

## VOLATILITY OF COAL AND ITS BY-PRODUCTS

By

J. K. Kuhn, D. Kidd, J. Thomas, Jr.,  
R. Cahill, D. Dickerson, R. Shiley,  
C. Kruse, N. F. Shimp

Illinois State Geological Survey  
Urbana, Illinois

### Abstract

*A number of projects are underway to assess the relationship of trace and minor elements to the volatile and residual products formed during the pyrolysis of coal. Physical and chemical demineralization of coals has shown that, with the exception of organic sulfur, all or nearly all of the trace and minor elements are associated with the mineral matter. Since the minerals cannot be totally removed with current commercial cleaning procedures, their volatility is as important to coal processing as that of the organic constituents.*

*Internal surface area measurements of coals and the chars produced upon pyrolysis show that the surface area is at a minimum at 350°C to 450°C. At this temperature range, most of the volatile matter has been expelled, and the greatest rate of sulfur loss occurs. The surface area increases (to the original area) above this temperature until the original structure is destroyed at 750°C to 800°C.*

*Six coals were pyrolyzed at 450°C and 700°C. Significant losses of some trace elements occurred at the lower temperature, whereas only slightly increased loss occurred at the higher temperature. Of the elements determined, S, In, Cl, Sn, Sb, As, Se, and Hg showed considerable volatilization, whereas others such as Cd and Zn exhibited a lesser degree of loss.*

### INTRODUCTION

The volatility of coal and the elements contained in it are of concern both environmentally and economically. The possible release of trace elements during power generation and conversion processes such as liquefaction and gasification may endanger the environment and be deleterious to catalysts in coal conversion.

A large portion of the many elements contained in the mineral matter of coal may be removed by physical cleaning. The determination of the association of these elements with the organic and inorganic portions of coal is necessary to assess the value of pretreatment procedures. Both the physical characteristics of the coal and the mode of occurrence of the elements in coal have significant effects on the volatility of products formed during power generation and conversion. The projects reported here are directed toward finding information that can be used in evaluating problems in coal utilization.

### Organically Associated Trace Elements

The type of association or combination in which an element occurs in natural materials can influence its reactivity or volatility. Analyses of fractions of coals obtained by specific gravity methods have produced data showing whether elements are associated with the mineral or the organic fractions of coal. A total separation of the mineral matter from the organic matter cannot be made by gravity methods alone, however. Consequently, we have combined physical and chemical methods to achieve more complete separation. Direct analysis of an almost entirely organic fraction should yield definitive information on those elements that are associated with organic matter. If the amounts of elements are sufficiently large, the volatilities of organically combined trace elements might be determined separately from the volatilities of the mineral elements.

To accomplish this, mineral matter was removed from cleaned coal by means of selective chemical dissolution, in which the coal organic fraction was relatively unaltered. A brief summary of the demineralization procedure follows:

1. Raw coal floated at 1.40 specific gravity
2. 2-hr reflux with 10 percent HNO<sub>3</sub>
3. 2-hr digestion with 48 percent HF at 70°C
4. 1-hr digestion with 25 percent HCl at 70°C
5. Vacuum-dry fractions

This procedure may oxidize some of the organic matter; however, any major effect should be indicated by a change in the organic sulfur con-

tent. Table 1 shows the extent of elemental extraction over time for major, minor, and trace elements. The values were normalized for loss of weight from removal of mineral matter.

The data show that acid extraction removes most of the mineral phases from coal. Removal of the mineral matter has little or no effect on the organic sulfur content of the coal; thus, we believe that for most coals the organic portion of the coal is nearly unaltered. After extraction, a total trace element concentration (including Si, Al, and others, but excluding S) of only about 250 ppm remains in most coals.

Table 2 shows the mode (the concentration occurring most frequently) and minima and maxima of the concentrations of some major, minor, and trace elements in the 25 raw and chemically cleaned coals studied in this project. In general, results of these analyses have confirmed conclusions drawn from earlier float/sink studies; e.g., Ge, Be, Sb, and Br have high organic associations in coal; Ni, Cu, Cr, and Hg tend to be in both organic and inorganic combinations; and Zn, Cd, As, and Fe are primarily associated with coal mineral matter. Boron is absent in the chemically cleaned coal, but float/sink data indicate that B is associated mainly with the organic fraction of coal. Therefore, we believe the chemical treatment removes B from the organic matter, perhaps as a fluoride.

