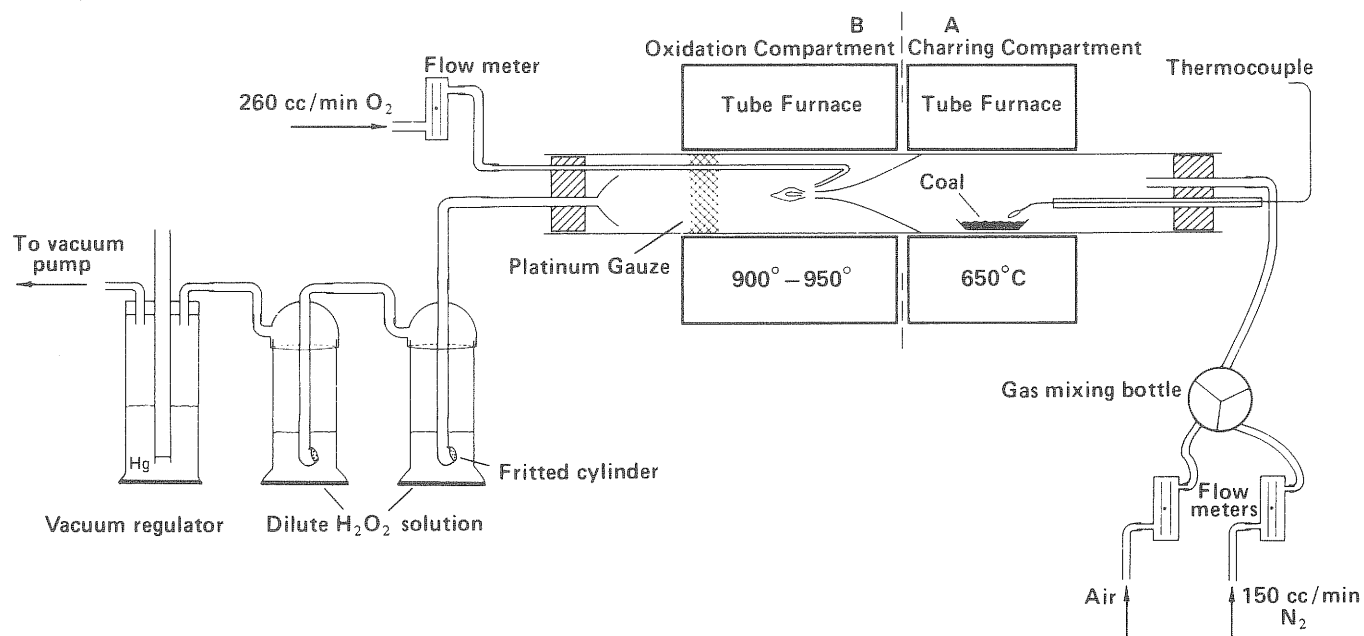


# Removal of sulfur from Illinois coals via charring and partial oxidation



R. R. Ruch • C. Chaven • C. W. Kruse

Illinois Department of Energy and Natural Resources  
STATE GEOLOGICAL SURVEY DIVISION

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## Abstract

*Illinois coals with different ash and sulfur compositions were charred and partially oxidized under various conditions of time and temperature (up to 900°C). A specially designed charring-combustion apparatus was utilized. The following parameters affected sulfur removal during both charring and partial oxidation: the ratio of pyrite to organic sulfur, rates of increase and holding times of temperatures, final temperatures, and particle sizes. The main conclusions are (1) regardless of conditions, the total range of sulfur removal is fairly narrow and pyritic sulfur is definitely lost in the charring step; (2) the parameters that maintain optimum charring and post-oxidation conditions are numerous, interrelated, and complex; and (3) in post-charring, partial-oxidation experiments, maximum loss of sulfur and minimum loss of carbon occurred when the temperature was initially dropped to about 240°C rather than maintained at 650°C, and pyrite-rich coals were more readily desulfurized with less loss of carbon than organic-sulfur-rich coals.*

## Background

Kruse and Shimp (1981) reported on a coal desulfurization method in which thin (2 to 3 mm) beds of Illinois coals were pyrolyzed at 600° to 700°C in a continuous-feed oven having counter-flow removal of volatile matter; the chars were leached with hydrochloric acid, then hydrogenated. The results indicated that more than 90 percent of the sulfur in the coal can be removed while the char retains about the same heat content per pound as the original coal. Kruse and Shimp (1981) studied coals in which the ratio of organic to pyritic sulfur ranged from 1.86 to 0.82. Analyses of the resulting chars indicated a stoichiometry approaching  $\text{FeS}_2$  regardless of the ratio of organic to pyritic sulfur in the original coal. They concluded that the retention of sulfur in the char is possibly related to the concentration of pyrite in the original coal.

A review of the literature on coking and desulfurization of coals via charring and oxidation (Appendix) provided the following generalizations:

- In coking or charring processes, pyrite decomposes to  $\text{FeS}$  with the release of sulfur. Sulfate is also reduced. Organic sulfur in the original coal is evolved over a range of temperatures. These reactions generally occur below 600°C, and most of the sulfur loss is accomplished by 700°C.
- The sulfur retained during coking or charring generally reflects the amounts of both the pyritic and organic sulfur in the feed coal and is dependent upon the volatile matter content.
- Desulfurization of char via oxidation is improved by small particle size, large pore size, high surface area, and generally lower temperature (300° to 400°C).

The present research was designed to clarify the processes occurring in counter-flow, low-temperature (CFLT) charring and also to explore thermal and oxidative treatment of the resulting char for further desulfurization. Specifically, the tasks include

- a study of several experimental variables of pyrolysis to determine conditions for maximum sulfur removal in the 650°C range.
- partial oxidation of the resulting chars by using limited amounts of air under different experimental conditions to maximize sulfur removal and minimize oxidation of carbon (it is desirable to evaluate this method as an alternative to chemical leaching and hydrosulfurization).
- a tracer study that employs a radioactive pyrite "spike" of coal and follows the loss of various forms of sulfur (pyritic and organic) upon charring. This work is described in a separate report (Frost et al., 1984).

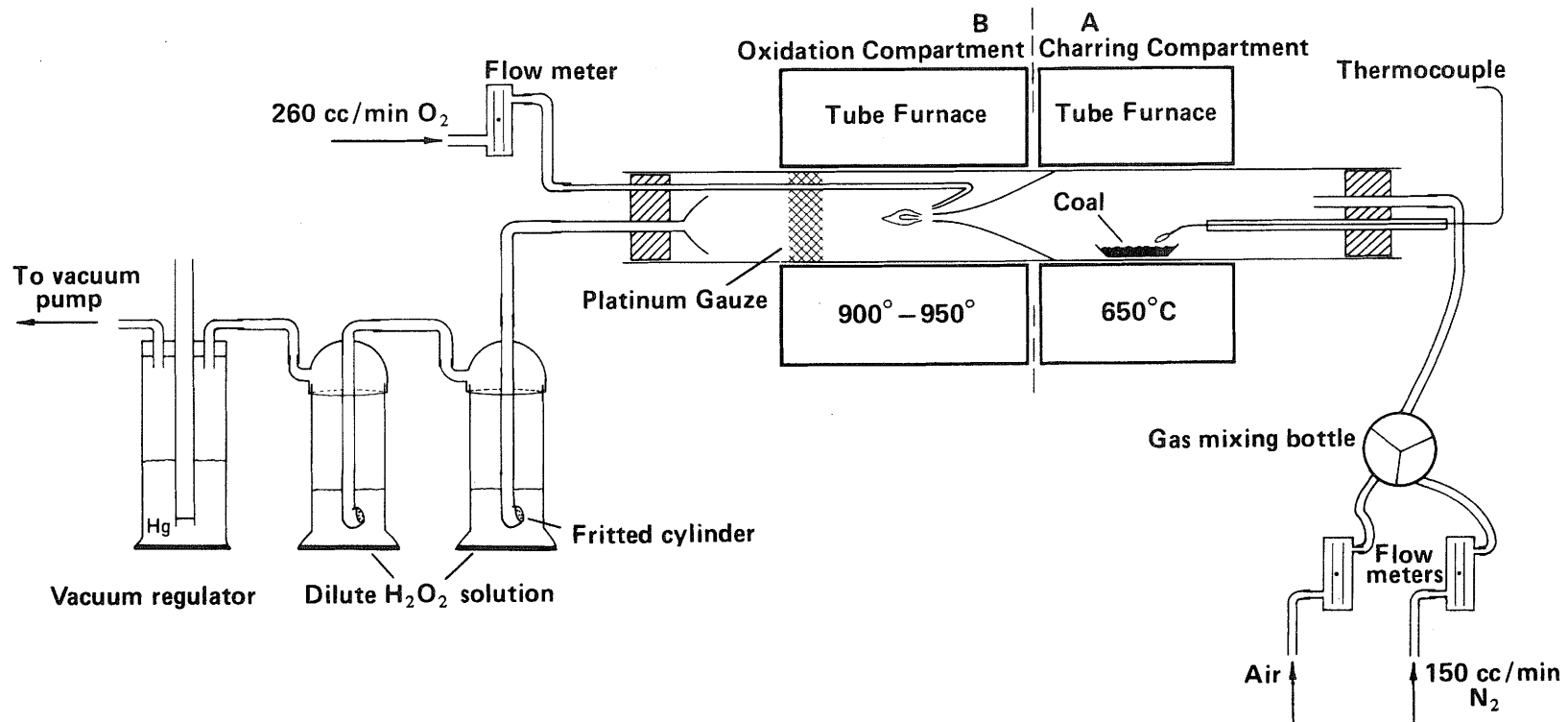


Figure 1 Schematic diagram of charring apparatus

**Table 1.** Coal Analysis (Air-Dried Basis)

%	C21054	C20586	C20620	C20712	C21164	C21169	C21625	C22151	C22173
Moisture	2.5	3.7	8.66	2.6	4.9	3.1	2.2	5.1	9.3
Volatile matter	34.8	39.1	33.7	36.6	34.9	34.9	40.5	39.9	36.5
Fixed carbon	48.0	45.8	—	52.6	46.2	41.6	46.3	54.9	44.4
Ash	14.7	11.4	—	8.2	14.0	20.4	11.0	10.1	9.8
Carbon	67.71	66.70	62.52	72.15	62.82	57.28	67.20	67.39	63.05
Hydrogen	5.13	—	—	5.22	5.04	4.47	4.95	4.81	5.47
Nitrogen	1.37	—	—	1.52	1.09	.99	1.16	1.24	1.10
Oxygen	10.3	—	—	10.47	13.31	8.66	11.28	12.35	16.46
Sulfur	.83	3.29	2.85	2.46	3.71	8.16	11.28	12.35	4.11
Pyritic sulfur	.28	1.67	1.32	.85	2.42	6.50	1.41	1.07	1.83
Organic sulfur	.54	1.60	1.43	1.52	.91	.79	2.99	2.86	1.97
Sulfatic sulfur	.005	.02	.01	.09	.38	.87	.02	.22	.31
Pyritic S/Organic S	.52	1.04	.92	.56	2.66	8.23	.47	.37	.93
C/S	81.6	20.3	21.9	29.3	16.9	7.0	15.2	16.2	15.3

