sulfur remains in the acid-leached chars. Very little to no iron or calcium remains in the acid-leached char for the H₂S to react with before escaping from the char matrix. As the hydrodesulfurization curves for the acid-leached chars in figures 14 to 17 indicate, hydrodesulfurization times required for acid-leached chars would be significantly



Figure 14 Sulfur evolution versus time for hydrodesulfurization at 800°C of three CR-B-1 chars

shorter than for untreated chars. Partially oxidized char has less total sulfur than does untreated char, but unlike the acid-leached char, the iron remains in an oxidized state. Thus, the iron is still available for reactions with escaping H_2S , which could prolong hydrodesulfurization relative to the acid-leached char.

Although the acid-leached chars gave the best hydrodesulfurization results, acid leaching would not be a very economical approach to desulfurization. However, post-pyrolysis partial oxidation appears to reduce the hydrodesulfurization time significantly, so post-pyrolysis oxidation followed by hydrodesulfurization would seem to be a feasible treatment for gas-phase thermal desulfurization.

Although the QGA monitoring system could not be used during the hydrodesulfurization experiments using

the H_2/H_2S mixture, it was used during corresponding post-hydrodesulfurization oxidation experiments. The QGA data for two of the experiments are shown in figure 18. As previously reported for post-pyrolysis oxidation, sulfur is preferentially oxidized during the first few minutes, after which carbon is preferentially oxidized. The width of the SO₂ peak for the RK-B-4 char reflects the high pyritic sulfur content of the original coal sample and its char equivalent.

CONCLUSIONS AND RECOMMENDATIONS

During thermal desulfurization, the sulfur removed by pyrolysis temperatures below 500°C is virtually all organic. Data collected on three different isotopically characterized Illinois coal samples consistently indicate



Figure 15 Sulfur evolution versus time for hydrodesulfurization at 800°C of three RK-B-4 chars



Figure 16 Sulfur evolution versus time for hydrodesulfurization at 800°C of three RK-B-5 chars

that most of the removable organic sulfur is released by the time pyrolysis temperatures reach 500 to 550°C. Higher pyrolysis temperatures result primarily in the removal of relatively small amounts of pyritic sulfur from the coal.

Studies on the effects of certain parameters during pyrolysis show that the maximum pyrolysis temperature is the most important factor controlling the amount of sulfur that can be removed during thermal treatment. To remove the most sulfur in the least amount of time, pyrolyses must be carried out at or above 550°C. Other parameters such as heating rate, particle size, and soak time appear to be minor contributing factors for total sulfur removal, although heating rate does directly affect the rate of sulfur evolution during pyrolysis. Generally, after a 550°C µyrolysis for 20 minutes the sulfur content



Figure 17 Sulfur evolution versus time for hydrodesulfurization at 800°C of three IBC-101 chars

of the char will be approximately 70 percent of that contained in the coal.

More "pyritic" sulfur can be removed by pyrolysis with a trace amount of oxygen and separation of the resulting magnetic iron sulfide by physical means. Pyrolysis of coal in the presence of a trace amount of oxygen results in the conversion of pyrite to magnetic pyrrhotite. The controlling parameters for this magnetic conversion appear to be oxygen concentration and pyrolysis temperature. The most magnetic pyrrhotite was obtained by adding 0.25 to 0.1 percent oxygen to the purging gas. A crude magnetic separation system (a hand magnet) was used to remove a significant amount of sulfur from a char produced at 550°C with a trace of oxygen. With more efficient magnetic separation, this type of process would be useful for coals with moderate organic sulfur and high pyritic sulfur.

Another method of reducing much of the pyritic sulfur in a coal is post-pyrolysis oxidation using a few percent oxygen in the purging gas. Significant amounts of sulfur can be removed using post-pyrolysis partial oxidation. The conditions of post-pyrolysis oxidation that gave the most sulfur removal with the least carbon loss were temperatures below 550°C and an oxygen concentration of 5 percent by volume in the purge gas. The per-



Figure 18 QGA data comparing the evolution of SO₂ and CO₂ during oxidation at 455°C of H_2 +0.44% H_2 S-treated chars

centage of sulfur removed during partial oxidation can vary significantly depending on the amount of pyritic sulfur present. After a 450°C pyrolysis followed by partial oxidation, the total sulfur content of the char generally is approximately 55 percent of that contained in the coal.