Results of chemical extraction of mineral matter from coal are in relative agreement with those obtained by gravity separations, except that the concentration levels of most trace elements in the chemically extracted coals (i.e., organically associated trace elements) are significantly lower than those contained in the lighter, organic-rich float fractions from the same coal. This raises the question of which values more nearly represent the organic portions of coal; those in chemically cleaned coals may be low and those in light gravity fractions may be high.

Recently we have compared some of the data on trace elements from chemically cleaned coals with the concentrations of organically combined trace elements estimated from washability and "organic affinity" curves. The following description of the manner in which such values are calculated was taken from

*Trace Elements in Coal: Occurrence and Distribution* by Gluskoter et al. (1977). Figure 1 presents both unadjusted (standard) and adjusted, normalized washability curves for zinc in a sample of the Herrin (No. 6) Coal Member. In the standard (unadjusted) washability curve (Figure 1a), the extrapolated ordinate intercept is approximately 4.5 ppm. The adjusted curve intercepts the ordinate at zero, and the curve reaches the zero zinc value at approximately 90 percent recovery (90 on the abscissa). A portion of the mineral matter estimated to be inseparable has been subtracted from the normal curve to produce the adjusted curve; the adjusted cumulative curve (Figure 1b) was constructed after the value,  $F$ , was determined, as in the following example for zinc, and subtracted from each of the 5 datum points.

$$\begin{aligned}
 F &= \frac{LTA(Light)}{LTA(1.60 S)} \times Zn(1.60 S) \\
 &= \frac{6.10}{77.80} \times 250 \text{ ppm} \\
 &= 19.6 \text{ ppm}
 \end{aligned}$$

$LTA(Light)$  is the percentage of low-temperature ash in the lightest float fraction.

$LTA(1.60 S)$  is the percentage of low-temperature ash in 1.60 sink fraction

$Zn(1.60 S)$  is the concentration in 1.60 sink fraction (ppm).

If the value of a datum point was negative after  $F$  was subtracted from the reported concentration, the value was taken to be zero. A fourth-order polynomial curve was drawn to best fit the data points. Thus, in the case of Zn, the net effect was a general lowering of the curve. The area beneath the curve is proportional to the element's organic affinity, and the intersection of the curve with the vertical axis is an estimate of the Zn concentration associated with organic material.

Tables 3, 4, and 5 are typical examples of element concentrations in raw coals and their respective organic-rich fractions which were

**TABLE 1**  
**EFFECT OF PHYSICAL AND CHEMICAL TREATMENT**  
**ON THE CONCENTRATIONS OF SOME ELEMENTS**  
**IN AN ILLINOIS NO. 6 COAL SAMPLE**

Element	Raw coal		1.40 float		1-hr treatment		2-hr treatment	
	%	ppm	%	ppm	%	ppm	%	ppm
Al	1.40		1.08			124		35
Si	3.20		2.15			250		41
Ca	.51		.094			33		25
K	.13		.11			1		1
Na	.04		.027			7		5
Cl	.05		.02			390		390
S	6.45		3.59		2.64		2.52	
Fe	2.60		.90			170		66
Ti	.06		.08			25		11
Organic S	2.55		2.66		2.64		2.52	
P		50		13		9.7		<1.0
As		3.4		2.8		.088		.062
Pb		<.1		<.1		<.1		<.1
Br		3.5		3.4		2.4		2.9
Cu		13		13		3.4		2.1
Ni		24		7.5		2.5		<1
Zn		43		20.5		8.8		4.4
V		36		28		6.1		3.5
Rb		23		10.3		<1		<1
Cs		2.0		.66		<.1		<.01
Ba		54		42		21		3.6
Sr		28		10.3		1.80		1.3
Sc		4.1		2.8		.88		.53
Cr		21		16.8		8.8		6.2
Co		5.5		3.7		.35		.35
Ga		2.4		2.8		.88		.62
Se		4.3		1.4		.18		.26
Sb		.49		.19		.088		.088
Hf		1.1		.46		.088		.088
W		.59		.28		.088		.052
La		6.1		3.4		.88		.61
Ce		25		7.3		1.8		1.5
Sn		.86		.8		.44		.35
Eu		.26		.19		.09		.088
Dy		1.2		.56		.53		.44
Lu		<.02		.02		.03		.02
Yb		.84		.46		.22		.20
Tb		.45		.09		.09		.09
Th		3.6		1.9		.88		.88
U		1.9		.46		.18		.09
Mo		18		3.5		.53		.44
Hg		.23		.066		.044		.044
Mn		60		10.3		.35		.26