## Experimental

**Apparatus.** To subject small (approximately 1 g) amounts of coal to various conditions of charring and partial air oxidation, a special tube-furnace system was constructed (fig. 1). The quartz tube has two compartments. In compartment A, the atmosphere is nitrogen or nitrogen mixed with a low concentration of oxidant, such as oxygen; a gas-mixing bottle is connected to the nitrogen inlet so that a blend of gases can be metered in and directed over the coal. During charring, nitrogen passes over the coal at the rate of about 150 cc per minute. Compartment A can be heated by a tube furnace, which takes the temperature up to 650°C or higher. A separate tube furnace heats the oxidation compartment B up to approximately 950°C while oxygen is metered in at about 260 cc per minute. Platinum gauze is used to catalyze oxidation.

During the run, suction was applied beyond the second absorption solution to ensure quantitative transfer of volatile material and to prevent pressure buildup. The vacuum drawn was adjusted to a constant value before heating of the coal began. This was accomplished by adjusting the flow meter on the air inlet to the gas-mixing bottle so as to permit about 100 mL of air to flow through the system together with the nitrogen and oxygen. The air flow was then shut off and 5 minutes allowed for purging all air from the charring oven.

**Characterization of Feed Coals.** Table 1 lists the chemical data on the coals studied. All coals are from Nos. 5 and 6 Coal seams in the Illinois Basin. Forms of sulfur, total sulfur, and proximate and ultimate analyses were determined using current ASTM methods.

**Procedure.** The stages of charring and of partial oxidation are presented schematically in figure 2. Approximately 1 gram of coal was placed in a high-temperature ceramic boat and charred in the apparatus shown in figure 1. The first stage of pyrolysis involved heating the coal to approximately 360°C (under nitrogen), then holding the temperature constant for about 5 minutes; this became the initial temperature for all runs. The coal was then heated to  $T_1$ , a temperature ranging from 450° to 900°C, and held for different periods of time (B). If the experiment involved pyrolysis only, the temperature was allowed to fall below approximately 100°C (under nitrogen) before the char was removed. It was stored in a desiccator until it was analyzed.

If post-pyrolysis partial oxidation was desired for the same sample, metered quantities of dried air were mixed with the incoming nitrogen immediately following pyrolysis. The temperature was allowed to drop to  $T_2$  and held there, or immediately raised to  $T_3$  and held. The actual times taken to complete steps A to F for individual runs are given in table 2.

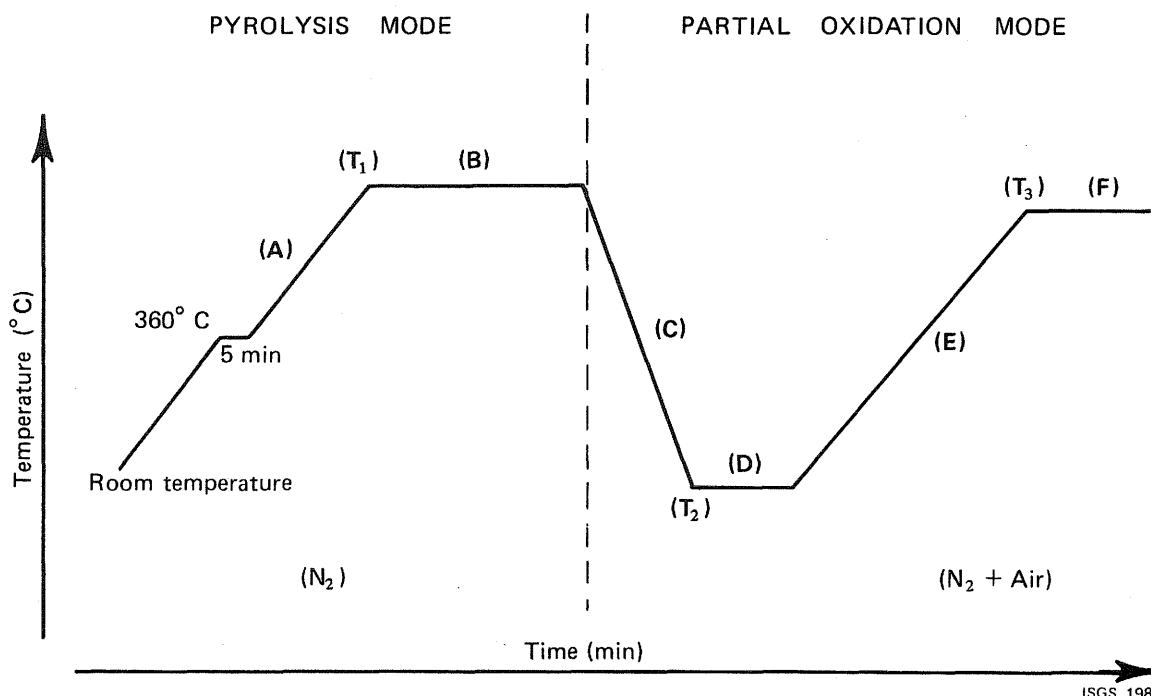


Figure 2 Schematic diagram of pyrolysis and partial oxidation modes

ISGS 1984

As noted in figure 2, the times and temperatures are varied. The evolved sulfur dioxide gas was quantitatively trapped in  $\text{H}_2\text{O}_2$  solution and the sulfur was analyzed as barium sulfate. The char was separately analyzed for sulfur.

**Chemical Analyses.** Results of chemical analyses are presented in table 2. Carbon, hydrogen, and nitrogen analyses on the feed coals and chars were performed on a Carlo Erba Elemental Analyzer. Sulfur contents of feed coals and product chars were determined by the ASTM method. Sulfur content of the evolved gas was analyzed by precipitating barium sulfate from the sulfuric acid formed in the hydrogen peroxide traps (ASTM, 1981). Mass-balance of sulfur, based on results of analyses for sulfur in the gases evolved and in the char compared to the amount in the original coal, was quantitative. For 12 runs on 6 different coals the total sulfur value for the products amounted to  $103.2 \pm 5.3$  percent of the known values obtained by ASTM methods (1981) on the feed coals.

Data on the charring and partial oxidation runs given in table 2 include conditions of time and temperature, percentages of sulfur loss and char yield, percentages of S-, C-, H-, N in the chars, percentage of sulfur in the trapped gas, and C/S ratios in the char. The desulfurization efficiency factor (DEF) is defined as

$$\text{DEF} = \frac{(\text{C/S})_{\text{char}}}{(\text{C/S})_{\text{coal}}} \times \text{char yield}$$

The DEF for each char produced is also listed in table 2. The experimental runs are identified by "run" number in the following discussion and figures.

Some of the data are plotted in figures 3 to 8 as sulfur loss (coal basis) relative to weight loss for a given experimental variable, such as final temperature or rate of temperature rise. Vertical lines on the weight-loss axis represent the maximum ASTM moisture loss (ML) value and the maximum combined moisture-and-volatile-matter loss (CMVML) value (ASTM procedure at  $950^\circ\text{C}$ ). A point corresponding to complete "organic sulfur" loss on the CMVML lines is plotted. A line is drawn from this point to the point at which the moisture-loss line intersects the horizontal axis (0% sulfur loss). The significance of these lines will be discussed later.



**Table 2. Charring and Partial Oxidation Data\***

	Run Number and Coal				
	39 C-21164	40 C-21164	43 C-21164	45 C-21164	48 C-21164
<b>Charring Mode</b>					
Time 360° to T <sub>1</sub> ° (A)	17	20	30	0	30
T <sub>1</sub> °	900°	560°	650°	360°	650°
Time at T <sub>1</sub> ° (B)	15	30	30	30	30
Special conditions other than 150 cc N <sub>2</sub> /minute					
<b>Partial Oxidation Mode</b>					
Time from T <sub>1</sub> ° to T <sub>2</sub> ° (C)					
T <sub>2</sub> °					
Time at T <sub>2</sub> ° (D)					
Time from T <sub>2</sub> ° to T <sub>3</sub> ° (E)					
T <sub>3</sub> °					
Special conditions other than 30 cc air /minute					
<b>Char</b>					
S	3.01	2.85	2.61	4.02	2.83
C	70.64	—	69.40	65.18	69.69
Yield	65.2	76.1	73.4	91.6	70.8
H	0.46	—	1.67	3.87	1.65
N	1.29	—	1.50	1.29	1.36
C/S ratio	23.5	—	26.6	16.2	24.6
% S loss (WC basis)	54.3	42.4	50.9	13.6	50.3
DEF**	.91	—	1.15	.88	1.03
<b>Gas</b>					
S (WC basis)	2.33	1.60	1.99		2.03

\* All times in minutes, temperatures in °C, and concentration in % unless otherwise noted.  
Absence of data for "Partial Oxidation Mode" indicates only "charring mode" conditions were executed in run.

$$**DEF = \frac{(C/S) \text{ char}}{(C/S) \text{ coal}} \times \text{char yield}$$

