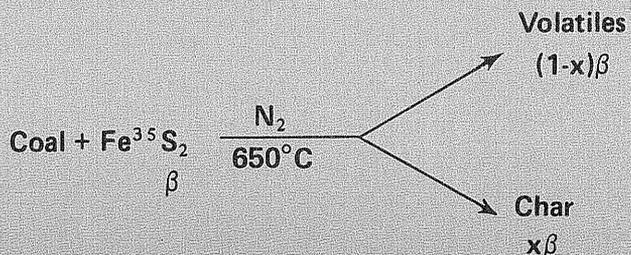


RADIOACTIVE SULFUR TRACER STUDY OF SULFUR REMOVAL IN THE CHARRING OF ILLINOIS COALS AT 650°C

Joyce K. Frost, Francesco Auteri, and R. R. Ruch



ISGS CONTRACT/GRANT REPORT 1984-3

Cover: Representation of the experimental method.

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CONTENTS

ABSTRACT.....	1
INTRODUCTION.....	2
EXPERIMENTAL.....	4
^{35}S Tracer as $\text{H}_2^{35}\text{SO}_4$ Solution.....	4
Synthesis of Pyrite and Radioactive Pyrite, Fe^{35}S_2	4
Preparation and Irradiation of 1.6 S.G. Sink Fraction of Coal Samples.....	4
Charring of Coal Spiked with Radioactive Pyrite or Irradiated 1.6 S.G. Sink, at 650°C	4
Combustion of Coal and Char for Determination of Total Sulfur and ^{35}S	6
Precipitation of Barium Sulfate for Total Sulfur and ^{35}S Analyses.....	6
Beta Counting of ^{35}S in Barium Sulfate.....	8
RESULTS AND DISCUSSION.....	10
SUMMARY AND CONCLUSIONS.....	22
ACKNOWLEDGMENTS.....	23
REFERENCES.....	23

FIGURES

1. Apparatus for charring coal and oxidizing and trapping volatile products.....	5
2. 1350°C combustion apparatus for determination of total sulfur in coal and char.....	7
3. Self-absorption effect for ³⁵ S in barium sulfate.....	9
4. Fractions of sulfur and pyritic sulfur evolved upon charring of coals.....	16
5. Fractions of sulfur and organic sulfur evolved upon charring of coals.....	17
6. Ash content of spiked coal samples and fraction of sulfur evolved upon charring of coals.....	18
7. Ash content and proportion of pyritic sulfur in spiked coal samples	19
8. Volatile matter content of spiked coal and fraction of sulfur evolved upon charring.....	20
9. Volatile matter and ash content of spiked coals.....	20
10. Organic S/pyritic S in spiked coals and fraction of sulfur evolved upon charring.....	21

TABLES

1. Chemical composition of coals.....	11
2. Composition of 1.6 S.G. sink fractions of coals.....	12
3. Composition of spiked coals charred.....	13
4. Results of charring coal plus radioactive synthetic pyrite at 650°C.....	14
5. Results of charring coal plus irradiated S.G. sink at 650°C.....	15

ABSTRACT

One gram samples of 13 high-volatile bituminous coals from Illinois, spiked with a small amount of radioactive synthetic pyrite, Fe^{35}S_2 , or with a small amount of irradiated 1.6 specific-gravity sink fraction prepared from five of the coals, were charred at 650°C in a nitrogen atmosphere for 30 minutes. The volatile matter evolved was combusted in an oxygen stream; and the sulfur oxides formed were trapped, then quantitatively separated as barium sulfate, which was weighed to give the amount of sulfur evolved on charring. In addition, the beta-radiation from ^{35}S was counted to determine the fraction of pyritic sulfur evolved upon charring. The char was also analyzed for sulfur content and ^{35}S activity. In 27 charring experiments, an average and range (as defined by one standard deviation about the mean) of $43\% \pm 5\%$ of the pyritic sulfur in the spiked coal was evolved, consistent with the well-known decomposition of pyrite to pyrrhotite with evolution of the sulfur. The volatilized material contained an average of $57\% \pm 5\%$ of the organic sulfur in the spiked coal. Thus, the larger the organic-to-pyritic sulfur ratio in a coal sample, the greater the fraction of total sulfur evolved upon charring; an average of $47\% \pm 5\%$ of the total sulfur was evolved upon charring the 23 different spiked coal samples investigated.

INTRODUCTION

The objective of this project was to determine the fate of the forms of sulfur in Illinois coals during charring. Kruse and Shimp (1981) developed a conveyor-feed, low-temperature charring technique in which the temperature of a thin (~5 mm) bed of coal increased to 650°C as it moved through the oven. The volatile matter was withdrawn counter current to the direction of the coal to prevent tar formed at one temperature from reacting with char formed at a higher temperature. When the resulting char was acid-leached and hydrogenated, the yield of the product from coal was 50% to 60%; and 75% to 90% of the sulfur in the original coal had been removed. From analyses of the chars produced from coals for which the ratio of pyritic sulfur to organic sulfur varied within a narrow range, Kruse and Shimp (1981) concluded that an amount of sulfur equivalent to the amount of organic sulfur in the feed coal could be removed during the charring process.

This was surprising because a review of the literature shows that all forms of sulfur in coal contribute to the sulfur evolved during charring or coking.

Powell (1920, 1921) reported that in the charring of coal, pyrite decomposed to pyrrhotite, sulfate decomposed to sulfide, and organic sulfur formed volatile organic compounds and hydrogen sulfide. These reactions were essentially complete by 600°C. Woolhouse (1935), who charred coals with different sulfur contents, also found that pyrite decomposed to ferrous sulfide and hydrogen sulfide at 600°C. Armstrong and Himus (1939) reported that the rate of organic sulfur removal generally correlated with the rate of removal of total sulfur. Thiessen (1935), from analyses of some 82 coals and cokes, found that the relationship between the sulfur in the coke and the pyritic and organic sulfur in the original coals was

$$S_{\text{coke}} = 0.62 S_{\text{pyritic}} + 0.45 S_{\text{organic}}$$

Eaton et al. (1948, 1949), using a radioactive sulfur tracer technique, showed that neither organic nor pyritic sulfur was preferentially evolved during a commercial coking run of a coal containing approximately the same amounts of organic and pyritic sulfur. Černić-Simić (1962), also using a radioactive tracer method, determined that in addition to the mineral matter content and total quantity of sulfur in the coal, the rank had a significant effect upon sulfur retention in the char.

It is important to understand the forms of sulfur retained in charring processes such as the conveyor-feed, low-temperature technique developed at the Illinois State Geological Survey for coals with a large range of pyritic- and organic-sulfur contents; further treatment of the char can be directed toward the efficient removal of the remaining forms. This study was specifically designed to investigate the fate of pyritic

sulfur in the charring of a series of Illinois coals with a wide range of pyritic to organic sulfur ratios, total sulfur contents, and ash contents.

A radioactive tracer method that involved the charring of coals spiked with tagged pyrite, Fe^{35}S_2 , and the measurement of the radioactive sulfur-35 in the evolved gases and resulting char, was developed. Two kinds of radioactive pyrite were used: (1) a radioactive pyrite was synthesized from iron and from sulfur that had been irradiated with thermal neutrons to produce ^{35}S ($t_{1/2} = 87$ days); and (2) the 1.6 specific-gravity (S.G.) sink fraction, in which pyrite is concentrated, was prepared from each of five coals, then irradiated with thermal neutrons.

It is presumed that pyrite separated from the coal, irradiated, and mixed with coal again, will undergo the same reactions it would have undergone had it not been separated and irradiated, although its reactivity may be greater because its surface was chemically cleaned. The use of the sink fractions suffers from the disadvantage that the radioactive sulfur is not all pyritic; the sink always contains small amounts of organic sulfur and sulfate, which introduces small errors into the calculation of the percentage of pyritic sulfur evolved upon charring. The synthetic radioactive pyrite, Fe^{35}S_2 , has the advantage of sulfur purity but the disadvantage that pyrite synthesized from laboratory-grade chemicals may have significantly different properties from pyrite formed authigenically in coal. The synthetic pyrite and the irradiated sinks can be expected to undergo reaction or reactions like those undergone mainly by coarse-grained pyrite. Not much, if any, direct information will be provided on the reactions involving the finely disseminated type of pyrite, although a small fraction of the pyrite in the 1.6 S.G. sink of a coal is of the finely disseminated type.