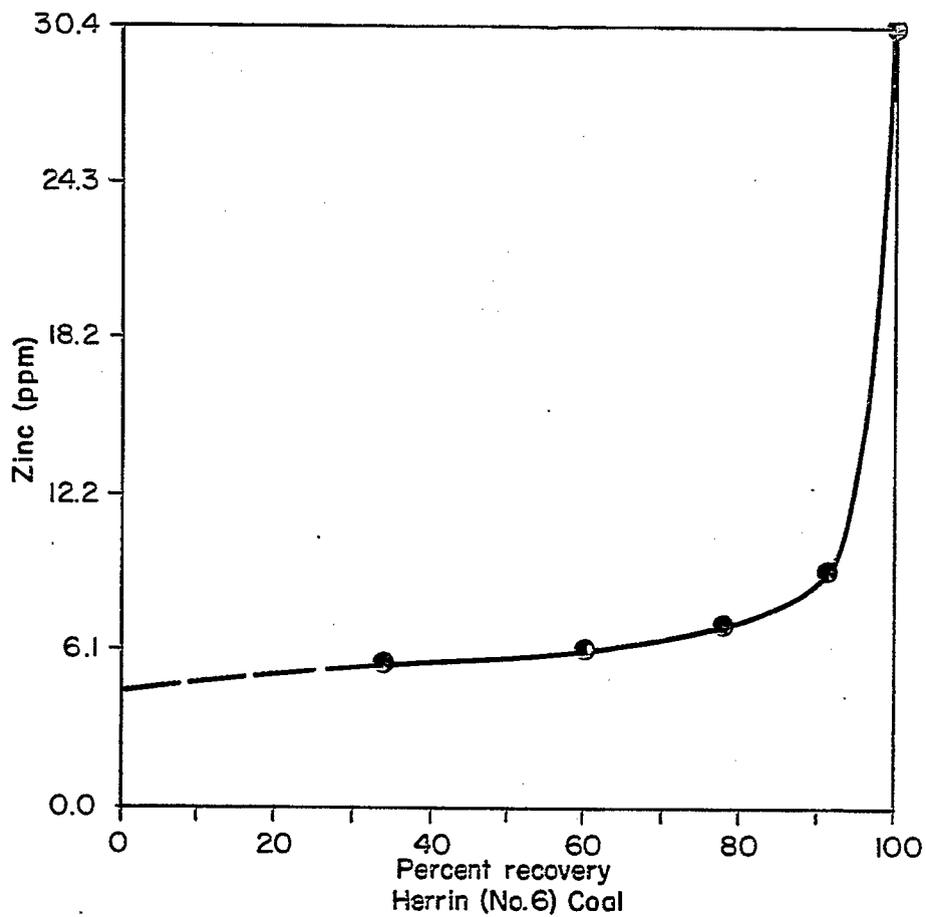
NOTE: All values normalized to raw coal.