Although pyrolysis combined with magnetic separation or pyrolysis plus partial oxidation can result in sufficient sulfur removal to produce a relatively low-sulfur fuel from certain Illinois coals (those with high pyritic sulfur and low organic sulfur), our results indicate that additional treatment will be necessary to produce a compliance fuel for most Illinois coals. Hydrodesulfurization at 800°C may be rather costly but it is effective in producing a low-sulfur solid fuel. Treatments such as acid leaching and partial oxidation before hydrodesulfurization help to increase the amount and rate of removal of sulfur from the char.

Hydrodesulfurization alone removes significant quantities of both organic and inorganic sulfur from a char and is capable of reducing the sulfur content of a char to near compliance levels (0.7% to 0.9% sulfur). Although acid leaching of char before hydrodesulfurization is probably not economically feasible, our results show that it yields the highest hydrodesulfurization rates and chars with the lowest char sulfur content (0.3% to 0.4% total sulfur). Partial oxidation before hydrodesulfurization has only a small effect on the reduction of total sulfur compared with no pre-hydrodesulfurization treatment. However, partial oxidation before hydrodesulfurization does help to reduce the time needed for hydrodesulfurization.

 H_2S back reactions may occur if iron oxides are present in the chars during hydrodesulfurization (Schrodt et al., 1982). Oxidation after hydrodesulfurization helps to overcome this problem. Two possible approaches are recommended: (1) use a few percent oxygen at lower temperatures after hydrogen treatment to oxidize the iron sulfides to iron oxides, or (2) use a trace of oxygen to form magnetic iron sulfides that can be magnetically separated from the char. Excluding the coal sample containing a high percentage of calcium, bench-scale experiments showed that both approaches of posthydrodesulfurization oxidation produced chars containing 1.2 to 1.4 percent sulfur from coals originally containing 4 to 6 percent sulfur.

These results are encouraging; however, the yield after magnetic separation was very low, probably because of char agglomeration and the crude magnetic separation methods used. Further investigation into magnetic mineral formation and especially separation of the magnetic sulfides is necessary in order to improve the yield of the cleaned char products. Coals with high calcium contents are poor candidates for hydrodesulfurization due to the formation of CaS, which remains in the char.

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APPENDIX

Three different bench-scale quartz tube reactor systems were used in investigating coal pyrolysis and postpyrolysis char desulfurization treatments. First, a stable sulfur isotope monitoring technique was developed to determine the fate of pyritic and organic sulfur in coals and chars during desulfurization treatments. Then, a pH monitoring technique was developed to measure sulfur evolution rates from coals during pyrolysis and chars during oxidative desulfurization. Finally, a quadrupole gas analyzer was used to monitor the evolution of both carbon and sulfur during coal pyrolysis, and oxidation and hydrodesulfurization of chars. Standard X-ray diffraction methods were used throughout the investigation to characterize changes in iron sulfur mineral content and structure during coal pyrolysis and char desulfurization treatments.

APPARATUS

Original Coal Pyrolysis Apparatus

This apparatus was designed so that coal pyrolysis could be carried out under an inert atmosphere and so that sulfur evolved during pyrolysis could be easily recovered for further analysis (fig. A1). The flow of the various gas streams through the apparatus was controlled by flow meters and valves. Volatiles driven off during pyrolysis were completely oxidized to CO₂, H₂O, and SO₂ or SO₃ in the combustion section, which was preheated to 900°C. CO₂ passed through the H₂O₂ traps, while the SO₂ and SO₃ were retained as H₂SO₄. This apparatus was used in almost all of the stable isotope monitoring experiments, in those experiments involving the conversion of pyritic to hexagonal and magnetic pyrrhotite, in development of the pH monitoring technique, and in preparation of char samples for use during desulfurization experiments in other apparatus.

The tube reactor was made from 30-mm-OD quartz tubing with outer \mathfrak{F} (standard taper) 34/45 joints on each end. The end caps were made from inner \mathfrak{F} 34/45 quartz

joints. The thermocouple and O_2 tube were inserted into the reactor through bored-out Cajon 1/4- to 3/8-in. reducing unions. The furnaces were 11/4-in.-ID by 8-in. split tubes with 1/2-in. transite end plates. The platinum (Pt) catalyst was a disk made from fine-mesh Pt screen and was held in place by the O_2 tube. The dual-temperature controller, which was built in-house, had a variable duty cycle (i.e., the percentage of time the charring furnace was heating could be varied to change the heating rate to the desired temperature).