The spiked coal samples were charred at 650°C in a tube furnace charring-and-oxidation apparatus (Ruch, Chaven, and Kruse, 1984); gases evolved in the charring were oxidized and the sulfur oxides collected. The sulfur products were radiochemically purified, measured, and beta-counted for ^{35}S activity, to determine the amount of sulfur evolved and the fraction of pyritic sulfur evolved upon charring of coal. The amount of sulfur and the fraction of radioactive sulfur remaining in the char were also determined.

The radiochemical purification done on the sulfur products collected was mainly to separate small amounts of isotopes of inorganic elements, such as selenium and mercury, that are concentrated in the 1.6 S.G. sink of coal and volatilized upon charring. The problem of the known interference of ^{32}P ($t_{1/2} = 14.3$ days) formed by the reaction $^{32}\text{S}(n,p)^{32}\text{P}$ was eliminated by a minimum 2-month decay period between irradiation and use of the radioactive pyrites. As chlorine is not concentrated in the 1.6 S.G. sink fraction of coal, interference from the reaction $^{35}\text{Cl}(n,p)^{35}\text{S}$ would be insignificant.

EXPERIMENTAL

³⁵S Tracer as H₂³⁵SO₄ Solution

Carrier-free sulfuric acid containing 2.0 millicuries/mL of ³⁵S (from New England Nuclear) was diluted 1:10,000 with water to provide a suitably active tracer for use in developing the radiochemical procedures.

Synthesis of Pyrite and Radioactive Pyrite, Fe³⁵S₂

Equal weights (3 g each) of iron filings and flowers of sulfur were mixed well and sealed in an evacuated Pyrex tube (1.2 cm i.d. x 15 cm length). The tube was heated in a small tube furnace at 480°C for 48 hours. The product was ground to a powder and boiled in 4 M HCl (10 mL/g of pyrite) for 2 hours. The insoluble material was filtered and washed with 4 M HCl, water, and ethanol, and dried at 110°C for 1 hour. The product was then refluxed with 200 mL of methylene chloride in a Soxhlet extractor for 12 hours, washed with ethanol, and dried for 3 hours at 110°C. X-ray diffraction analysis of the purified product showed only peaks for pyrite, indicating a purity of at least 98%.

Pyrite containing ³⁵S was prepared by this procedure using 99.999% pure sulfur that had been irradiated in a thermal neutron flux of $2.8 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ for 4 hours. This pyrite was ground to -60 mesh.

Preparation and Irradiation of 1.6 S.G. Sink Fraction of Coal Samples

Five coals were dried, put through a roll mill, and sized through 10-, 20-, and 30-mesh screens. About 1000 g of the -20 + 30 mesh fraction was gravity separated with a 1.6 specific gravity mixture of ethylene dibromide in petroleum ether. The sink fraction was collected, dried, washed first with water, then with acetone, and ground to -60 mesh. The sinks were irradiated for the equivalent of 4 hours in a flux of 2.8×10^{12} thermal neutrons $\text{cm}^{-2} \text{ sec}^{-1}$.

Charring of Coal Spiked with Radioactive Pyrite (Fe³⁵S₂) or Irradiated 1.6 S.G. Sink, at 650°C

Approximately 1 g of air-dried coal (-60 mesh) spiked with 0.01 to 0.03 g of radioactive pyrite (Fe³⁵S₂) or irradiated sink fraction was charred under a nitrogen atmosphere ($\approx 150 \text{ cc N}_2/\text{min}$) in the apparatus illustrated in figure 1. During the charring run, suction was applied beyond the second absorption solution bottle 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; the flow meter on the air inlet to the gas-mixing bottle was adjusted to permit 100 mL of air per minute 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.

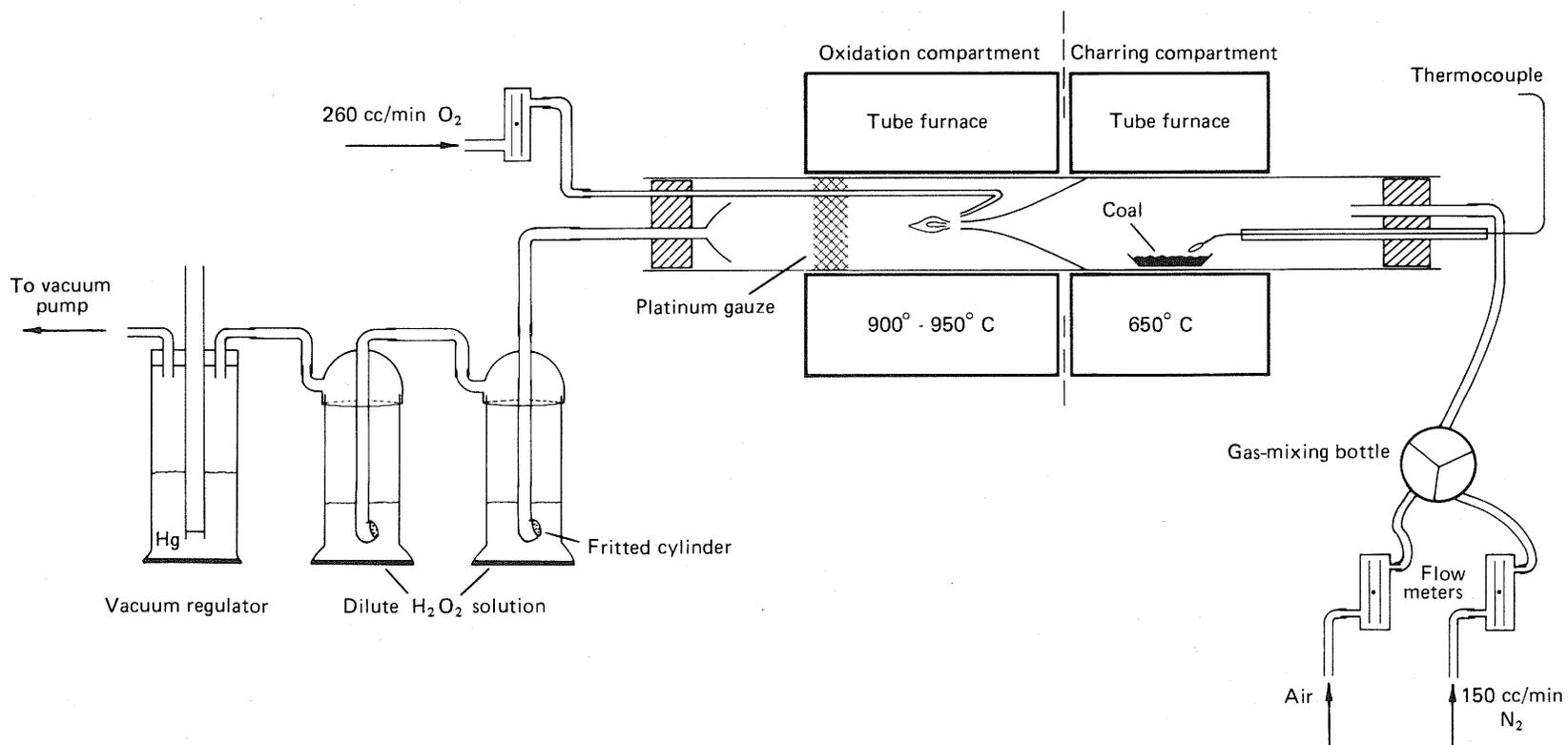


Figure 1
Apparatus for charring coal at 650° C and oxidizing and trapping volatile products.