**Table 2.** Charring and Partial Oxidation Data\* Continued

	Run Number and Coal				
	53 C-21164	60 C-21164	61 C-21164	62 C-21164	63 C-21164
<b>Charring Mode</b>					
Time 360° to T <sub>1</sub> ° (A)	50	30	30	30	19
T <sub>1</sub> °	650°	650°	650°	650°	650°
Time at T <sub>1</sub> ° (B)	5	30	5	0	30
Special conditions other than 150 cc N <sub>2</sub> /minute					
<b>Partial Oxidation Mode</b>					
Time from T <sub>1</sub> ° to T <sub>2</sub> ° (C)		5	5	0	6
T <sub>2</sub> °		250°	250°	650°	225°
Time at T <sub>2</sub> ° (D)		0	0	25	0
Time from T <sub>2</sub> ° to T <sub>3</sub> ° (E)		26	28		35
T <sub>3</sub> °		650°	650°		650°
Special conditions other than 30 cc air/minute					
<b>Char</b>					
S	3.09	1.32	1.21	2.09	1.21
C	70.12	68.43	65.92	68.20	66.77
Yield	68.5	66.8	61.8	64.4	60.7
H	1.98	1.76	1.72	1.58	1.55
N	1.51	1.53	1.51	1.49	1.57
C/S ratio	22.7	51.8	54.5	32.6	55.2
% S loss (WC basis)	42.7	79.2	81.9	67.3	83.1
DEF**	.92	2.24	1.99	1.24	1.98
<b>Gas</b>					
S (WC basis)	1.58	3.36	3.39	2.76	3.58

\* All times in minutes, temperatures in °C, and concentration in % unless otherwise noted.  
Absence of data for "Partial Oxidation Mode" indicates only "charring mode" conditions were executed in run.

$$**DEF = \frac{(C/S) \text{ char}}{(C/S) \text{ coal}} \times \text{char yield}$$

**Table 2.** Charring and Partial Oxidation Data\* Continued

	Run Number and Coal				
	64 C-20586	65 C-21625	66 C-21164	67 C-21164	68 C-21164
<b>Charring Mode</b>					
Time 360° to T <sub>1</sub> ° (A)	18	20	20	19	17
T <sub>1</sub> °	650°	650°	650°	650°	650°
Time at T <sub>1</sub> ° (B)	30	30	30	30	30
Special conditions other than 150 cc N <sub>2</sub> /minute					
<b>Partial Oxidation Mode</b>					
Time from T <sub>1</sub> ° to T <sub>2</sub> ° (C)	6	6	7	2	3
T <sub>2</sub> °	225°	250°	130°	360°	380°
Time at T <sub>2</sub> ° (D)	0	0	0	0	0
Time from T <sub>2</sub> ° to T <sub>3</sub> ° (E)	28	33	30	16	26
T <sub>3</sub> °	650°	650°	650°	650°	650°
Special conditions other than 30 cc air/minute					
<b>Char</b>					
S	1.50	1.90	1.33	1.47	1.42
C	69.41	66.69	67.46	68.52	68.38
Yield	60.8	52.9	62.7	67.0	60.5
H	1.76	1.64	1.62	1.59	1.54
N	1.43	1.46	1.57	1.48	1.54
C/S ratio	46.3	35.1	50.7	46.6	48.2
% S loss (WC basis)	74.9	76.4	78.8	75.9	76.0
DEF**	1.39	1.22	1.87	1.84	1.72
<b>Gas</b>					
S (WC basis)	2.71	3.30	3.09	3.09	2.73

\* All times in minutes, temperatures in °C, and concentration in % unless otherwise noted.  
Absence of data for "Partial Oxidation Mode" indicates only "charring mode" conditions were executed in run.

$$**DEF = \frac{(C/S) \text{ char}}{(C/S) \text{ coal}} \times \text{char yield}$$

**Table 2.** Charring and Partial Oxidation Data\* Continued

	Run Number and Coal				
	69 C-21164	70 C-21164	71 C-21164	74 C-21625	78 C-21625
<b>Charring Mode</b>					
Time 360° to T <sub>1</sub> ° (A)	18	19	9	30	30
T <sub>1</sub> °	650°	650°	650°	650°	650°
Time at T <sub>1</sub> ° (B)	30	30	30	30	30
Special conditions other than 150 cc N <sub>2</sub> /minute					
<b>Partial Oxidation Mode</b>					
Time from T <sub>1</sub> ° to T <sub>2</sub> ° (C)	0	10	6		
T <sub>2</sub> °	650°	110°	225°		
Time at T <sub>2</sub> ° (D)	25	15	0		
Time from T <sub>2</sub> ° to T <sub>3</sub> ° (E)		29	31		
T <sub>3</sub> °		650°	650°		
Special conditions other than 30 cc air/minute		-1-			
<b>Char</b>					
S	2.00	1.34	1.28	3.01	3.86
C	67.48	65.26	64.89	74.80	74.74
Yield	65.3	64.8	62.6	70.4	72.8
H	1.54	1.54	1.50	1.75	1.56
N	1.48	1.49	1.52	1.24	1.27
C/S ratio	33.7	48.7	50.7	24.8	19.4
% S loss (WC basis)	68.9	79.6	80.7	45.3	31.8
DEF**	1.30	1.87	1.87	1.15	.93
<b>Gas</b>					
S (WC basis)	2.90	3.39	3.35	1.84	1.31

\* All times in minutes, temperatures in °C, and concentration in % unless otherwise noted.  
Absence of data for "Partial Oxidation Mode" indicates only "charring mode" conditions were executed in run.

$$**DEF = \frac{(C/S) \text{ char}}{(C/S) \text{ coal}} \times \text{char yield}$$

-1- Run 70; 100% air at 110°C for 15 minutes

**Table 2. Charring and Partial Oxidation Data\* Continued**

	Run Number and Coal				
	81 C-21164	82 C-21164	84 C-21164	85 C-21164	86 C-21164
<b>Charring Mode</b>					
Time 360° to T <sub>1</sub> ° (A)	8	9	30	7	5
T <sub>1</sub> °	650°	650°	650°	465°	650°
Time at T <sub>1</sub> ° (B)	5	30	5	30	30
Special conditions other than 150 cc N <sub>2</sub> /minute					
<b>Partial Oxidation Mode</b>					
Time from T <sub>1</sub> ° to T <sub>2</sub> ° (C)					0
T <sub>2</sub> °					650°
Time at T <sub>2</sub> ° (D)					30
Time from T <sub>2</sub> ° to T <sub>3</sub> ° (E)					
T <sub>3</sub> °					
Special conditions other than 30 cc air/minute					
<b>Char</b>					
S	3.44	3.35	3.32	4.08	2.30
C	71.14	70.60	69.92	64.54	68.01
Yield	76.1	74.2	74.3	85.6	65.2
H	1.92	1.60	1.90	3.51	1.40
N	1.55	1.52	1.52	1.42	1.58
C/S ratio	20.7	21.1	21.1	15.8	29.6
% S loss (WC basis)	38.5	41.5	42.3	21.0	64.7
DEF**	.93	.93	.93	.80	1.14
<b>Gas</b>					
S (WC basis)	1.64	1.76	1.81	0.93	2.75

\* All times in minutes, temperatures in °C, and concentration in % unless otherwise noted. Absence of data for "Partial Oxidation Mode" indicates only "charring mode" conditions were executed in run.

$$**DEF = \frac{(C/S) \text{ char}}{(C/S) \text{ coal}} \times \text{char yield}$$

**Table 2.** Charring and Partial Oxidation Data\* Continued

	Run Number and Coal				
	87 C-21164	88 C-21164	89 C-21164	90 C-21164	91 C-21164
<b>Charring Mode</b>					
Time 360° to T <sub>1</sub> ° (A)	18	19	19	40	30
T <sub>1</sub> °	650°	650°	650°	750°	650°
Time at T <sub>1</sub> ° (B)	30	30	30	30	30
Special conditions other than 150 cc N <sub>2</sub> /minute					
<b>Partial Oxidation Mode</b>					
Time from T <sub>1</sub> ° to T <sub>2</sub> ° (C)	6	7	0		
T <sub>2</sub> °	240°	230°	650°		
Time at T <sub>2</sub> ° (D)	0	0	35		
Time from T <sub>2</sub> ° to T <sub>3</sub> ° (E)	31	33			
T <sub>3</sub> °	650°	650°			
Special conditions other than 30 cc air/minute					
<b>Char</b>					
S	1.46	1.39	2.22	3.34	3.35
C	69.12	65.44	66.94	70.30	69.48
Yield	65.2	64.0	60.7	70.2	73.1
H	1.58	1.64	1.32	1.02	1.60
N	2.34	1.47	1.43	1.24	1.35
C/S ratio	47.3	47.1	30.2	21.0	20.7
% S loss (WC basis)	77.6	79.4	66.8	43.3	42.6
DEF**	1.82	1.78	1.08	.87	.89
<b>Gas</b>					
S (WC basis)	3.29	3.42	2.72	1.79	1.84

\* All times in minutes, temperatures in °C, and concentration in % unless otherwise noted.  
Absence of data for "Partial Oxidation Mode" indicates only "charring mode" conditions were executed in run.

$$**DEF = \frac{(C/S) \text{ char}}{(C/S) \text{ coal}} \times \text{char yield}$$

**Table 2. Charring and Partial Oxidation Data\* Continued**

	Run Number and Coal				
	92 C-21625	94 C-21164	95 C-21625	96 C-20712	97 C-20154
<b>Charring Mode</b>					
Time 360° to T <sub>1</sub> ° (A)	30	19	14	11	12
T <sub>1</sub> °	650°	650°	900°	900°	900°
Time at T <sub>1</sub> ° (B)	30	30	5	6	5
Special conditions other than 150 cc N <sub>2</sub> /minute					
<b>Partial Oxidation Mode</b>					
Time from T <sub>1</sub> ° to T <sub>2</sub> ° (C)		40			
T <sub>2</sub> °		250°			
Time at T <sub>2</sub> ° (D)		0			
Time from T <sub>2</sub> ° to T <sub>3</sub> ° (E)					
T <sub>3</sub> °					
Special conditions other than 30 cc air /minute					
<b>Char</b>					
S	2.99	1.54	2.90	1.75	0.77
C	73.57	65.82	75.52	79.82	74.76
Yield	69.3	71.6	67.0	66.8	71.7
H	1.72	1.56	0.54	0.56	0.56
N	1.24	1.39	0.99	1.31	1.22
C/S ratio	24.6	42.6	26.0	45.6	97.1
% S loss (WC basis)	50.8	73.7	53.7	51.4	35.3
DEF**	1.12	1.80	1.14	1.04	.85
<b>Gas</b>					
S (WC basis)	2.14	3.09	2.25	1.24	0.30