Second Coal Pyrolysis-Char Desulfurization Apparatus

This apparatus was coupled with two systems to monitor the evolution of sulfur during coal pyrolysis and char desulfurization treatments (fig. A2). The first system, a pH monitor, was used to determine the effects of various parameters on total sulfur evolved during coal pyrolysis and char oxidative desulfurization. The pH monitoring system was based on the fact that H₂SO₄ produced in the H₂O₂ trap completely ionizes, thereby decreasing the pH (= $-\log[H^+]$) of the H₂O₂ solution. The second system, a quadrupole gas analyzer (QGA), monitored the evolution of both carbon and sulfur during coal pyrolysis and char oxidative desulfurization. The QGA system was also used to monitor the evolution of H₂S during char hydrodesulfurization experiments in which the H₂S was trapped in cadmium acetate. During hydrodesulfurization experiments, the combustion chamber was heated to about 800°C and continuously flushed with pure N₂.

The main reactor tube was made from 30-mm-OD quartz tubing with an inner \$ 34/45 joint on the inlet end. The end cap consisted of a cut-off \$ brass joint and a brass end plate attached to the joint with machine screws. A neoprene gasket was used between the plate and joint. The thermocouple was inserted into the reactor through a bored-out Cajon ultra-torr male connector. The push-pull rod was inserted into the reactor through a special fitting containing a rubber septum. The fur-



Figure A1 First coal pyrolysis apparatus

naces were 1¹/₄-in.-ID by 8-in. split tubes with ¹/₂-in. transite end plates. In use, the left-hand end plates were removed from the pyrolysis furnace and the right-hand end plates of the combustion furnace were grooved to accommodate the 6-mm-OD gas inlet tube. The Pt catalyst was a disk made from fine-mesh Pt screen and was held in place by a length of quartz tubing inserted into the main quartz tube.

An LFE Corporation model 2011 microprocessorbased temperature controller was used for the pyrolysischar desulfurization chamber. The controller had a RS232 interface by means of which the various control parameters were changed, and the temperature within the chamber was read by an IBM PC. The temperature controller could be programmed to run a ramp and soak routine, e.g., heat to 650°C at 20°C/min, hold the temperature at 650°C for 15 min, cool to and hold the temperature at 450°C for 15 min, and then switch the furnace off.

Chromel/alumel (type K) thermocouple assemblies were made using pieces of 1/e-in.-OD two-hole ceramic insulators and 15- to 20-in. lengths of 6-mm-OD quartz tubing. Silicone sealant was used to create a gas-tight seal between the thermocouple wire, ceramic insulators, and the inside of the quartz tubing.

pH monitoring The pH meter, Fisher Accumet model 825MP, had an RS232 interface through which pH data could be transmitted to the IBM PC computer every few seconds (fig. A3). A BASIC program was written to accept the pH data from the meter, record the temperature within the pyrolysis-char desulfurization chamber from the LFE controller, and record the computer's clock time. The pH electrode used was an Orion #810200 Ross combination electrode. The H_2O_2 trap was a tall 16-oz glass bottle with a cap outfitted with plastic bulk head tube fittings to hold the pH electrode, automatic temperature compensation probe (not shown), and gas dispersion tube (coarse). The trap was connected to the pyrolysis apparatus with a Cajon ultratorr union, and during an experiment the trapping solution was stirred with a magnetic stirring bar.

Quadrupole gas analyzer monitoring The quadrupole gas analyzer (QGA) was a Dycor Electronics Inc. model M200 with a Faraday cup detector (fig. A4). Control commands can be sent to and data received from the M200 control unit by the IBM PC computer, A BASIC program was written that can tell the M200 to scan 12 different masses and transmit the mass data (ion currents) to the PC, ask the LFE temperature controller for the temperature within the pyrolysis-char desulfurization chamber, and record the computer's clock time. The glass capillary tubing (50 µm ID, about 1 m long) was heated during experiments by wrapping a 1/2-in.-wide heating tape around a length of 1/4-in.-OD copper tubing. The vacuum manifold and valve were heated during experiments by a Dycor heating jacket (not shown). The H₂O₂ traps were two gas washing bottles connected in series (fig. A1.) The cadmium acetate traps were made from 500-mL Erlenmeyer flasks, two-hole rubber stoppers, and lengths of 6-mm-OD Pyrex tubing. Gas dispersion tubes could not be used because the H₂S is trapped by the precipitation of CdS,