The coal sample, accurately weighed into a ceramic boat, was heated from 100° to 650°C in about 30 minutes. Charring at 650°C was allowed to continue for 30 minutes, then the char was cooled to room temperature in the nitrogen stream. Developmental work in the charring of coal by Ruch, Chaven, and Kruse (1984) showed that this procedure gave fairly reproducible results for sulfur loss. The volatile products exiting from the charring chamber were oxidized in a stream of oxygen (~260 cc/min) in the quartz chamber in the second tube furnace set at 960°C. The oxidized gases were trapped in two sequential bubblers, each containing 125 mL of 3% H₂O₂ solution. The sulfur oxides collected as sulfate were precipitated as barium sulfate (described in a following section) for weight determination of sulfur and for beta counting. Also, the resulting char was tared, then combusted at 1350°C to measure the total amount of sulfur and the fraction of radioactive sulfur in the char.

Combustion of Coal and Char for Determination of Total Sulfur and ³⁵S

Samples of coal (1 g) or char (0.5 to 0.7 g) were combusted at 1350°C according to the high-temperature combustion method in ASTM standard D3177-82 for total sulfur in coal and coke. The experimental setup is diagrammed in figure 2. The combustion boat contained a weighed amount (0.5 to 1.0 g) of coal or char covered with ~0.5 g activated alumina. The boat was pushed into the combustion zone at a rate slow enough to avoid thermal shock; it was held in the 1350°C zone for 4 minutes. The sulfur oxides formed were collected in two sequential hydrogen peroxide solution scrubbers (125 mL of 3% H₂O₂ in each). The scrubber solutions were transferred to an Erlenmeyer flask, the collecting bottle and the flare tube were washed with water, and the washings were added to the Erlenmeyer flask.

Preliminary experiments were conducted with coal samples spiked with H₂³⁵SO₄ tracer to confirm the complete recovery of radioactivity and of sulfur⁴ from the combustion procedure at 1350°C.

Precipitation of Barium Sulfate for Total Sulfur and ³⁵S Analyses

The hydrogen peroxide scrubbing solutions obtained from the high-temperature combustion or from a charring experiment were acidified to pH 1 with hydrochloric acid, then boiled to remove all carbon dioxide and hydrogen peroxide and to reduce the volume to about 150 mL. The cooled solution was passed through a cation-exchange column (15 cm of Dowex 50W-X8 in a 1 cm diameter x 30 cm length tube), and the column was rinsed with 100 mL of 0.1 N HCl. The solution plus rinse from the column was heated to boiling, then cooled, and 0.1 M BaCl₂ solution in excess, usually about 25 mL, was added. For those samples where a low weight of BaSO₄ (<0.08 g) was expected, a known amount of 0.1 N H₂SO₄ was added to the solution before the barium chloride addition to bring the expected weight of barium sulfate to about 0.15 g. The barium sulfate precipitated was digested for 6 hours. The precipitate was

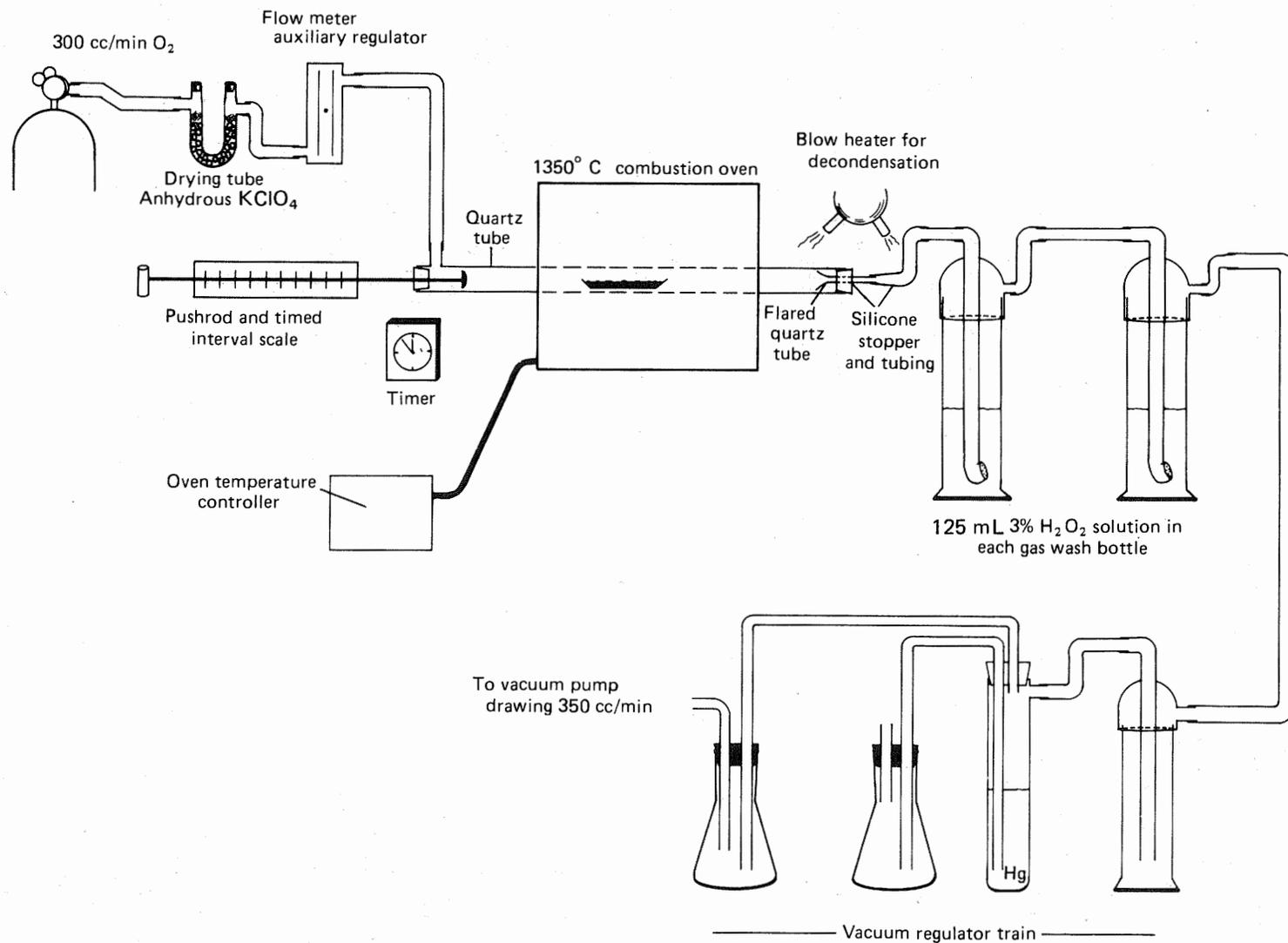


Figure 2
1350°C combustion apparatus for determination of total sulfur in coal and char.

separated by filtration with a Millipore filtration apparatus, using tared polyvinyl chloride Millipore filters (BDWP, 0.6 μm pore size). The precipitate was washed with distilled water and ethanol. The Millipore filter was placed on a tared stainless steel planchet, held flat with a stainless steel retainer ring, and dried in a 110°C oven for 1 hour. The planchet was cooled and weighed. The precipitate was covered with a light, even coat of Krylon prior to beta counting for ^{35}S content.

Preliminary experiments were done with chars from coal samples spiked with the $\text{H}_2^{35}\text{SO}_4$ tracer (1) to test complete recovery of radioactivity in the process of purification of the volatile products and in the precipitation of barium sulfate, and (2) to develop the procedure for precipitation of barium sulfate on the Millipore filter such as would give a reproducible solid sample for beta counting.

The recovery of sulfur from a spiked coal sample, as calculated from the determined weight of BaSO_4 , agreed with the value calculated from the analyzed sulfur contents of the coal and the spike. Yields were, therefore, essentially quantitative, generally between 97% and 101%.

A mass balance for sulfur from a charring run was calculated from the determined weights of the BaSO_4 precipitates from the volatile products collected during charring and from the 1350°C combustion of the char, compared to the analyzed sulfur content of the spiked coal. Yields were thus determined to be quantitative.