\* All times in minutes, temperatures in °C, and concentration in % unless otherwise noted.  
Absence of data for "Partial Oxidation Mode" indicates only "charring mode" conditions were executed in run.

$$^{**}\text{DEF} = \frac{(\text{C/S}) \text{ char}}{(\text{C/S}) \text{ coal}} \times \text{char yield}$$

**Table 2. Charring and Partial Oxidation Data\* Continued**

	Run Number and Coal				
	98 C-21169	99 C-20712	100 C20154	101 C-21169	102 C-20620
<b>Charring Mode</b>					
Time 360° to T <sub>1</sub> ° (A)	12	30	30	30	12
T <sub>1</sub> °	900°	650°	650°	650°	900°
Time at T <sub>1</sub> ° (B)	5	30	30	30	6
Special conditions other than 150 cc N <sub>2</sub> /minute					
<b>Partial Oxidation Mode</b>					
Time from T <sub>1</sub> ° to T <sub>2</sub> ° (C)					
T <sub>2</sub> °					
Time at T <sub>2</sub> ° (D)					
Time from T <sub>2</sub> ° to T <sub>3</sub> ° (E)					
T <sub>3</sub> °					
Special conditions other than 30 cc air/minute					
<b>Char</b>					
S	7.52	1.80	0.76	7.52	2.56
C	63.89	78.22	72.63	63.22	70.10
Yield	66.1	73.9	75.2	71.8	63.1
H	0.46	2.08	1.82	1.50	0.58
N	1.04	1.58	1.42	1.20	0.80
C/S ratio	8.5	43.4	95.6	8.4	27.4
% S loss (WC basis)	41.4	45.3	29.6	37.7	45.3
DEF**	.80	1.09	.88	.86	.79
<b>Gas</b>					
S (WC basis)	3.51	1.10	0.24	3.27	1.34

\* All times in minutes, temperatures in °C, and concentration in % unless otherwise noted.  
Absence of data for "Partial Oxidation Mode" indicates only "charring mode" conditions were executed in run.

$$**DEF = \frac{(C/S) \text{ char}}{(C/S) \text{ coal}} \times \text{char yield}$$



**Table 2.** Charring and Partial Oxidation Data\* Continued

	Run Number and Coal				
	103 C-20620	105 C-21164	107 C-21173	108 C-21164	109 C-21173
<b>Charring Mode</b>					
Time 360° to T <sub>1</sub> ° (A)	30	18	30	(14)	13
T <sub>1</sub> °	650°	650°	650°	650°	900°
Time at T <sub>1</sub> ° (B)	30	30	30	30	15
Special conditions other than 150 cc N <sub>2</sub> /minute				-3-	
<b>Partial Oxidation Mode</b>					
Time from T <sub>1</sub> ° to T <sub>2</sub> ° (C)		9			
T <sub>2</sub> °		240°			
Time at T <sub>2</sub> ° (D)		0			
Time from T <sub>2</sub> ° to T <sub>3</sub> ° (E)		10			
T <sub>3</sub> °		450°			
Special conditions other than 30 cc air/minute		-2-			
<b>Char</b>					
S	2.52	1.37	3.17	3.10	3.25
C	71.54	67.52	73.98	70.89	76.72
Yield	68.1	70.0	64.9	72.0	60.0
H	1.76	1.61	1.80	1.68	0.44
N	1.10	1.40	1.32	1.46	1.06
C/S ratio	28.4	49.3	23.3	22.9	23.6
% S loss (WC basis)	43.2	76.6	48.8	46.4	51.5
DEF**	.91	2.03	.99	.97	.92
<b>Gas</b>					
S (WC basis)	1.31	3.14	1.95	1.93	2.07

\* All times in minutes, temperatures in °C, and concentration in % unless otherwise noted. Absence of data for "Partial Oxidation Mode" indicates only "charring mode" conditions were executed in run.

$$^{**}\text{DEF} = \frac{(\text{C/S}) \text{ char}}{(\text{C/S}) \text{ coal}} \times \text{char yield}$$

-2- Run 105; Remained at 450°C for 20 minutes with usual air/nitrogen mixture.

-3- Run 108; Time of rise (14 minutes) is from 100° to 650°C.

**Table 2.** Charring and Partial Oxidation Data\* Continued

	Run Number and Coal		
	110 C-22151	111 C-22151	112 C-22151
<b>Charring Mode</b>			
Time 360° to T <sub>1</sub> ° (A)	(15)	(15)	17
T <sub>1</sub> °	650°	650°	650°
Time at T <sub>1</sub> ° (B)	15	15	30
Special conditions other than 150 cc N <sub>2</sub> /minute	-4-	-5-	
<b>Partial Oxidation Mode</b>			
Time from T <sub>1</sub> ° to T <sub>2</sub> ° (C)			8
T <sub>2</sub> °			225°
Time at T <sub>2</sub> ° (D)			0
Time from T <sub>2</sub> ° to T <sub>3</sub> ° (E)			29
T <sub>3</sub> °			650°
Special conditions other than 30 cc air/minute			-6-
<b>Char</b>			
S	2.76	2.96	2.22
C	73.94	73.73	71.57
Yield	66.0	68.0	59.6
H	1.96	1.87	1.60
N	1.33	1.34	1.42
C/S ratio	26.8	24.9	32.2
% S loss (WC basis)	55.3	50.2	66.2
DEF**	1.09	1.05	1.19
<b>Gas</b>			
S (WC basis)	2.25	2.03	3.00

\* All times in minutes, temperatures in °C, and concentration in % unless otherwise noted. Absence of data for "Partial Oxidation Mode" indicates only "charring mode" conditions were executed in run.

$$** \text{DEF} = \frac{(\text{C/S}) \text{ char}}{(\text{C/S}) \text{ coal}} \times \text{char yield}$$

-4- Run 110; Time of rise (15 minutes) is from 90° to 650°C.

-5- Run 111; Time of rise (15 minutes) is from 90° to 650°C. -10 mesh coal.

-6- Run 112; -10 mesh coal.

## Results and Discussion

### Charring Experiments

*Influence of Pyritic-to-Organic Sulfur Ratios upon Sulfur Removal.* Figure 3 shows the results of charring seven coals under comparable conditions at 650° and 900°C; each had a different ratio of pyritic sulfur to organic sulfur in the feed coal. Table 2 gives the details of these charring experiments. Sulfur removal for each coal is plotted as total sulfur removed relative to total weight loss (volatile matter plus moisture). On the horizontal scale only the high percentage range is shown for each coal. (The plots are similar to presentations in figures 4 to 7 with the lower portions of the horizontal scale eliminated.) Line C is the hypothetical "sulfur loss" (%) that would occur if (1) only organic sulfur were lost; (2) all organic sulfur were lost when "weight loss" (%) became equal to the sum of moisture and volatile matter in the coal; and (3) its loss were directly proportional to the "weight loss" (%) after the moisture was removed. The maximum loss for moisture and volatile matter (by ASTM D3175) for each coal is noted on the weight-loss scale. The rectangular "error bar" (standard deviation of results on runs 43, 48, and 91) for sample C-21164 indicates the precision of results for sulfur and volatile-matter loss on the 650°C runs.

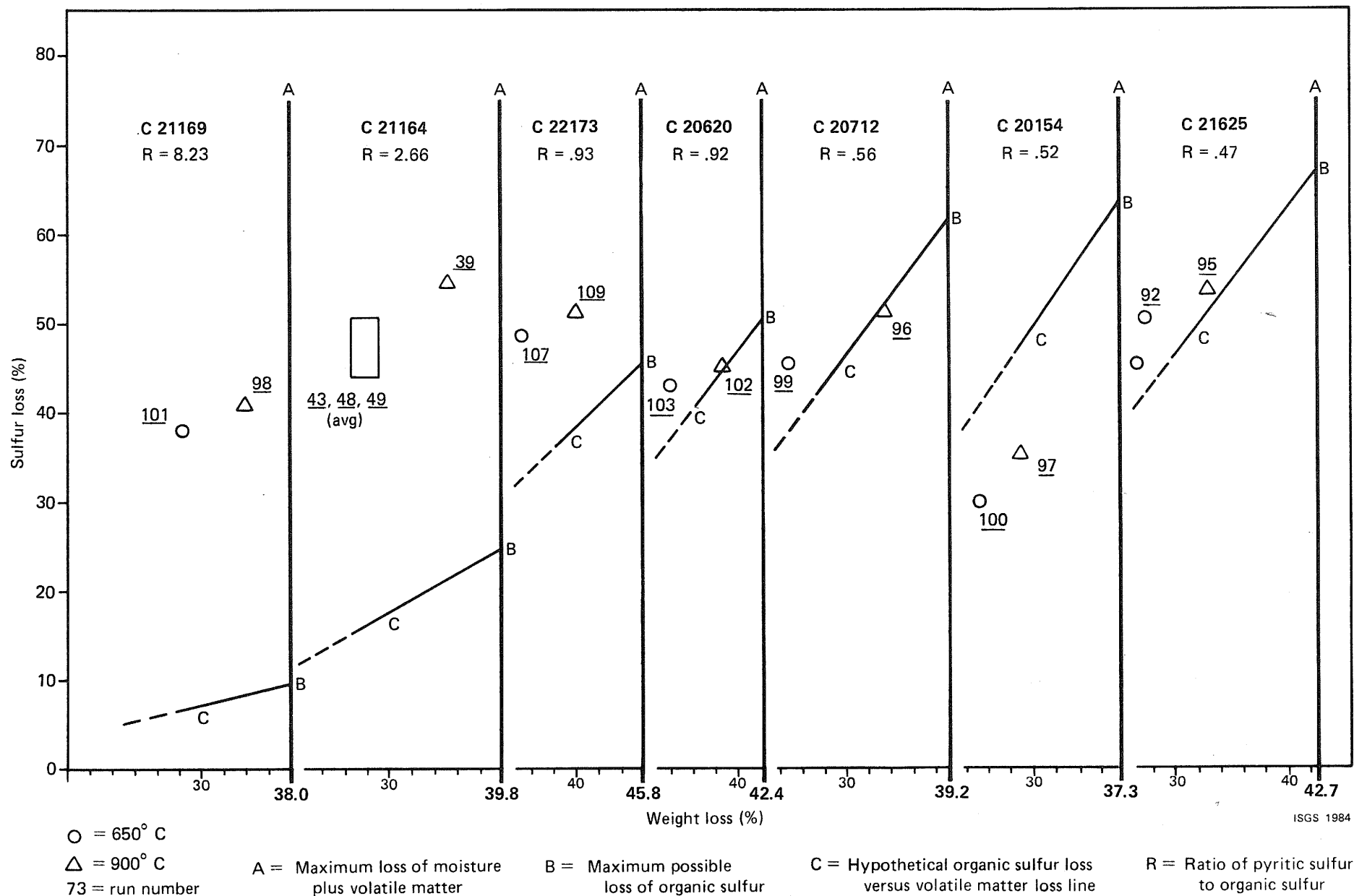
With the exception of C-20154, the total sulfur removed during the 900°C runs ranges between about 40 and 55 percent and during the 650°C experiments ranges between about 38 and 50 percent. These rather narrow ranges strongly imply that several reactions take place and that both inorganic and organic sulfur are evolved.