Figure A2 Second coal pyrolysis-char desulfurization apparatus



Figure A3 pH monitoring system (the quartz tube reactor is shown in fig. A2)

which would plug up the fritted dispersion tubes. Although one cadmium acetate trap was always 100 percent effective, standard practice was to use two traps in series. The tee (fig. A4) was a Cajon ultra-torr union with a length of small-bore ¹/₁₆-in.-OD stainless steel tubing silver-soldered at its midpoint.

Flash Pyrolysis Apparatus

A maximum heating rate of 50° to 60°C/min could be used with the two previously described pyrolysis apparatus. At higher heating rates, the rate at which volatiles are produced is too high for the volatiles to be completely oxidized as they pass through the combustion chamber. Figure A5 is a diagram of the apparatus constructed to carry out pyrolysis experiments with high heating rates. Flow meters and valves controlled the flow of the various gas streams through the apparatus, which was placed in a fume hood. The apparatus was also used in some char hydrodesulfurization experiments that included the use of an H₂/H₂S (0.44%) mixture. In these experiments, the blast burner used to combust the volatiles was replaced with two cadmium acetate traps, and the temperature recorder was connected to the thermocouple within the reactor.

The basic reactor was made from 30-mm-OD quartz tubing with an inner \$ 34/45 joint on the inlet end. The reactor was mounted on a trolley, which permitted rapid insertion of the reactor into the preheated furnace. The reactor end cap was made from an outer \$ 34/45 Pyrex joint. The furnace used was a split-tube laboratory furnace with an ID of 11/4 in. and a heated length of 6 in. The temperature controller was an LFE Corporation microprocessor-based model 2010.

EXPERIMENTAL METHODS AND TECHNIQUES

Coal Sample Selection

Several coal samples were collected from two underground mines in Illinois. The coals were selected on the basis of a previous sulfur isotope study of Illinois coal by Westgate and Anderson (1984). More recently, additional coal samples were collected from other mines. The coal samples were collected by hand at a freshly cut face and sealed in labeled plastic bags. When they were brought to the laboratory, the samples were transferred into air-tight aluminum canisters filled with nitrogen.

Stable Sulfur Isotope Characterization

Standard methods The coal samples were crushed to less than 60 mesh and split for chemical and isotopic analysis. To separate the forms of sulfur (sulfate, pyritic, and organic) from the coal for isotopic analysis, a representative split was pulverized to less than 230 mesh (62.3 μ m). The pulverized coal was then washed in dilute hydrochloric acid (HCI) to remove any sulfates or soluble sulfides, as well as any carbonates present in the sample. The amount of sulfate sulfur and soluble sulfide sulfur collected during this step was minuscule (<0.01%). Thus, no isotopic data are reported for sulfate sulfur or soluble sulfide sulfur.



Figure A4 Quadrupole gas analyzer monitoring system



Figure A5 Flash pyrolysis apparatus

Pyritic sulfur was quantitatively extracted from the acid-washed coal by the reductive lithium aluminum hydride (LAH) method (Kuhn, Kohlenberger, and Shimp, 1973; Price, 1977; Westgate and Anderson, 1982). The sulfide released from the pyrite was trapped in cadmium acetate solution as cadmium sulfide (CdS) and converted to Ag₂S for measurement. The organic sulfur was obtained by combusting the LAH-extracted coal under pure oxygen at 1350°C (modified ASTM D1377-82, Frost, Auteri, and Ruch, 1984). The organic sulfur, oxidized to SO₂, was trapped in a hydrogen peroxide (H₂O₂) solution and precipitated as barium sulfate (BaSO₄) for measurement.