Beta Counting of ^{35}S in Barium Sulfate

Beta counting was done on a gas-proportional alpha beta counter (Gamma Products, Inc.). A ^{14}C ($\beta = 0.156$ MeV) disc-reference source was used to establish the optimum operating voltage (1870 volts) for counting ^{35}S with $\beta = 0.167$ MeV. The carbon-14 source was also counted with each series of samples to measure efficiency (about 10%), which is very dependent on gas flow rate and gas composition. All sample counts were corrected to the same efficiency. Samples were typically beta counted for 40 minutes, for a total count of 60,000 to 150,000. Background was monitored but was less than 1 count per minute and was not subtracted.

To obtain reproducible results from beta counting, it was necessary to prepare barium sulfate precipitates in the same manner each time. Filtration with deposition of barium sulfate onto the Millipore filter was always carried out in the same manner to obtain an even layer of precipitate. Stainless steel planchets and retainer rings were of uniform size. Spraying the dried precipitate with Krylon helped to prevent flaking and to limit moisture absorption.

Several samples were beta counted at intervals of one month or more and gave $t_{1/2} = 87$ days, the reported half-life of ^{35}S , indicating that the radiochemical purification was sufficient.

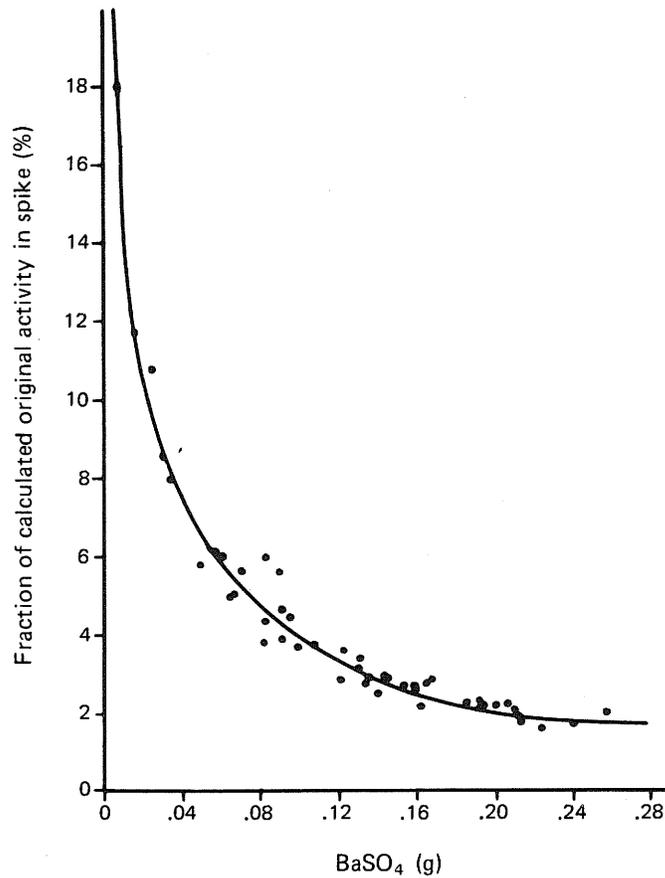


Figure 3
Self-absorption effect for the beta radiation of ^{35}S in barium sulfate.

To compare beta counts from one sample to another, it was necessary to correct for self-absorption of the ^{35}S beta by the barium sulfate. An empirical correction curve (fig. 3) of fraction of self-absorption relative to the weight of barium sulfate precipitate was made. The experimental data were counts on barium sulfate precipitates prepared from the radioactive H_2SO_4 tracer, the radioactive synthetic pyrite, and coals spiked with these or with the radioactive 1.6 S.G. sinks.

Beta counts on samples were compared after standardizing for counting efficiency, counting time, date of count (i.e., decay from a reference T_0), weight of BaSO_4 precipitate, and chemical yield. Total radiochemical yield of the two fractions from a charring run was calculated as a percentage of the $\text{Ba}^{35}\text{SO}_4$ radioactivity obtained from the high-temperature combustion of coals spiked with the same radioactive pyrite sample (either the synthetic pyrite or one of the five 1.6 S.G. sinks).

The amount of activity in a spike for a given weight of BaSO_4 was read from a curve of beta count, which was standardized to the same weight of radioactive spike and corrected to 100% chemical yield of sulfur, relative to the weight of barium sulfate precipitate made for each of the sinks and for the synthetic radioactive pyrite.

RESULTS AND DISCUSSION

The coal samples tested were prepared from one of 13 coals; 11 were from the Herrin (No. 6) Coal, one was from the Springfield (No. 5) Coal, and one was from the Colchester (No. 2) Coal. The results of proximate, ultimate, and sulfur analyses of these coals are listed in table 1. All the coals are high-volatile bituminous in rank. The sulfur, moisture, and ash contents of the five irradiated 1.6 S.G. sinks are listed in table 2. Thirty-one charring experiments were run; the compositions of the spiked coals and their calculated total sulfur and forms of sulfur contents are listed in table 3.

The results of the charring experiments are listed in tables 4 and 5. The fraction of pyritic sulfur evolved in charring was equated to the fraction of the ^{35}S activity measured in the volatile products. The ^{35}S activity in the volatile products and in the char accounted satisfactorily for the total ^{35}S activity in the spiked coal sample. The fraction of the total sulfur evolved in charring was calculated from the weighed amounts of barium sulfate collected from analysis of the volatile products and of the char. Knowing the total, pyritic, organic, and sulfate sulfur in the spiked coal, as well as the percentages of total and pyritic sulfur evolved upon charring, we then calculated the amount and fraction of organic sulfur evolved, with the assumption that the sulfate sulfur remained in the char (although probably as sulfide, [Powell, 1921]). The sulfate sulfur ranged from 0.3% to 8.3% and averaged 3.5% of the total sulfur in the spiked coal samples, so this was not an important source of error.

In 19 charring experiments of coals spiked with synthetic radioactive pyrite, an average and range as defined by one standard deviation about the mean of $42.5\% \pm 5.0\%$ of the pyritic sulfur, $47.4\% \pm 5.7\%$ of the total sulfur and $57.8\% \pm 7.0\%$ of the organic sulfur was evolved. In 9 charring experiments of coals spiked with an amount of irradiated 1.6 S.G. sink fraction, an average ($\pm s$) of $44.0\% \pm 3.8\%$ of the pyritic sulfur, $45.6\% \pm 4.2\%$ of the total sulfur, and $51.5\% \pm 6.9\%$ of the organic sulfur was evolved. (Results for run 158, shown in table 5, are anomalous and will be discussed separately.) The effect of a small amount (1% to 10% of the pyritic sulfur) of organic sulfur in the irradiated sink spikes, when all the radioactivity was calculated as arising from pyritic sulfur, is to overestimate the fraction of pyritic sulfur evolved, and consequently underestimate the fraction of organic sulfur evolved. The effect of a small amount (0.5% to 2% of the pyritic sulfur) of sulfate sulfur in the spike is, similarly, to underestimate the fraction of pyritic sulfur evolved.

Table 1. Chemical composition of coals (as received basis)

Constituent (wt %)	Herrin (No. 6)											Spring- field (No. 5)	Colchester (No. 2)
	C22167	C22169	C22170	C22171	C22172	C22174	C22175	C22176	C22267	C22444	C22447	C22173	C22396
Sulfur	2.33	2.49	2.22	3.60	3.56	0.89	0.99	2.33	3.78	5.10	2.80	4.11	3.61
Pyritic sulfur	0.99	1.42	0.84	2.31	1.37	0.38	0.57	1.38	1.14	2.08	0.67	1.83	2.29
Organic sulfur	1.27	0.94	1.19	1.15	2.08	0.50	0.40	0.87	2.57	2.54	2.12	1.97	1.26
Sulfatic sulfur	0.07	0.13	0.19	0.14	0.11	0.01	0.02	0.08	0.07	0.48	0.01	0.31	0.06
Moisture	6.5	7.3	5.9	5.0	8.5	5.5	5.4	3.7	8.3	10.4	9.0	9.3	1.8
Volatile matter	35.9	32.3	34.6	31.0	36.5	35.2	31.0	30.2	38.8	34.4	37.7	36.5	42.0
Fixed carbon	48.6	47.0	49.8	41.7	42.9	53.8	44.4	43.7	43.5	44.9	44.8	44.4	50.1
Ash	9.0	13.4	9.7	22.3	12.1	5.5	19.2	22.4	9.4	10.3	8.5	9.8	6.0
Carbon	67.20	61.73	66.20	55.41	60.58	71.19	58.77	57.42	62.38	64.77	70.75	63.05	71.88
Hydrogen	5.38	5.02	5.20	4.43	5.32	5.20	4.58	3.96	5.12	4.60	4.70	5.47	6.80
Nitrogen	1.43	1.34	1.38	1.16	1.05	1.15	1.28	1.10	1.01	1.26	1.24	1.10	1.27
Oxygen	14.66	15.98	15.33	13.15	17.40	15.65	15.22	12.79	18.31	13.97	12.01	16.46	10.40
CaO	0.19	0.56	0.37	0.88	0.54	0.12	0.74	0.34	0.48	0.38	0.52	0.76	0.071
MgO	0.070	0.12	0.080	0.22	0.11	0.057	0.26	0.23		0.076	0.082	0.072	0.028
Organic S/ Pyritic S	1.28	0.66	1.42	0.50	1.52	1.32	0.70	0.63	2.25	1.22	3.16	1.08	0.55