Data for the "organic-rich" coals (such as C-21625 with organic sulfur content significantly higher than pyritic sulfur content) show that sulfur loss generally follows the slope of line indicating "organic sulfur loss relative to volatile matter loss." Sulfur loss for coals that are rich in pyritic sulfur (such as C-21169 and C-21164) is generally much higher than can be accounted for by only organic sulfur loss.

The relative sulfur loss in charring C-20154 is the lowest result, possibly due to a combination of a low, total-sulfur content in the coal (0.85% versus 2% to 4% for others) and the higher ash content (15% versus 8% to 12% for others). It has been reported (Černič-Simeć, 1962) that coals containing higher percentages of ash, especially those containing iron or calcium minerals (such as pyrite and calcite), tend to trap sulfur. These minerals could be very effective sulfur scavengers for low-sulfur coals. This explanation may also apply in part for sample C-21169, which also showed less evolved sulfur than did five of the coals. Although this coal has a very high ash (approximately 20%) content, total sulfur is also high (approximately 8%).

When desulfurization efficiency factors (DEFs) are compared for chars formed under similar conditions from different coals, there appears to be no significant difference: for instance, the values for chars prepared at 650°C range only from .86 to 1.15 for the whole series of coals having widely varying pyritic-sulfur-to-organic-sulfur ratios and total sulfur concentrations.

*Effect of Final Temperature upon Sulfur Removal.* Figure 4 shows the results of maintaining the same rate of increase in temperature (approximately 10°C/min) then holding the final temperature for 30 minutes for a pyrite-rich coal: C-21164. The amount of sulfur evolved upon charring appears to rise sharply after 360°C and level out at 750°C. As expected, there is a significant loss of volatile matter and sulfur up to 560°C, but beyond 560°C those losses are limited. This may mean that pyrite transformation is essentially completed around 600°C and that the sulfur evolved after that is a small amount of organic-derived sulfur. It is observed that the maximum weight loss of volatiles obtained at 950°C, as determined by ASTM 3175, is not obtained under these conditions. The DEFs are very similar (Table 2). When faster heating rates (approximately 30°C/min) and higher temperatures (900°C) are used, the sulfur and weight losses are greater; these results will be discussed later.



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**Figure 3** Dependence of sulfur removal upon ratio (R) of pyritic sulfur to organic sulfur

*Rate of Temperature Rise.* Figure 5 shows the effects of changing the rate of temperature increase during the charring of a pyrite-rich coal, C21164. The rate was increased from approximately 5°C per minute to approximately 32°C per minute (runs 81, 84, and 53), then stopped at 650°C and held at that temperature for 5 minutes. The data indicate that the longer is the time required to reach 650°, the greater is the loss of volatile matter; but the increase in the sulfur loss is only minor.

When samples of C21164 were charred at comparable fast-heating rates (approximately 35° to 39°C/min) to different temperatures, 650° and 900°C (fig. 6), it was observed that the higher charring temperature resulted in significantly greater loss of sulfur and volatile matter.

The DEFs are almost identical for all runs presented in table 2.

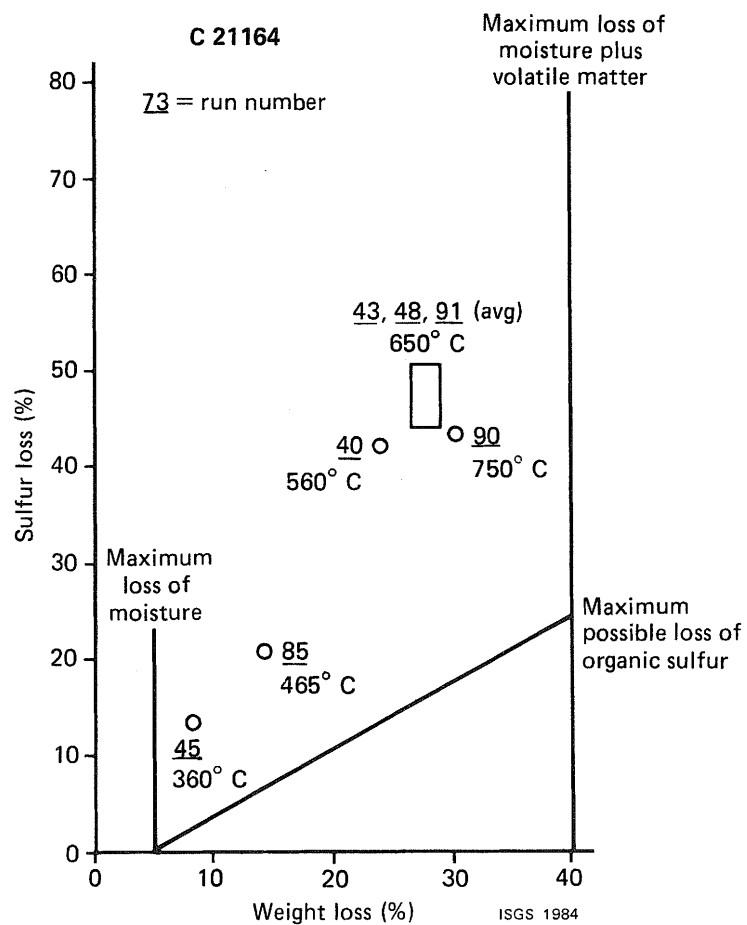
*Holding at Designated Temperature.* Figure 7 shows the results of heating pyrite-rich C-21164 to 650°C, then holding for 5 (runs 81 and 84) or for 30 minutes (runs 82, 45, 48, and 91) at that temperature. It is apparent that holding at the designated temperature for longer times gives greater sulfur removal. This is true whether the rate of increase in temperature to 650°C is rapid (runs 81 and 82) or slow (runs 84, 45, 48, and 91). It is probable the additional time at the final temperature allows sulfur gases to diffuse out of the pore system and kinetically controlled reactions to occur more completely. The DEFs are very similar.

### Partial Oxidation Experiments

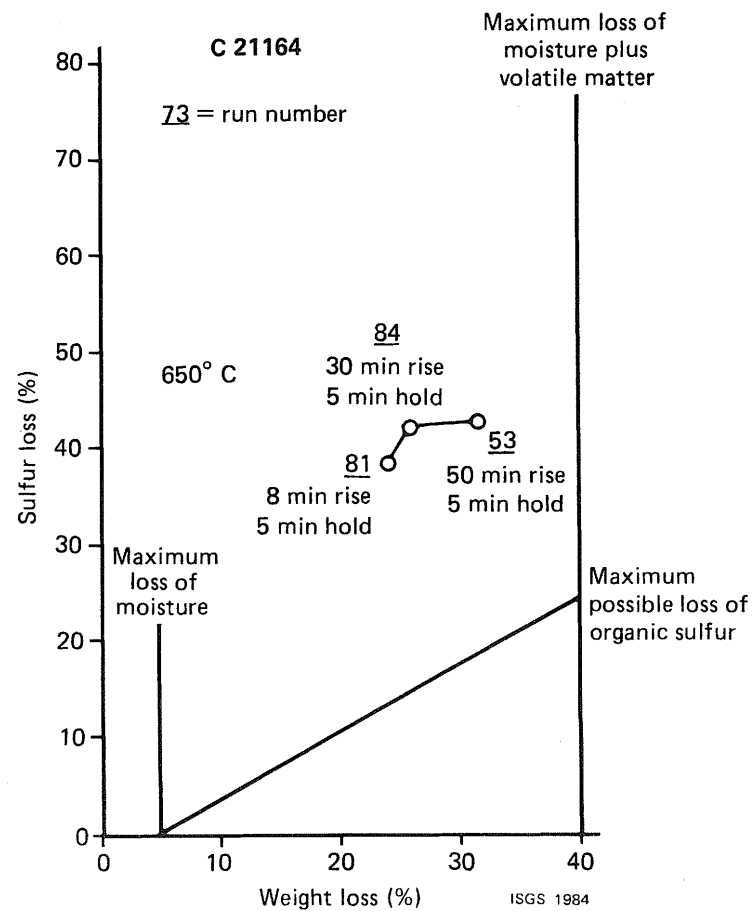
*Temperature-Dependent Air Oxidation.* Limited-air oxidation of chars prepared at 650°C was done to evaluate sulfur removal. Experiments were made on pyrite-rich C-21164. Immediately after completing the charring phase (raising the temperature to 650°C and holding at that temperature for a predetermined time under nitrogen, a small, metered amount of air was allowed to mix with the nitrogen and pass over the char. In this limited oxidizing environment, the temperature was allowed to drop and then rise again to various temperatures.