After the different species of sulfur were separated and in the form of Ag_2S or $BaSO_4$, they were converted to SO_2 for analysis on the mass spectrometer. The Ag_2S was converted to SO_2 by combustion with cupric oxide (CuO) at 950°C as described by Fritz, Drimmie, and Norwicki (1974). The $BaSO_4$ was converted to SO_2 by reacting $BaSO_4$ with sodium metaphosphate (NaPO₃) at 950°C as described by Halas, Shakur, and Krouse (1982). The SO_2 released during each reaction was trapped and purified on a high vacuum line. The isotopic composition of each form of sulfur was determined on a Nuclide RMS Isotope Ratio 6-60 mass spectrometer. Isotopic ratios are expressed in delta notation as the per mil difference between the ${}^{34}S/^{32}S$ ratio of a sample and the ${}^{34}S/^{32}S$ ratio of a standard:

$$\delta^{34}S = \frac{{}^{34}S/{}^{32}S_{(smpl)} - {}^{34}S/{}^{32}S_{(std)}}{{}^{34}S/{}^{32}S_{(std)}} \times 1000$$

All delta values are reported relative to the international sulfur standard, Canyon Diablo Troilite (CDT). The precision of the isotopic determinations is ± 0.20 per mil.

After a coal sample was found with a sufficiently large difference between the isotopic composition of the organic and pyritic sulfur (about 10 + ∞), further isotopic characterization of the forms of pyritic sulfur (massive and disseminated) was completed. The massive pyrite was separated by density using an agitated water medium. After physical separation, massive and disseminated pyritic sulfur were extracted, using the LAH method, and analyzed isotopically. Samples with similar δ^{34} S values for the massive and disseminated pyritic sulfur were the subscription of the study.

Quick method Determining the isotopic composition of the pyritic and organic sulfur in coal samples is tedious and time consuming, so we developed a quick method to screen coal samples. This method resulted from some experiments carried out during the first half of the project that showed that pyrolysis at 450°C yields only organic sulfur and that partial oxidation at 450°C immediately after pyrolysis releases sulfur enriched in pyritic sulfur. The two sulfur fractions are recovered by BaSO₄ precipitation and analyzed isotopically as described above. The isotopic difference between the pyrolysis and oxidation-derived sulfur can be used to calculate the minimum isotopic difference between the pyritic and organic sulfur in the coal sample. If the isotopic difference was at least 6 per mil, then the coal sample was characterized in more detail using the chemical methods described earlier.

Coal Pyrolysis and Char Oxidation Procedures

A sample of dried coal (0.5 to 1.0 g) was spread evenly, 1 to 2 mm thick, in a ceramic or guartz boat, which was placed in the center of the pyrolysis chamber of the reactor. The entire reactor was flushed with nitrogen for 10 min at a rate of 250 mL/min. Oxygen was then introduced at a rate of 350 mL/min into the combustion section of the reactor, which had been preheated to 900°C. The H₂O₂ traps filled with 3 percent H₂O₂ solution were attached to the reactor. The coal sample was heated to the maximum pyrolysis temperature at approximately 30°C/min. Pyrolysis was usually carried out at the maximum temperature for 30 min. The gas pressure within the reactor was about 1 psi above atmosphere because of the back pressure created by the gas dispersion tubes in the H2O2 traps. If the experiment included post-pyrolysis oxidation of the char, then the sample was cooled to the desired temperature, and oxygen was admitted into the nitrogen stream to produce the desired oxygen concentration. A second set of H₂O₂ traps was used during post-pyrolysis exidation.

After an experiment was completed, the sulfur trapped in the H_2O_2 solutions was precipitated as $BaSO_4$, filtered, weighed, and stored for isotopic analysis. The sulfur remaining in the char was collected for isotopic analysis using the modified ASTM D1377 high-temperature combustion method mentioned earlier.

Calculation of sulfur composition in products The relative proportions of organic and pyritic sulfur in the volatiles and in the char were calculated from the isotopic values of the volatilized sulfur and the char sulfur. The calculations for the proportions of pyritic and organic sulfur in the products were based on a straightline mixing relationship in which the end members were the isotopic compositions of the pyritic sulfur and the pure organic sulfur (fig. A6). For example, for the isotopic compositions of the pyritic and organic sulfur for coal sample R-B-3, a mixture of sulfur with an isotopic composition of +10 per mil consisted of 54 percent organic sulfur and 46 percent pyritic sulfur.

Conversion of coal pyrite to magnetic pyrrhotite The initial experiments at 550°C indicated that only a trace of oxygen was needed to produce magnetic pyrrhotite. To facilitate the task of determining the actual concentration of oxygen necessary for magnetic conversion, we used two cylinders containing 0.1 and 1.0 percent oxygen in nitrogen.