Table 2. Sulfur, moisture, and ash content of 1.6 S.G. sink fractions from float-sink separations of coals (as received basis)

Constituent (wt %)	Original coal of 1.6 S.G. sink				
	C22169	C22171	C22173	C22175	C22267
Sulfur	8.77	10.20	14.24	2.66	13.71
Pyritic sulfur	8.21	9.89	13.78	2.50	12.38
Organic sulfur	0.41	0.13	0.24	0.15	1.22
Sulfatic sulfur	0.15	0.18	0.22	0.01	0.11
Moisture	0.3	1.0	0.2	1.5	1.5
Ash	68.1	73.3	49.7	76.6	49.8

Also included at the end of table 5 are the results of a charring experiment (starred) run on a sample of coal C22447 at 650° under nitrogen in an experimental system very similar to the one used in this project (D. D. Coleman, 1983, personal communication). In this experiment, Coleman and coworkers used detectable differences in the natural $^{34}\text{S}/^{32}\text{S}$ ratio of the pyritic sulfur and organic sulfur fractions of this coal to measure the percentages of pyritic sulfur and organic sulfur evolved upon charring. They found that of the sulfur evolved (58%), 28% was pyritic and 66% was organic sulfur.

Experimental error accounts for some of the range in the values for the fraction of sulfur or type of sulfur evolved in coal charring. The reproducibility of the technique for charring a coal under nitrogen at 650°C using this experimental system is indicated by the results of Ruch, Chaven, and Kruse (1984); they reported the yield of char from coal was 73.4%, 70.8% and 73.1%, and the fraction of sulfur lost was 50.9%, 50.3% and 42.6% in three different runs. Table 4 includes the results of four sets of replicates: (1) runs 149 and 163, (2) runs 138 and 160, (3) runs 151 and 164, and (4) runs 144, 150, and 159. Runs 152 and 153 were done with samples prepared from the same coal (C22170) but with different amounts of the radioactive synthetic pyrite as spike: 1.66% and 0.92%, respectively. In table 5, runs 154 and 167 are replicates. Results from runs 150 and 159 agree well, as do results from runs 151 and 164; however, results on the other sets of replicates show that the experimental difference in fraction of total sulfur evolved may be 2% to 5% absolute. Similarly, the error in fraction of pyritic sulfur evolved via radioactivity measurement may be 2% to 5% absolute. Some inhomogeneity in the coals may account for some differences.

Table 3. Composition of spiked coals charred (as received basis)

Charring Run	Coal (wt %)	Spike (wt %)	S (wt %)	Pyritic S (wt %)	Organic S (wt %)	Sulfatic S (wt %)	Ash (wt %)
135	C22173 (98.97)	Pyrite (1.03)	4.62	2.36	1.95	0.31	10.7
136	C22267 (98.79)	Pyrite (1.21)	4.39	1.78	2.54	0.07	10.5
137	C22267 (97.75)	1.6 sink (2.25) of C22267	4.00	1.39	2.54	0.07	10.3
138	C22396 (98.96)	Pyrite (1.04)	4.13	2.83	1.25	0.06	6.9
139	C22173 (98.00)	1.6 sink (2.00) of C22173	4.30	2.07	1.93	0.30	10.6
140	C22171 (97.29)	1.6 sink (2.71) of C22171	3.78	2.52	1.12	0.14	23.7
141	C22169 (96.70)	1.6 sink (3.30) of C22169	2.70	1.64	0.92	0.13	15.2
142	C22171 (98.95)	Pyrite (1.05)	4.12	2.85	1.14	0.14	23.2
143	C22169 (98.45)	Pyrite (1.55)	3.28	2.22	0.92	0.13	14.8
144	C22447 (99.19)	Pyrite (0.81)	3.20	1.09	2.10	0.01	9.2
145	C22167 (98.98)	Pyrite (1.02)	2.85	1.51	1.26	0.07	9.9
146	C22167 (96.94)	1.6 sink (3.06) of C22169	2.53	1.21	1.24	0.07	10.8
147	C22172 (98.98)	Pyrite (1.02)	4.06	1.90	2.06	0.11	13.0
148	C22172 (97.10)	1.6 sink (2.90) of C22173	3.88	1.73	2.03	0.12	13.1
149	C22176 (99.03)	Pyrite (0.97)	2.83	1.89	0.86	0.08	22.3
150	C22447 (99.19)	Pyrite (0.81)	3.20	1.09	2.10	0.01	9.2
151	C22444 (98.88)	Pyrite (1.12)	5.64	2.66	2.51	0.47	11.3
152	C22170 (98.34)	Pyrite (1.66)	3.07	1.72	1.17	0.19	11.2
153	C22170 (99.08)	Pyrite (0.92)	2.69	1.32	1.17	0.19	10.5
154	C22170 (97.41)	1.6 sink (2.59) of C22171	2.43	1.08	1.16	0.19	11.35
155	C22176 (97.48)	1.6 sink (2.52) of C22171	2.53	1.59	0.85	0.08	23.6
156	C22174 (98.87)	Pyrite (1.13)	1.48	0.98	0.49	0.01	6.5
157	C22175 (99.04)	Pyrite (0.96)	1.49	1.07	0.40	0.02	20.0
158	C22175 (90.22)	1.6 sink (9.78) of C22175	1.15	0.75	0.37	0.02	25.0
159	C22447 (99.19)	Pyrite (0.81)	3.20	1.09	2.10	0.01	9.2
160	C22396 (98.96)	Pyrite (1.04)	4.13	2.83	1.25	0.06	6.9
163	C22176 (99.03)	Pyrite (0.97)	2.83	1.89	0.86	0.08	22.3
164	C22444 (98.88)	Pyrite (1.12)	5.64	2.66	2.51	0.47	11.3
165	--	Pyrite (100)	53.45	53.45	--	--	--
166	--	1.6 sink (100) of C22173	14.24	13.78	0.24	0.22	49.7
167	C22170 (97.41)	1.6 sink (2.59) of C22171	2.42	1.08	1.16	0.19	11.35

Beyond experimental error, reasons for the range of results relate to the reactions of sulfur in coal upon charring. When a high-volatile bituminous coal is heated in an inert atmosphere such as nitrogen, loss of volatile material becomes rapid above about 350°C, peaks between 400°C and 500°C, and slows appreciably after about 550°C (Rostam-Abadi and Kruse, 1983). Organic sulfur is evolved with the organic compounds, some as hydrogen sulfide and some as volatile compounds of carbon and sulfur. Pyrite begins to break down at about 500°C (Given and Jones,

Table 4. Fraction of sulfur, pyritic sulfur and organic sulfur evolved, and yield of char in the charring of coal plus radioactive synthetic pyrite at 650°C. Replicate runs of the same spiked coal sample are bracketed. Results are on the basis of weight of the spiked coal.