The results of these experiments are shown in table 3. The temperatures for each experiment type are schematically diagrammed at the left of the table. In separate runs the temperature of the char was allowed to drop to 360° to 380°C (type C, runs 67 and 68), 225° to 240°C (type B, runs 63, 87, 88), and 110° to 130°C (type A, runs 66 and 70), and then returned to 650°C. In another series the chars were left at 650°C during partial oxidation (type D, runs 62, 69, 86, and 89). In another experiment the temperature was allowed to slowly drop to 250°C (type E, run 94). In another run, the temperature was allowed to fall to 240°C, then increased to 450°C and held for 20 minutes (type F, run 105). The total time of the oxidation stage for a run was from 25 to 40 minutes, depending upon the time it took to go from 650°C to the low temperature in the charring stage. The times to go from the lower temperature back up to 650°C were similar (27 to 33 min). In all runs except run 70, the amount of air mixed into the nitrogen stream was a constant 35 cc per minute. This rate or amount was chosen because it did not produce visible "ashing" for the times specified; whereas definite ashing was observed in the boats when higher concentrations of air were used.

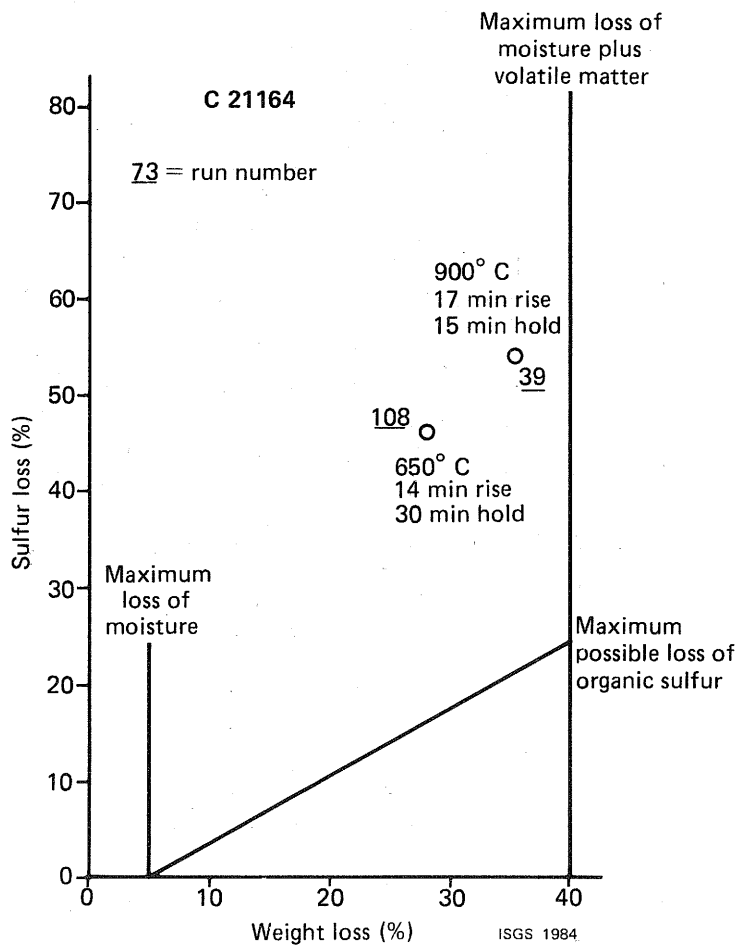
For comparable amounts of oxidation (as measured by the percentage of original carbon remaining in the char), the sulfur removed (76% to 83%) was higher for runs in which the temperature was allowed to drop and then raised again (type A, B, C runs) than in runs (type D) in which the temperature was maintained at 650°C while partial oxidation was carried out (65% to 68% of the sulfur removed). The percentage of original carbon left for the runs was essentially the same (67% to 69%); therefore the ratio of carbon to sulfur in the oxidized char is higher for those runs in which the temperature was initially dropped. At lower temperatures, the internal pore structure of the char is more accessible, allowing oxygen to penetrate more completely (Tomkov et al., 1977a; and Schmidt, 1945).



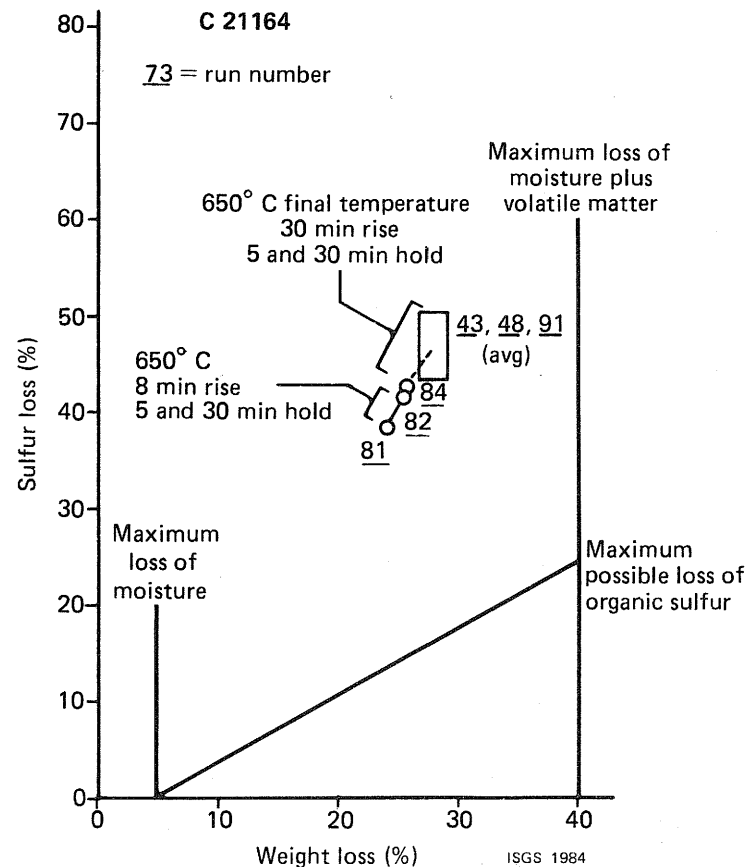
**Figure 4** Dependence of sulfur removal upon final charring temperature



**Figure 5** Dependence of sulfur removal upon rise time

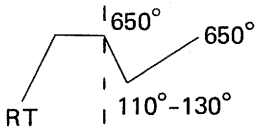
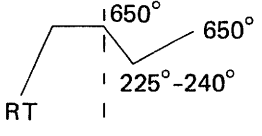
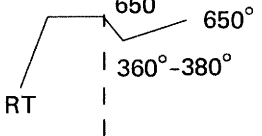
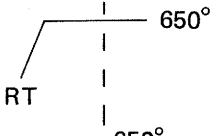
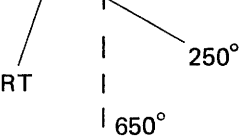
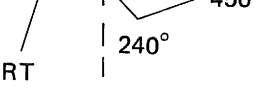


**Figure 6** Comparison of sulfur removal at 650°C and 900°C for fast rise time condition



**Figure 7** Dependence of sulfur removal on holding time

**Table 3.** Results of Partial Oxidation of Char

Type run	Mode		Run	S lost %	C/S	DEF	S in char %	Original C %
	Charring	Oxidation						
A	RT		66, 70	79.2 ± 0.4	50	1.87	1.3	67
B	RT		63, 87, 88	88.0 ± 2.3	50	1.86	1.4	68
C	RT		67, 68	76.0 ± 0.1	47	1.78	1.4	69
D	RT		62, 69, 86, 89	66.9 ± 1.5	32	1.19	2.2	69
E	RT		94	73.7	43	1.80	1.5	75
F	RT		105	76.6	49	2.03	1.4	75

In run 70 (similar to run 66 in which the temperature was dropped to 110°C and then raised to 650°C), only air was passed over the char at 110°C for 15 minutes before the temperature was raised to 650°C. When the temperature was raised to 650°C, the usual 35 cc per minute air and 150 cc per minute nitrogen was again imposed on the system. The percentage of sulfur loss and the ratio of carbon to sulfur in the char were very similar to results from run 66 in which the char was not subjected to an air flow at 110°C. This might mean that the process of oxygen sorption into the pores is fairly rapid at the lower temperature, but when the temperature is raised, there is little chance for more oxygen to get into the pores.

Data for run 94 (type E) indicate that when char is allowed to oxidize while the temperature is slowly reduced from 650° to 250°C, the relative loss of sulfur is also higher than when the char is oxidized just at 650°C (74% loss of sulfur versus 65% to 68%). The C/S ratio is somewhat higher (43% versus 32%) and the percentage of available carbon left in the char is higher (75% versus 69%), indicating less oxidation of carbonaceous material.

In the oxidation of the char in run 105, the temperature was reduced from 650° to 250°C then raised to 450°C rather than to 650°C, and held for 20 minutes. The percentage of sulfur loss was quite high (77%). The percentage original carbon in the char and the C/S ratio were somewhat higher than chars oxidized at 650°C only, indicating more efficient



**Table 4.** Dependence of Sulfur Removal During Partial Oxidation of Char upon Different Ratios of Pyritic Sulfur to Organic Sulfur of Feed Coals

Mode			Ratio of pyritic S to organic S	S lost %	C/S	DEF	Original C %
Charring	Oxidation	Run					
		63	2.66	83.1	55	1.98	64.5
		64	1.04	74.9	46	1.34	63.3
		65	.47	76.4	35	1.22	52.4

sulfur removal. The greater amount of carbon remaining in the char (75%) also means that a final oxidation temperature of 420°C is more efficient than 650°C.

The DEFs generally follow the trend of the C/S values (table 3); however, the highest value of 2.03 for the type F run also indicates this may be the best approach, i.e. using a lower post-charring partial-oxidation temperature.

*Sulfur Removal during Partial Oxidation Stage: Dependence upon the Ratio of Organic Sulfur to Pyritic Sulfur.* Table 4 shows the results of charring and partially oxidizing three coals with similar compositions of total sulfur but with different ratios of organic sulfur to pyritic sulfur. The percentage of sulfur removed was slightly higher for the coal

rich in pyritic sulfur (run 63) than for the others. There is a general trend: the coal with a higher ratio of organic sulfur to pyritic sulfur results in a lower ratio of carbon to sulfur and lower DEFs in the char. This indicates that more carbon (or heating value) is lost for roughly the same percentage of sulfur removed from organic-sulfur-rich coal compared to pyritic-sulfur-rich coal under comparable oxidizing conditions.