A sample of dried coal (0.5 to 1.0 g) was spread evenly, 1 to 2 mm thick, in a quartz boat, that was placed in the center of the pyrolysis chamber of the reactor. The entire reactor was flushed with the 0.1 percent O_2/N_2 gas mixture for 10 min at a rate of 250 mL/min. Oxygen was then introduced at a rate of 350 mL/min into the combustion section of the reactor, which had been preheated to 900°C. The H_2O_2 traps filled with 3 percent H_2O_2 solution were attached to the reactor. The coal sample was heated to the maximum pyrolysis temperature at approximately 30°C/min. Pyrolysis was carried out at the maximum temperature for 18 to 30 minutes.



Figure A6 Isotopic mixing relationship of pyritic and organic sulfur in coal sample R-B-3

After an experiment was completed, the sulfur trapped in the H_2O_2 solutions was precipitated as $BaSO_4$, filtered, and weighed to determine the amount of sulfur evolved. The char samples were analyzed by X-ray diffraction. The char sample from a single experiment was not large enough to carry out a magnetic separation. Therefore, several char samples were prepared under identical conditions and combined into a composite sample. This sample was separated with a hand magnet into nonmagnetic and magnetic fractions. The two fractions were submitted for X-ray diffraction analysis and their sulfur contents determined by the high-temperature combustion method.

Magnetic susceptibility measurements were made on chars prepared under different pyrolysis conditions by a Squid magnetic susceptibility magnetometer located at the Physics Department, University of Illinois. Preliminary runs were carried out on chars prepared at temperatures ranging from 425° to 600°C (with a temperature interval of 25°C between each charring). Approximately 0.1 g of char sample was first weighed and then loaded and capped in a small plastic capsule. The capsule was then attached and lowered into the magnetometer using a measured length of string threaded through the upper portion of the capsule. All of the magnetic susceptibility measurements were conducted at room temperature with a magnetic field strength of 2000 gauss.

Coal pyrolysis with high heating rates The furnace was preheated to the described maximum pyrolysis temperature. A sample of dried coal (about 0.7 g) was spread evenly in a quartz boat that was placed in the reactor about 3 in, from the end. The reactor was flushed with nitrogen for 5 min at a rate of 25 mL/min. The blast burner was ignited. The reactor was rolled into the furnace so that the reactor exit tube extended into the chimney on top of the blast burner (fig. A5). The temperature within the reactor was monitored with a microprocessor-based temperature recorder. Heating rates of greater than 200°C/min were measured. After the sample had been at the maximum pyrolysis temperature for the desired soak time, the reactor was withdrawn from the furnace and cooled to room temperature. The char sample was weighed to determine char vield, analyzed by X-ray diffraction, and then combusted to determine its sulfur content.

pH Monitoring of Sulfur

pH monitoring was used to follow the evolution of sulfur during coal pyrolysis and char oxidative desulfurization. Some of the sulfur evolved was lost to absorption on the walls of the apparatus because the entire length of the gas stream could not be heated to prevent condensation of SO₂ and SO₃ before it entered the H₂O₂ trapping solution. The single H₂O₂ trap used was not 100 percent efficient in removing SO₂ and SO₃ from the gas stream. Also, the response time of the pH electrode was found to be slower than the maximum rate of sulfur evolution during coal pyrolysis. For the above reasons, the pH monitoring technique produced only qualitative or semiquantitative results.

Procedure A sample of dried coal (about 0.7 g) was spread evenly in a quartz boat that was placed in the center of the pyrolysis chamber of the reactor. The entire reactor was flushed with nitrogen for 10 min at a rate of 250 mL/min. Oxygen was then introduced at a rate of 200 mL/min into the combustion section of the reactor, which had been preheated to 900°C. The special H₂O₂ trap was connected to the reactor and filled with 350 mL of 3 percent H₂O₂ solution, which had been acidified to about pH 3.5 to reduce CO₂ absorption and which contained NaCl (2.0 g/L) to increase its ionic strength. The pH meter and electrodes were calibrated using 10⁻², 10⁻³, and 10⁻⁴ N H₂SO₄ solutions prepared from Acculute 0.1 N H₂SO₄ standard volumetric solution. The calibration solutions also contained 3 percent H₂O₂ and 2.0 g NaCl/L. After calibration, the pH electrode was inserted into the H₂O₂ trap. The temperature controller was programmed via a BASIC program on the IBM PC with the desired ramp (heating rate) and soak (time spent at maximum pyrolysis temperature) routine. The pH meter was set to transmit pH data to the IBM PC every few seconds, and the ramp and soak routine was started. If the experiment had a post-pyrolysis oxidation of the char, a cooling ramp and a second soak time and temperature were included in the programming of the temperature controller. After the char oxidation temperature was reached, dry air was blended into the nitrogen stream to produce the desired oxygen concentration. After an experiment was over, the char sample was cooled to room temperature and weighed to determine char yield. The amount of sulfur in the H_2O_2 trap was determined by $BaSO_4$ precipitation. Char samples were analyzed by X-ray diffraction and combusted to determine their sulfur contents.