Run no.	Coal	Char yield(%)	Fraction of radioactivity evolved/in char	Radioactivity yield(%)	Amount(wt%) of S evolved/in char	Grav. S yield(%)	Fraction of total S evolved(%)	Fraction of organic S evolved(%)
145	C22167	65.4	45.3/54.7	99.4	1.32/1.36	94.4	49.3	56.8
143	C22169	68.1	38.0/62.0	100.	1.34/1.82	96.2	42.4	59.0
152	C22170	67.7	45.1/54.9	93.5	1.40/1.66	99.7	45.8	54.2
153	C22170	68.7	42.0/58.0	101.	1.17/1.48	98.4	44.2	53.8
142	C22171	71.7	32.9/67.1	98.8	1.57/2.34	94.9	40.2	63.4
147	C22172	66.2	43.8/56.2	106.	2.14/2.13	105.	50.1	58.5
135	C22173	64.4	46.7/53.3	83.8	2.08/2.34	95.7	47.1	55.3
156	C22174	68.9	51.9/48.1	93.7	0.86/0.68	104.	55.8	64.7
157	C22175	71.7	37.3/62.7	86.0	0.57/1.02	107.	35.8	33.6
149	C22176	70.6	38.3/61.7	99.8	1.18/1.48	94.0	44.6	62.0
163	C22176	72.0	42.6/57.4	96.2	1.25/1.50	97.3	45.5	56.0
136	C22267	63.6	41.0/59.0	101.	2.24/2.11	99.3	51.5	60.2
138	C22396	64.8	32.6/67.4	97.6	1.54/2.44	96.4	38.7	54.3
160	C22396	65.0	42.5/57.5	91.9	1.89/2.15	97.5	46.8	58.8
151	C22444	62.1	42.8/57.2	94.2	2.70/2.84	98.3	48.7	64.1
164	C22444	64.9	42.6/57.4	114.	2.91/2.96	104.	49.6	66.3
144	C22447	62.0	44.0/56.0	103.	1.71/1.31	94.1	56.6	63.4
150	C22447	62.0	48.5/51.5	99.2	1.68/1.41	96.2	54.4	57.0
159	C22447	63.8	48.8/51.2	100.	1.77/1.52	102.	53.8	56.6
165	--	69.8	46.4/53.6	101.	25.3/27.4	98.5	48.0	--
† SUMMARY								
Avg ± s		(19)42.5				(19)47.4	(19)57.8	
		±5.0				±5.7	±7.0	
		(18)42.7				(18)48.1	(18)59.1	
		±5.0				±5.1	±4.0	

† The summary gives the mean and range (one s) of results for the number of runs in parenthesis. Summary of 18 runs omits run 157.

Table 5. Fraction of sulfur, pyritic sulfur and organic sulfur evolved, and yield of char in the charring of coal plus irradiated 1.6 S.G. sink at 650°C. Replicate runs of the same spiked coal sample are bracketed. Results are on the basis of weight of the spiked coal.

Run no.	Coal	Char yield(%)	Fraction of radioactivity evolved/in char	Radioactivity yield(%)	Amount(wt%) of S evolved/in char	Grav. S yield(%)	Fraction of total S evolved(%)	Fraction of organic S evolved(%)
146	C22167	66.1	37.6/62.4	74.7	1.15/1.19	106.	49.1	63.1
141	C22169	69.6	42.6/57.4	88.5	1.03/1.45	91.8	41.5	45.4
154	C22170	69.2	40.0/60.0	106.	1.02/1.38	99.3	42.5	51.8
167	C22170	70.5	44.0/56.0	76.1	1.05/1.43	102.	42.3	47.6
140	C22171	74.4	42.9/57.1	97.0	1.45/2.06	93.0	41.3	42.9
148	C22172	65.6	46.1/53.9	101.	2.06/2.00	105.	50.7	57.6
139	C22173	63.8	46.1/53.9	104.	1.97/2.17	96.2	47.6	56.7
158	C22175	75.1	38.0/62.0	103.	0.35/0.85	104.	29.2	12.8
155	C22176	71.1	45.8/54.2	105.	1.03/1.31	92.5	44.0	44.7
137	C22267	64.1	50.7/49.3	107.	2.07/1.93	100.	51.8	53.9
166	--	78.7	42.5/57.5	70.4	5.45/9.44	105.	36.6	--
*	C22447	59	28 pyritic S				58	66
† SUMMARY								
Avg ± s			(9)44.0 ±3.8				(9)45.6 ±4.2	(9)51.1 ±6.9

* Run by Coleman (personal communication), described in text.

† The summary gives the mean and range (one s) of results for the number of runs in parenthesis. Run 158 is omitted.

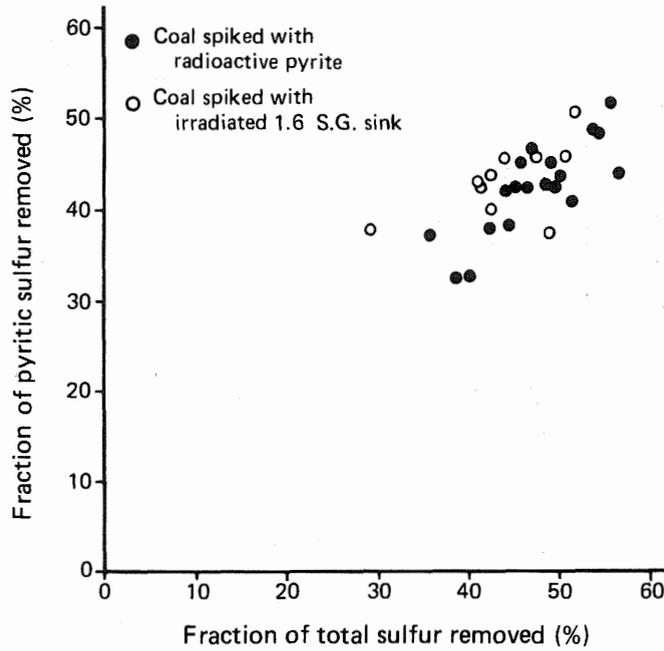
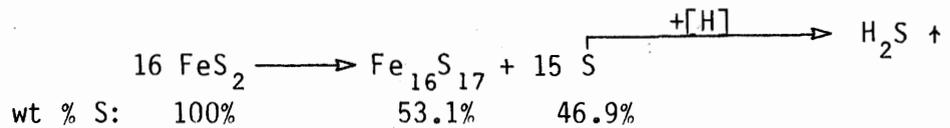


Figure 4
Relationship between fractions of sulfur and pyritic sulfur evolved upon charring of coals at 650°C.

1966) to form pyrrhotite and sulfur, which is evolved mainly as hydrogen sulfide, although reaction with volatile organic material to form volatile compounds of carbon and sulfur is surely possible. A number of investigators, including Černič-Simić (1962), have shown that not all of the sulfur released during the decomposition of coal material or of pyrite escapes: some reacts with other coal material to form new carbon-sulfur compounds, stable and solid to 650°C; and some reacts with other iron compounds and calcium compounds to form iron and calcium sulfides.

X-ray diffraction analysis of coal chars (R. E. Hughes and H. D. Glass, 1983, personal communication) shows that the pyrrhotite formed during the charring at 650°C has a composition approximately $Fe_{16}S_{17}$. If all the pyrite in the coal decomposed thus and all the released sulfur was evolved, according to the equation



46.9% of the pyritic sulfur would be evolved and 53.1% would be left in

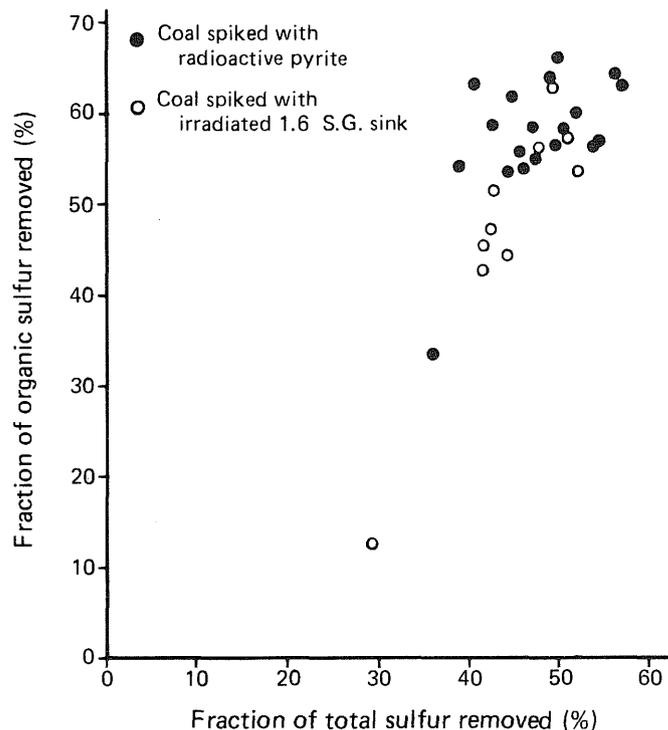


Figure 5
Relationship between fractions of sulfur and organic sulfur evolved upon charring of coals at 650°C.