Table 5 gives the loss of sulfur during the charring and partial-oxidation stages. The results for the oxidation step were obtained by subtracting the amount of sulfur and carbon lost upon charring alone (runs 91 and 92) from the amounts lost in charring plus oxidation (runs 63 and 65). More sulfur and carbon are lost in the charring of the organic-sulfur-rich coal than in the charring of the pyritic-sulfur-rich coal. During the partial oxidation step, however, the loss of more sulfur but less carbon is observed for the pyritic-sulfur-rich coal compared to the organic-sulfur-rich coal.

**Table 5.** Sulfur and Carbon Loss Related to Charring or Partial Oxidation Mode

		Mode			
		Char		Oxidation	
Run		S lost %	C lost %	S lost %	C lost %
Pyrite-rich sulfur coal (C21164)	63, 91	43	19	40	16
Organic-rich sulfur coal (C21625)	65, 92	51	24	26	24

**Table 6.** Effect of Varying Charring Conditions upon Partial Oxidation of Coal (C-21164)

Mode			Rise Time	Holding Time	S	S in	
Charring	Oxidation	Run	"A" (min)	"B" (min)	lost %	char %	DEF
"A"	"B"	71	9	30	80.7	1.3	1.87
	650°C 680°C	63	19	30	83.1	1.2	1.98
	225° -	60	30	30	79.2	1.3	2.24
	250°C	61	30	5	81.9	1.2	1.99

*Dependence of Sulfur Removal upon Varying the Charring Conditions Prior to Partial Oxidation.* For comparable partial-oxidation conditions (table 6), it appears there is no significant difference in the percentage of sulfur removed due to varying either the rate of temperature increase to 650°C or the charring time at 650°C prior to partial oxidation. The percentage of sulfur lost ranged only from 79 to 83 percent when charring conditions were varied as shown. The best DEF was noted for run 60 where both 30-minute-rise and 30-minute-holding times were used in the charring mode.

*Fate of Nitrogen and Hydrogen during Charring and Partial Oxidation.* Table 7 lists the C/H and C/N ratios of chars produced by charring samples of C-21164 to different final temperatures. It is apparent that more hydrogen but not nitrogen is lost, relative to carbon, at higher charring temperatures. Data on runs 53, 81, and 82 (table 2) indicate also that

**Table 7.** Dependence of C/H and C/N Ratios in Chars upon Final Charring Temperatures





Run #	Final temperature (°C)	C/H	C/N
45	360°	17	50
85	465°	18	45
91	560°	43	52
90	750°	69	57
39	900°	157	55

neither the rate of temperature increase nor holding time appears to have any significant effect upon the C/N ratio; however, longer holding times at 650°C appear to result in a greater loss of hydrogen.

Table 8 indicates that different intermediate temperatures during the partial oxidation of char have little effect on the C/N ratio. The C/H ratio is greater, however, when partial oxidation is done completely at 650°C than when the char is taken to lower temperatures (runs 66, 88, 68) and then back to 650°C.

*Effect of Particle Size upon Sulfur Loss.* Figure 8 shows the effect of particle size under similar conditions of charring and partial oxidation of coal rich in organic sulfur. C-22151 and C-21625 are splits from the same coal sample. It is apparent that charring proceeds more easily on the smaller particle-size (60 mesh; <250 µm) coal, because more sulfur and volatile matter are lost. The effect of particle size appears to be more pronounced in the partial-oxidation stage than in the charring stage.

**Table 8.** Dependence of C/H and C/N Ratios in Chars upon Temperature Conditions During Partial Oxidation

Run	Condition	C/H	C/N
	Charring      Oxidation		
66		42	43
88		40	44
68		44	44
89		51	47

## Conclusions

Results of charring coals, primarily coals rich in pyritic sulfur, under different conditions show the following:

- There is a narrow range of relative sulfur loss from coals charred under comparable conditions, regardless of the ratio of organic sulfur to pyritic sulfur in the feed coal. This is definite evidence that some pyrite-derived sulfur is evolved in charring. Radioactive tracer experiments involving "spiked" pyrite ( $\text{Fe}^{35}\text{S}_2$ ) have confirmed this (Frost et al., 1984).
- The parameters that need to be considered in order to obtain optimum charring conditions are numerous, interrelated, and complex. Only one coal rich in pyritic sulfur was studied initially. It appears that the rate of temperature increase, charring time, and charring temperature all have a significant effect upon the total amount of sulfur evolved. Limited data show that a slow rate of temperature increase combined with a longer charring time at higher temperatures results in greater losses of sulfur.
- In post-charring partial-oxidation experiments, it was observed for comparable levels of oxidation that maximum loss of sulfur occurred when the temperature was initially dropped to  $<240^\circ\text{C}$  and returned to  $650^\circ\text{C}$  or a lower temperature ( $450^\circ\text{C}$ ) rather than maintained at  $650^\circ\text{C}$  for the partial oxidation. Limited data showed that pyritic-sulfur-rich coal is more easily desulfurized with less loss of carbon in the partial oxidation stage than an organic-sulfur-rich coal. Comparison of DEFs is useful in judging the best approach.

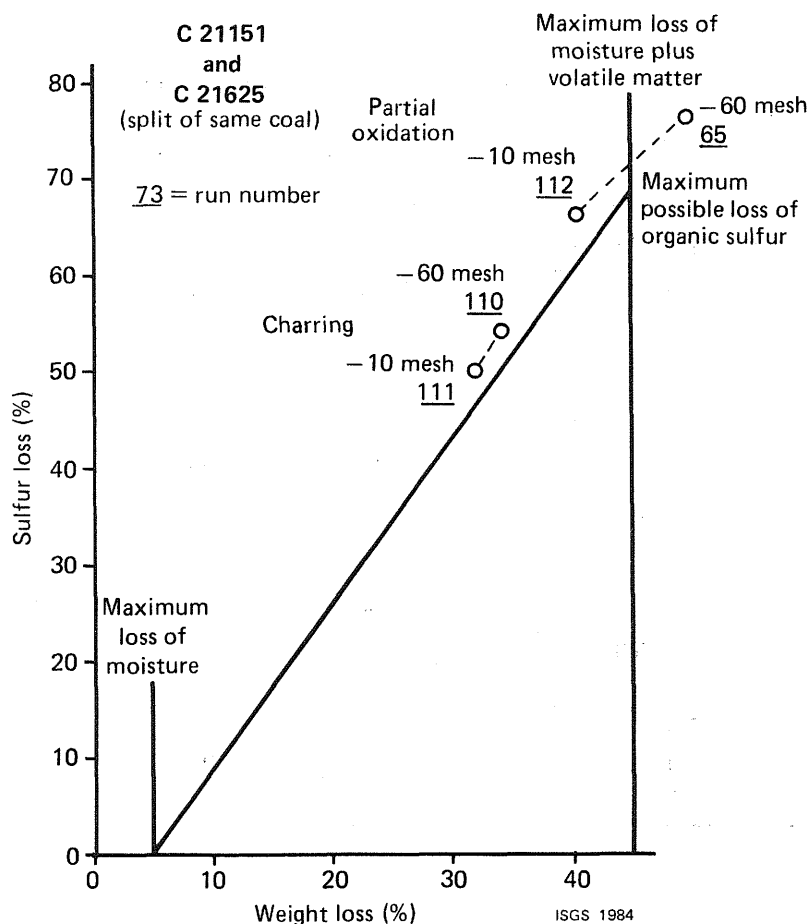


Figure 8 Dependence of sulfur removal on mesh size

## Recommendations

Further work is needed to systematically characterize the effects of the following parameters in charring and post-charring partial oxidation—temperature, time to reach charring temperature, charring time, particle size, type of coal, optimized time and temperature sequence, and oxygen concentration for post-charring partial oxidation.

Experiments with radioactive pyrite tracer and use of natural variations in the  $^{34}\text{S}/^{32}\text{S}$  ratio of different forms of sulfur are being directed toward elucidating the speciation of the forms of sulfur during post-charring partial oxidation and should greatly aid in interpretation of the chemical processes involved.

With optimization of the conditions for charring and partial oxidation, possibly more than 90 percent of the sulfur in a coal can be eliminated while most of the heating value is retained. This would give a product whose combustion would be in compliance with existing regulations on sulfur emissions.

## Acknowledgments

We thank the following colleagues for their valuable assistance in various phases of this work: L. Camp, D. Coleman, J. Cooper, J. Frost, V. Jones, L. Kohlenberger, and J. Liu.

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## Appendix: Literature Review

### General Background—Carbonization in Relation to Sulfur Removal

Early work by Powell (1920, 1921) showed that pyrite and marcasite decomposed to ferrous sulfide, pyrrhotite, and hydrogen sulfide beginning about 300°C; the reaction reached a maximum rate between 400° to 500°C and was complete at approximately 600°C. In his experiments he demonstrated that sulfates were reduced to sulfides, (the reaction being complete at 500°C), that a significant portion of organic sulfur was volatilized as hydrogen sulfide, and that part of the organic sulfur formed other volatile compounds, especially at lower temperatures. Of significance was his finding that between 400° and 500°C part of the organic sulfur formed complexes with carbon and these complexes show none of the properties of the original sulfur in the feed coal. He also concluded that some ferrous sulfide formed when the pyrite reacts with the carbon.

Foerster and Geissler (1922), working with brown coals, obtained results in disagreement with those of Powell: at 500°C only about one-half the pyrite and sulfate decomposed. They also found the greater amount of volatilized sulfur came from inorganic compounds, and the organic sulfur content was practically unchanged. Upon carbonization of brown coals high in organic sulfur, about 70 percent of the total sulfur was volatilized as H<sub>2</sub>S, most of which had to come from organic sulfur compounds.

Campbell (1916) reported on a carbonization run of a coal in which most of the sulfur was present as pyrite. Some 42 percent was volatilized with the remainder existing in the coke as pyrrhotite.