Processing of data The cumulative amount of sulfur evolved at any given time *t* during an experiment is given by the following equation:

$$\frac{\text{sulfur (g)}}{100 \text{ g coal}} = 1.603 \times (\text{H}_{\text{f}} - \text{H}_{\text{o}}) \times \frac{\text{V}}{\text{SW}}$$
where $\text{H}_{\text{f}} = 10^{-\text{pH}_{\text{f}}}$
 $\text{H}_{\text{o}} = 10^{-\text{pH}_{\text{f}=0}}$
 $\text{V} = \text{volume of H}_2O_2 \text{ solution (mL)}$
 $\text{SW} = \text{ sample weight (g)}$

A BASIC program was written for the IBM PC to process the pH, temperature, and time data acquired during an experiment. Also, the program calculated smoothed cumulative sulfur evolved versus time and smoothed rate (first derivative of cumulative curve) versus time curves by the simplified least-squares procedures described by Savitzky and Golay (1964).

QGA Monitoring of Carbon and Sulfur

The QGA was used quite successfully to monitor the evolution of carbon and sulfur during coal pyrolysis and various char desulfurization treatments. The basic problems of the pH monitoring technique were avoided with the QGA. However, a new problem arose that was not solved before experiments for this report were completed. A small amount of H_2SO_4 formed in the combustion section of the quartz tube reactor. After a while, the H_2SO_4 plugged the 50-µm-ID capillary tubing, necessitating its replacement. Worse yet, a pool of H_2SO_4 apparently formed inside the QGA system and absorbed a significant fraction of the SO₂ or H_2S pumped into the system during an experiment.

Procedure The turbomolecular pumping system was turned on with the capillary tubing valve closed. The vacuum manifold was heated to about 130°C. The analyzer head was cooled by an air stream while the vacuum manifold was being heated. Pumping was continued for several hours before an experiment. The turbomolecular pumping system was left on between experiments unless several days lapsed between them.

A sample of dried coal or char (0.5 to 0.75 g) was spread evenly in a quartz boat that was placed in the center of the pyrolysis chamber of the reactor. The entire reactor was flushed with nitrogen for 10 min at a rate of 250 mL/min. In experiments involving pyrolysis and/ or oxidative desulfurization, oxygen was then introduced at 200 mL/min into the combustion section of the reactor, which had been preheated to 900°C. In oxidative desulfurization experiments, the gas fed into the flow meter feeding the pyrolysis chamber was simply switched from nitrogen to a cylinder of 5 percent oxygen-95 percent nitrogen mixture. When hydrodesulfurization was carried out after pyrolysis and/or oxidative desulfurization, the combustion section of the reactor was cooled to about 800°C and the oxygen was replaced with nitrogen at 50 mL/min. Also, after the hydrodesulfurization temperature was reached, pure hydrogen was introduced into the pyrolysis chamber at 200 mL/min. Other gas mixtures containing hydrogen could also be used in hydrodesulfurization experiments. For pyrolysis or oxidative desulfurization experiments, the gas washing bottles filled with 3 percent H₂O₂ solution were connected to the reactor. When oxidative desulfurization followed pyrolysis, a second set of gas washing bottles was used during the oxidative desulfurization. For hydrodesulfurization experiments, the cadmium acetate traps containing 300 mL of cadmium acetate solution were attached to the reactor at the beginning of the experiment or after the combustion chamber was flushed with nitrogen if prior desulfurization treatments were carried out.