the char. In the present study, an average value of $42.8\% \pm 4.8\%$ pyritic sulfur evolved in 29 charring runs may be evidence that 1% to 5% of the sulfur dissociated from the pyrite is retained in the char. However, it also may be that $Fe_{16}S_{17}$ does not well represent the pyrrhotite formed in every experiment; a more sulfur-rich pyrrhotite such as $Fe_{11}S_{12}$ may better apply to the formulation. It is also possible that not all the pyrite in a sample decomposes in each charring experiment.

Evidence for incomplete decomposition of pyrite is as follows. Figures 4 and 5 show the relationship between the fractions of pyritic sulfur and of organic sulfur evolved upon charring of the spiked coal samples and the total amount of sulfur evolved. Figure 4 shows that the more total sulfur evolved, the greater is the fraction of pyritic sulfur evolved. But as shown in figure 5, in most of the samples 50% to 65% of the organic sulfur is evolved without regard to the percentage (between 40% and 55%) of total sulfur evolved. These facts are consistent with the observation that organic sulfur comes off easily with the volatile organic matter below 500°C, or rapidly at 650°, and the sulfur released later in the charring process is from the decomposition of pyrite beginning about 500°C; this higher temperature reaction may not be complete in every experiment.

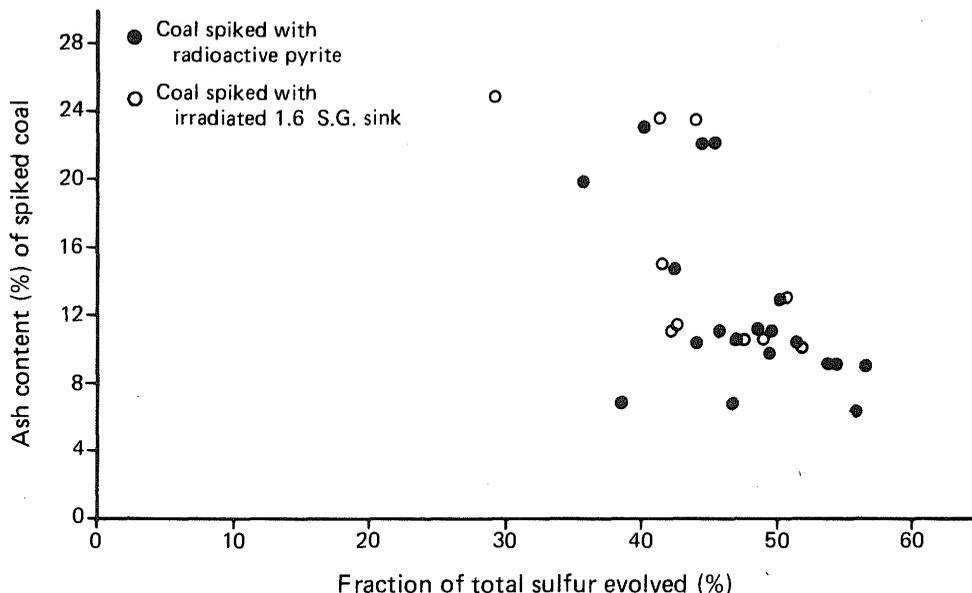
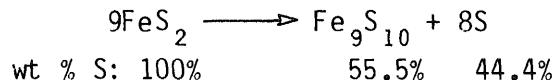


Figure 6
Relationship between ash content of spiked coal samples and fraction of sulfur evolved upon charring of coals at 650°C.

The decomposition of pyrite in coal, when coal is charred at 650°C, can occur both by hydrogen reduction, which is favored at lower temperature, and by thermal decomposition. But when pyrite alone is heated in nitrogen to 650°C it must decompose by thermal decomposition alone (Lambert, 1982). The auto-reduction is not so effective and a more sulfur-rich pyrrhotite, about Fe_9S_{10} in composition as shown by X-ray diffraction analysis (R. E. Hughes and H. D. Glass, 1983, personal communication), results, according to the following equation:



In the one experiment in the present study in which radioactive synthetic pyrite alone was heated at 650°C under nitrogen, run 165, the fraction of sulfur evolved was 46.4% as measured by ^{35}S activity and 48.0% as measured by weight of sulfur. The difference from expected results probably represents experimental error.

Let us consider the effect of coal composition in the discussion of the reasons for the range in the percentages of pyritic sulfur and organic sulfur evolved in the 29 coal charring experiments of this project. Tables 4 and 5 show that the percentages of pyritic sulfur and organic sulfur evolved are fairly consistent among all runs on samples containing the same coal, such as C22170 (runs 152, 153, 154, and 167). Similarly results from runs 147 and 148, using coal C22172, are consistent, as are results from runs 135 and 139 using coal C22173. But

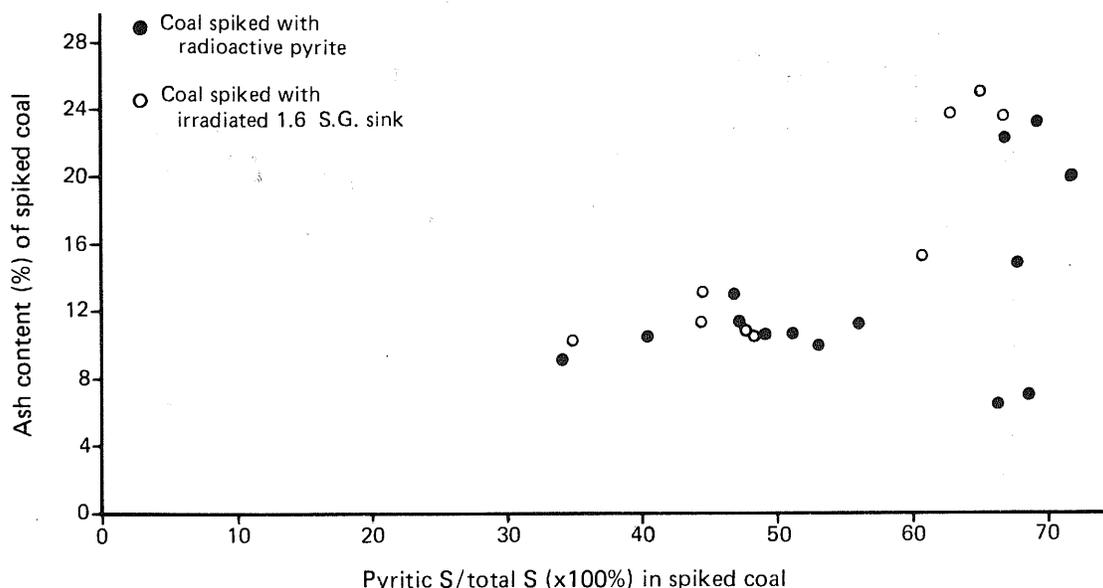


Figure 7
Relationship between ash content and proportion of pyritic sulfur in spiked coal samples.

differences are sometimes large between the results from charring runs on spiked coal samples (i.e. feed coals) prepared with different coals. In particular, the results from runs on samples containing coal C22175 (runs 157 and 158) showed relatively low (37% and 38%) evolution of pyritic sulfur and significantly lower (34% and 13%) evolution of organic sulfur than did results from runs on other coals. C22175 is a very unusual coal: it is high in ash but low in sulfur. Recent results of analysis of the volatile fraction from coal pyrolysis via gas chromatography, (Mei-In M. Chou, 1984, personal communication), indicate that the organic sulfur in C22175 is in a more condensed phase (relatively more aromatic--and therefore less easily degraded) than the organic sulfur in the typical Illinois high-volatile bituminous coal.