TABLE 2

**MODES, MAXIMA, AND MINIMA OF CONCENTRATIONS  
OF ELEMENTS FOR 25 RAW AND CHEMICALLY CLEANED COALS**

Element	Raw coal				Mineral-free coal					
	Mode		Minimum		Mode		Maximum		Minimum	
	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Al	1.10	1.60	.36		41		143		22	
Si	2.59	3.47	.71		37		62		26	
Ca	.51	3.30	.18		18		57		7	
K	.14	.21	.02		4		200		<1	
Na	.04	.15	.01		5		25		<1	
S	1.43	6.45	.49		.79		2.52		.28	
Organic S	.77	2.52	.25		.79		2.52		.28	
Fe	1.95	2.96	.31		86		110		66	
Ti	.06	.08	.02		18		35		2.1	
P	50	200	10		4.5		19		<1	
As	4	9.4	1.2		.25		.50		.046	
Pb	4	56	<.1		.7		1.1		<.1	
Mo	14	26	.7		.44		.55		.37	
Cu	12	92	2.1		3.4		8.8		.7	
Ni	18	29	2.9		2.1		4.6		<1	
Zn	46	328	16		4		4.6		<1	
V	36	62	5.4		3.5		6.4		2	
Ba	78	500	41		10		20.9		2.9	
Cr	16	46	6		3		7		.28	
Br	15	33	.9		7		24		.1	
Mn	42	69	12		.28		.7		.19	
Co	7	15	.6		.34		1.5		<.04	
Ga	2.4	3.8	.8		.47		1.0		.38	
Se	2.0	4.3	1.1		.26		.7		<.1	
Sb	.4	2.5	.19		.28		.46		.088	
Hg	.14	.23	.06		.055		.060		.044	
Sr	32	190	23		4.6		15		<1.3	

(1a)



(1b)