After a set of traps was connected to the reactor, the capillary valve was opened. The capillary tubing heater had been turned on a few minutes earlier. The temperature controller was programmed via a BASIC program on the IBM PC with the desired ramp and soak routine. The BASIC program was also used to instruct the QGA to scan 12 different masses every 6 sec and report the results to the PC. After data collection began (12 ion currents, pyrolysis chamber temperature and time), the ramp and soak routine was started. After an experiment was completed, the char sample was cooled to room temperature under nitrogen and weighed to determine char yield. The amount of sulfur in a set of H₂O₂ traps was determined by BaSO₄ precipitation. The amount of sulfur in the first cadmium acetate trap was determined by conversion of the CdS to Ag₂S. The char sample was submitted for X-ray diffraction analysis after which it was combusted to determine its sulfur content.

Processing of data The QGA was in effect an ion gauge that measured partial pressures (as ion currents) of the gases present within the vacuum manifold; we assumed that these partial pressures were equal to those present in the gas stream exiting the reactor. The relationship between the current and partial pressure is usually represented by the following equation:

$$C_n = I_n^+ / S_n$$

where $C_n = \text{partial pressure of component } n$

 I_n^+ = ion current measured for component *n*

 $S_n = QGA sensitivity for component n$

If S_n is known, as well as the total pressure and flow rate of the gas stream exiting the reactor, then the hydrodesulfurization rate at the time of the mass scan could be calculated by the following equation:

rate (mg S/g char/min) =
$$\frac{C_{H_2S}}{TP} \times \frac{FR}{SW} \times FACT$$

where C_{H_2S} = partial pressure of H_2S

TP = total pressure exerted by gas stream

FR = flow rate (mL/min)

SW = sample weight (g)

FACT = factor to convert $H_2S(mL)$ to sulfur (mg)

If $l_{H_2S}^+$ or $l_{SO_2}^+$ is measured as a function of time, a rate versus time curve can be calculated. Integration of the rate curve then yields a cumulative sulfur evolved versus time curve.

In practice, S_n values are not easy to obtain and are subject to change as the filaments of the QGA age. Therefore, a method was developed to convert sulfur ion current versus time curves into actual sulfur rate versus time curves. Since only a small fraction of the sulfur evolved in an experiment was pumped into the QGA system, we assumed that the amount of sulfur trapped in the H₂O₂ or cadmium acetate traps equaled the total amount of sulfur evolved (S_T). The area (A_t) up to time t and total area (A_T) under the ion current curve was obtained by graphic integration. The amount of sulfur (S_t) evolved to time t is given by

$$S_t = \frac{A_t}{A_T} \times S_T$$

Thus, the cumulative sulfur evolved versus time curve could be generated. The cumulative sulfur curve was smoothed and differentiated to produce smoothed rate versus time curves by the simplified least-squares procedures described by Savitzky and Golay (1964). The calculations described were carried out using a BASIC program written for the IBM PC.

Char Hydrodesulfurization Procedures

A sample of dried char (0.5 to 1.0 g) was spread evenly in a quartz boat that was placed in the reactor at the center of the heated zone. The reactor was rolled into a cold furnace and flushed with nitrogen for 5 min at a rate of 250 mL/min. The cadmium acetate traps were attached to the reactor. The char sample was heated at about 30°C/min in the nitrogen stream to the hydrodesulfurization temperature. Then the gas stream was switched from nitrogen to hydrogen or the H₂ with 0.44 percent H₂S mixture for the desired length of time, after which the reactor was again flushed with nitrogen. The char sample was cooled to room temperature and weighed to determine char yield. When pure hydrogen was used, the amount of the sulfur in the first cadmium acetate trap was determined by conversion of the CdS to Ag₂S. The char sample was submitted for X-ray diffraction analysis, then combusted to determine its sulfur content. If the char had been produced from a coal suitable for stable sulfur isotope monitoring, then the Ag₂S and the combusted sulfur was isotopically characterized. When the H₂/H₂S mixture was used, the cadmium acetate solution and the CdS were simply discarded. The char sample was either analyzed by X-ray diffraction after hydrodesulfurization and then combusted to determine its sulfur content or it was subjected to oxidative desulfurization with QGA monitoring at 450°C and then analyzed by X-ray diffraction and its sulfur content determined. Several chars that were hydrodesulfurized with the H₂/H₂S mixture were cooled to room temperature by an N₂/0.1 percent O₂ mixture to test the conversion of the nonmagnetic iron sulfide present in the sample after the hydrodesulfurization to a magnetic iron sulfide. The chars were separated by a hand magnet into two fractions, which were then subjected to standard total sulfur analyses.