Parr (1904) reported on 150 Illinois coals that had been volatilized. The average percentage of sulfur remaining in the coke was 48.5; values ranged from 16 to 96.

Using specific gravity separations of a coal, McCallum (1909) secured fractions having increasing ratios of pyrite to organic sulfur but essentially a constant organic sulfur content. The ratio of pyritic sulfur to total sulfur ranged from 0.15 to 0.62. Upon carbonization the ratio of sulfur in the resulting chars (as calculated back to the original coal basis) to the sulfur content of the original coal ranged from 0.477 to 0.581.

Thiessen (1935) found the relationship between sulfur in coke and the pyritic and organic sulfur in the original coal was  $S_{\text{coke}} = 0.62 S_{\text{pyrite}} + 0.45 S_{\text{organic}}$ , based upon data on 82 samples analyzed by ASTM methods.

Woolhouse (1935) studied coals with different sulfur contents, reporting that pyrite decomposed completely at approximately 600°C to FeS and H<sub>2</sub>S, and organic sulfur yielded H<sub>2</sub>S and other volatile compounds. Sulfur was retained in the coke because of the stability of FeS and C-S complexes and because of its inertness to hydrogen at higher temperatures.

Armstrong and Himus (1939) found that evolution of sulfur was essentially complete at approximately 700°C, that pyrite decomposed at lower temperatures, that organic sulfur removal generally followed removal of total sulfur, and that with a reduction of pressure during carbonization coke tended to retain sulfur, particularly at high temperatures.

Wibaut (1931) concluded that part of the organic sulfur in coke was present in solid solution or held physically by adsorption.

Eaton et al., (1948, 1949) confirmed previous views that there was a simple relation between the total sulfur in the feed coal carbonized and the sulfur in the resulting coke. They mixed radioactive pyrite with a coal prior to carbonization. By measuring the radioactivity in the gaseous products and in the resulting coke, they found the proportions of pyritic and organic sulfur in the coke were nearly the same as in the coal. The coke contained 66 percent of the pyritic sulfur and 73 percent of the organic sulfur, whereas the gases contained 23 and 26 percent of the pyritic and organic sulfur respectively. Apparently pyrite decomposed to FeS and some pyrite-derived sulfur remained in the coke. The results indicated neither form of sulfur was preferentially lost during the coking process.

In another radioactive tracer experiment, Medvedev and Petropolskaya (1958) "spiked" coal with  $\text{Ca}^{35}\text{SO}_4$  and found sulfate was reduced initially to sulfide, then converted to organic sulfur during carbonization from  $900^\circ$  to  $1000^\circ\text{C}$ .

Černič-Simeć (1962) extensively studied sulfur evolution upon carbonization of coal spiked with radioactive pyrite. Factors that determined the retention of sulfur in coals during the carbonization process included

1. *the rank of the coal*: high amounts of volatile matter in low rank coals tended to carry the volatile sulfur away from the coal particles during charring. The type of bonding of the organic sulfur in the coal molecule appeared to be more stable in high-rank coals. The lower the rank, the greater the proportion of organic sulfur released, probably because of evolution of more volatile matter, which scavenged the released sulfur before it could be "fixed" by iron or calcium compounds (probably forming sulfides). Volatile matter also helped carry away the sulfur obtained from decomposition of  $\text{FeS}_2 \rightarrow \text{FeS} + \text{S}$ . Tracer studies showed coals higher in rank and lower in volatiles were less reactive and apparently could not accept or react with "transformed" organic sulfur (made from conversion of pyrite), whereas lower rank coals can. The paper claimed a direct proof of the transformation during carbonization of sulfur from inorganic to organic forms; the extent of such transformation depended upon the chemical reactivity of the coal.
2. *the quantity and composition of the mineral matter*: compounds of calcium and iron that form sulfides during the carbonization process retained much of the sulfur that would normally leave with the volatile gases.
3. *the quantity of sulfur in the coal*: the greater the amount of sulfur in the coal, the more sulfur retained upon charring, possibly due to suppression of the forward reaction in the equilibrium of  $2\text{H} + \text{RS} \rightarrow \text{R} + \text{H}_2\text{S}$  (where R is either an organic substrate or mineral ion).

Okladnikova and Kalechits (1955) reported an incomplete reaction between sulfur and organic matter to form hydrogen sulfide; ferrous sulfide (from decomposition of pyrite) exerted an inhibiting effect on the decomposition of organic sulfur compounds.

Thiessen (1935, 1937) found the sulfur content of coke was not as low as expected when pyrite was oxidized before the coal was carbonized. The iron sulfates from oxidized pyrite increase the retention of sulfur in the coke.

Given and Jones (1966) found some sulfur derived from pyrite upon coal carbonization became "fixed" in the organic matter; this took place essentially from  $350^\circ$  to  $500^\circ\text{C}$ . They stated that some known sulfur compounds decomposed at  $500^\circ$  to  $600^\circ\text{C}$  with the formation of hydrogen sulfide or mercaptans, and that these compounds could react elsewhere on the coal surface to produce firmly bound sulfur-carbon complexes. These findings, which are consistent with other references, indicated that part of the "inorganic" sulfur converted to "organic" sulfur under certain charring conditions.

Maa et al. (1975) determined the forms of sulfur upon charring of a Kentucky No. 9 coal under nitrogen atmosphere up to approximately  $850^\circ\text{C}$ . Their results indicated that pyrite began to evolve sulfur at about  $300^\circ$  to  $400^\circ\text{C}$  and at  $740^\circ\text{C}$  apparently completely transformed into sulfide. Sulfate showed a maximum concentration in the char at  $550^\circ\text{C}$  and then decreased. Analyses of the char for forms of sulfur showed that 51.5 percent of the sulfur was organic, 4.6 percent was pyritic, 3.1 percent sulfatic, and 40.8 percent sulfidic; whereas the sulfur in the original coal was 58.9 percent organic, 40.0 percent pyritic, and 1.1 percent sulfatic.

Huang and Pulsifer (1977) reported that when high-sulfur Iowa coal was charred in a nitrogen atmosphere up to  $700^\circ\text{C}$ , about 80 percent of the inorganic sulfur was lost. They confirmed that some inorganic sulfur was "transformed" into an organic form in the char. The total sulfur loss was proportional to the weight loss.



## General Background—Partial Oxidation of Chars and Coals to Remove Sulfur

Many factors affect the partial-oxidation process, including surface area, mineral composition, temperature and contact time, rate of heating, and the use of different oxidants and reagents.

Available surface area, for example, allows adsorption of more oxygen at lower temperatures. Jenkins et al. (1973) found that preparing chars at 600° to 700°C increased surface area to a maximum. Rank of the original coal was also extremely important: the surface area of char from lignite was higher than the surface area of char from HvA bituminous coals by a factor of approximately 100.

Jenkins et al. (1973) also found mineral matter (especially that containing Fe and Ca) tended to make chars more reactive; but many other factors were involved in the reactivity. Robinson (1976) removed the minerals containing iron and calcium to increase the effectiveness of hydrodesulfurization. Kruse and Shimp (1981) found that hydrochloric acid leaching of iron made hydrodesulfurization of 650°C char more complete—achieving approximately 90 percent removal of sulfur.

Temperature and contact time are dominant factors in partial oxidation. Breen and Evans (1963) reported oxygen adsorbed on char surfaces of brown coal at temperatures as low as 300°C, indicating a carbon-oxygen complex. They report it took a long time (up to 1 year for chunks of char 2 x 1½ inches thick) for oxygen to reach equilibrium in the inner regions of the coal particles. Tomkov et al. (1977a), using oxygen to activate chars, found that at higher temperatures oxygen does not effectively penetrate the interior of a char particle; its reaction is restricted to the outer parts of the char particle. Schmidt (1945) alludes to this phenomenon in his statement that “at high temperatures the rate of oxidation of the internal area (of char) becomes small relative to the rate of oxidation of the external area because of slowness of diffusion of oxygen to the pores.” Young (1981) stated that the rate of combustion of char is restricted by external mass transfer and pore diffusion of oxygen.

Sinha and Walker (1972) studied low-temperature (350° to 450°C) air oxidation of coal (approximately 100 mesh) as a means of desulfurization; they found that generally oxidation resulted in a decrease in both volatile matter and calorific value. Desulfurization efficiency increased with higher temperature and shorter oxidation time. For instance the calorific values of char made at 450°C for 15 minutes and the amount of sulfur removed is also greater. One possible explanation given was chemisorption of more oxygen at 400°C than at 450°C. Their studies also point out that the removal of pyritic sulfur is controlled by resistance to the diffusion of oxygen into the microporous structure of the coal and that removal of sulfur is greater when the particle size of the coal is smaller.

Nsakola et al. (1978) stated that chars prepared under rapidly heated conditions have more surface area and porosity, which allows adsorption of more oxygen at lower temperatures. Leon et al. (1981) showed that coals heated with nitrogen or nitrogen plus air from 300° to 1000°C showed the greatest increase (100-fold) in surface area for pores 0.5 mm or greater at about 400° to 450°C. Tomkov et al. (1977b) reported that reaction with oxygen develops microporosity in coal; but they noted surface complexes are formed on the activated surfaces, tending to block the entrances of micropores and to inhibit further activation. This phenomenon does not seem to interfere with the larger micropores.

Oda et al. (1981) reported that coals pre-oxidized in air for as long as 10 hours at 150°C, prior to charring with N<sub>2</sub>, produce chars with higher micropore volumes than those not pre-oxidized.

Several reports deal with oxidants and reagents other than air. Boron et al. (1981) reported on experiments treating coal with H<sub>2</sub>O<sub>2</sub> over periods as long as 384 hours. Pyritic sulfur was essentially removed, but much organic matter was lost and most of the organic sulfur remained. Steinberg et al. (1977) reported on unsuccessful attempts to remove

sulfur via ozone addition to fine-mesh coal at temperatures from 25° to 100°C. Warzinski et al. (1978) reported on the air/water oxydesulfurization of coal. Air is fed through a pressurized batch system at 150° to 200°C and 500 to 155 psig. As much as 90 percent of the pyritic sulfur and up to 40 percent of the organic sulfur is removed. Joshi and Shah (1981) reported on the kinetics of the pressurized-oxidation process.