To determine whether the percentages of pyritic sulfur, organic sulfur, and total sulfur evolved in charring coals were related to the chemical properties of the feed coals, these three sets of sulfur data were plotted with data on carbon, hydrogen, hydrogen/carbon, volatile matter, ash, calcium (as oxide), magnesium (as oxide), sulfur, and volatile matter on a mineral-matter-free basis (which is the best indicator of coal rank available here) in the feed coals. None of the graphs showed significant correlation between the variables.

Figure 6 is the plot of ash content of the feed coal sample relative to the fraction of total sulfur evolved upon charring. It shows that a greater percentage of the sulfur is evolved when a coal with a lower mineral content is charred. However, figure 7 shows that feed coals with higher ash content are the ones with a higher proportion of pyritic

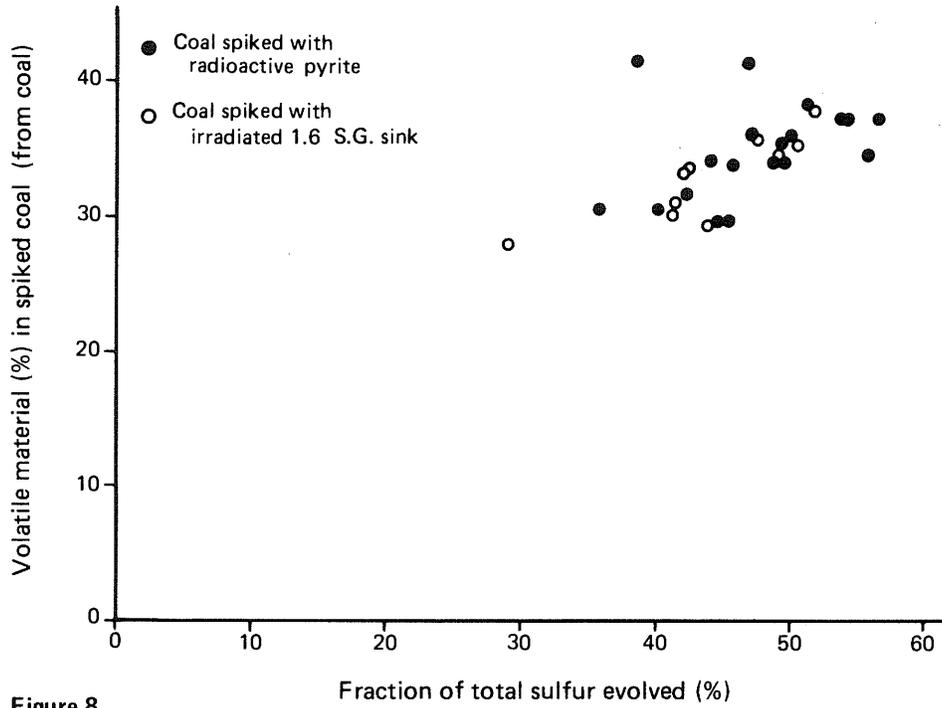


Figure 8
Relationship between volatile matter content of spiked coal (volatile matter content from the whole coal component only) and fraction of sulfur evolved upon charring at 650°C.

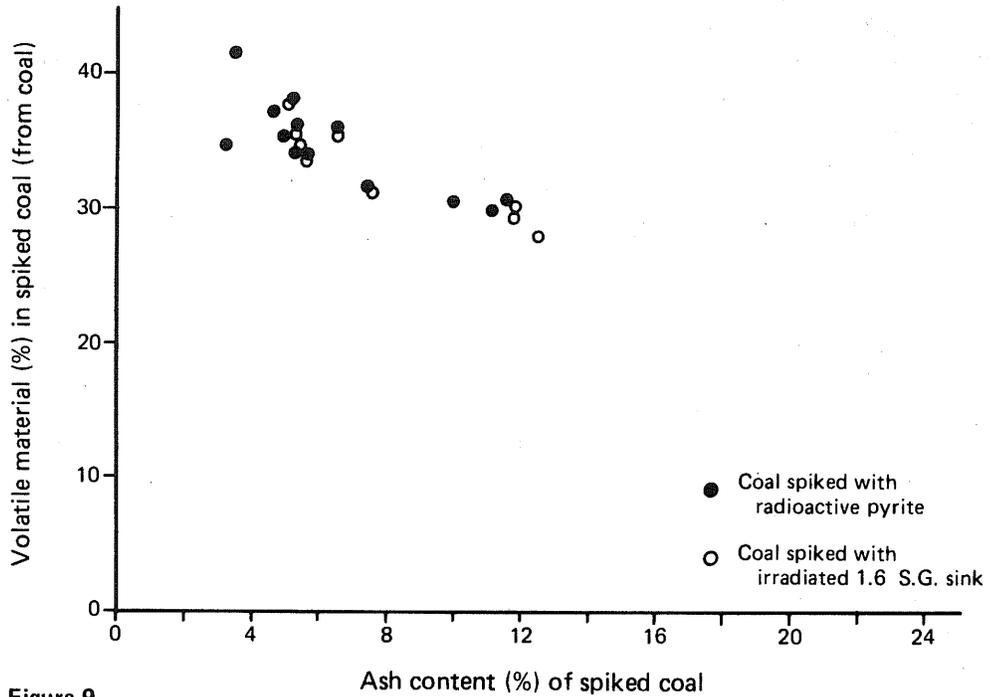


Figure 9
Relationship between volatile matter (volatile matter content from the whole coal component only) and ash content of spiked coals.

study presented, but also the result from the charring of C22447 at 650° under nitrogen by Coleman (D. D. Coleman, 1983, personal communication). In addition, figure 10 shows data from Kruse and Shimp (1981) on chars produced at 650°C. Kruse and Shimp (1981) charred Illinois coals from Saline County (runs CF-134 and CF-135) and Gallatin County (CF-136, -137, -138, and -140) at 650°C in a large charring oven; as a thin bed of coal moved on a conveyor belt through the oven, the volatilized material was bled off in the opposite direction. As their experimental system significantly differed from the laboratory scale system of Ruch, Chaven, and Kruse (1984) that was used both in this project and, with some adaptation, by Coleman (1983 personal communication), data from Kruse and Shimp (1981) need not fit well with the trend of the rest of the data in figure 10. Differences in efficiency of sulfur removal from one project to another will occur because of different experimental parameters such as flow rates, particle size, and rate of temperature increase to charring temperature.

SUMMARY AND CONCLUSIONS

Charring experiments carried out with coals spiked with ³⁵S tracer in this project provided direct evidence concerning the fate of pyritic sulfur and organic sulfur when coal is pyrolyzed. Summarized are the results of charring, at 650° for 30 minutes in a nitrogen atmosphere, 18 samples of Illinois coals spiked with radioactive synthetic pyrite and 9 samples of Illinois coals spiked with an amount of an irradiated 1.6 S.G. sink fraction. (Results from two runs with one low-sulfur coal [C22175] are not included because the coal and the data on its char were considered atypical.)

- An average 43% of the pyritic sulfur in the feed coals was lost on charring. Values ranged from 33% to 52% but most were from 38% to 48%. The results are consistent with the decomposition of pyrite to pyrrhotite and sulfur, which further reacts and is evolved with the volatile matter.
- An average 57% of the organic sulfur in the feed coals was lost on charring. Results ranged from 43% to 66%, but most ranged from 51% to 63%.

Since more organic than pyritic sulfur is evolved and lost with the volatile matter on charring an Illinois coal at 650°, it follows that the greater the ratio of organic to pyritic sulfur in the feed coal, the greater will be the fraction of total sulfur evolved on charring the coal. In the 23 different spiked coal samples charred in this project, organic to pyritic sulfur ratio ranged from 0.37 to 1.93, and an average of 47% of the total sulfur was evolved. Results ranged from 39% to 57% but most were between 42% and 52%.

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