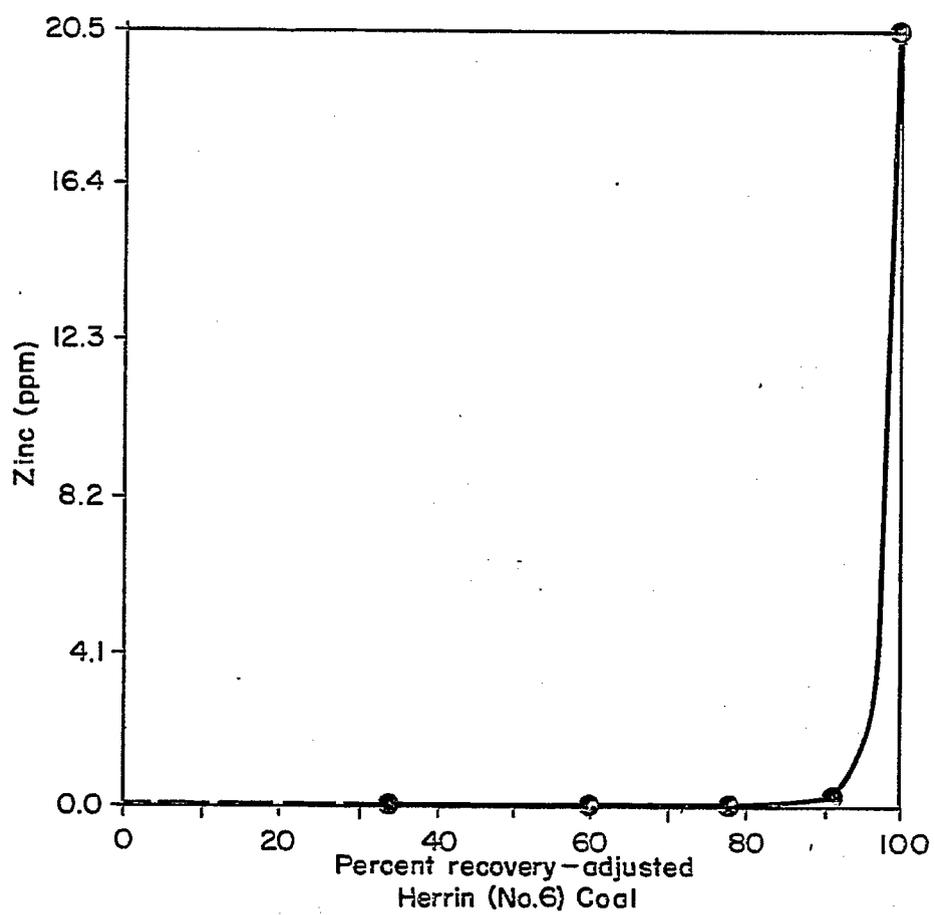


Figure 1

**TABLE 3**  
**ELEMENTAL CONCENTRATIONS**  
**IN AN EASTERN COAL (C-1<sup>0</sup>820)**

Element	Raw Coal		F/S EXT		MMF	
	%	ppm	%	ppm	%	ppm
Al	1.41		0.0			69
Ca	.56		.11			34
Fe	.56		.34			72
K	.23		.0			<10
Si	2.51		.0			56
Ti	.12		.01			19
Mg	.06		.00			18
Na	.07		.00			.5
Organic S	.50		.60		.47	
Br		24		27		16
P		26		13.7		.1
V		22		.00		1.5
Mn		14		1.6		.5
Sn		.3		1.0		<.1
B		12		2.0		9.7
Cu		20		6.7		6.5
Co		7.5		7.9		6.5
Ni		12		12		5
Be		.88		.94		.11
Cr		20		3.5		6.3
Mo		4.6		1.7		<1.0
Sr		96		82		50
Pb		1.6		.6		LD
Zn		12		1.1		.3
Cd		<.1		.09		<.1
As		15		.29		<.5
Ga		4.2		1.1		.7
Se		5.8		1.1		1.0
U		1.0		.15		.2
Ba		180		118		33
Ce		31		7.5		.1
Hf		1.5		.19		.2
La		19		5.8		5
Lu		.12		.04		.05
Rb		<.1		0.0		<.1
Cs		2.0		.0		.2
Sc		3.3		.9		2.0
Sm		1.5		.76		.9
Tb		.4		.13		.27
Dy		2		.86		.9
I		2.6				1.4
Ta		.12		.05		.09
Yb		.6		.24		.06
Te		.3				<.1
Th		6.2		.53		1.1
W		.5		.43		.12
Eu		.47		.19		.2
Sb		4.6		.36		<.4

ISA

129 m<sup>2</sup>/g

TABLE 4  
ELEMENTAL CONCENTRATIONS IN  
AN ILLINOIS NO. 6 COAL (C-18560)

Element	Raw Coal		F/S EXT		MMF	
	%	ppm	%	ppm	%	ppm
Al	1.40		0.0			41
Ca	.51		0.0			25
Fe	2.60		0.0			66
K	.13		.02			<1.0
Si	3.20		0.0			41
Ti	.06		.01			20
Mg	.06		0.0			21
Na	.04		.01			6
Organic S	1.87		2.36		1.81	
Br		13.4		24		3.3
P		50		0.0		<1.
V		36		34.5		3.5
Mn		62		0.0		.3
Sn		.4		0.0		<.1
B		200		38		6.6
Cu		13		2.3		2.1
Co		7.2		1.42		.36
Ni		24		5.5		<1.0
Be		1.4		.68		.03
Cr		20		21		6.8
Mo		11				.52
Sr		33		1.7		1.5
Pb		<1		.03		<1
Zn		57		.0		1
Cd		<.1		0.0		<.1
As		3.4		0.0		<.07
Ga		2.4		0.0		.73
Se		4.3		0.0		.26
U		1.9		5.3		.09
Ba		54		0.0		.2
Ce		25		0.0		.1
Hf		1.1		.05		.11
La		6.1		0.0		.72
Lu		.1		.02		.03
Rb		23		0.0		<1.0
Cs		2.0		.01		.1
Sc		4.1		.57		.65
Sm		.86		.11		.41
Tb		.1				.1
Dy		1.2		.61		.5
I		1.2				<.8
Ta		.12		.03		.09
Yb		.84		.05		.23
Te		1.				<.1
Th		3.6		.33		1.0
W		.6				.06
Eu		.26		.05		.1
Sb		.5		.47		.09

ISA

173 m<sup>2</sup>/g

**TABLE 5**  
**ELEMENTAL CONCENTRATIONS**  
**IN A WESTERN COAL (C-19000)**

Element	Raw Coal		F/S EXT		MMF	
	%	ppm	%	ppm	%	ppm
Al	1.40		0.0			87
Ca	.46		.64			20
Fe	.40		.27			65
K	.02		.00			<10
Si	1.40		0.0			87
Ti	.06		0.0			54
Mg	.07		.06			<20
Na	.17		.15			1.4
Organic S	.38		.38		.32	
Br		.9		1.2		1.0
P		120		91		<4
V		7.1		8.1		<5
Mn		8.3		.68		.4
Sn		<.2		0.0		<.2
B		37		37		5.3
Cu		4.7		2.0		<3
Co		.9		.5		.5
Ni		2.6		1.14		<1.5
Be		.39		.33		.03
Cr		3.4		.98		1.4
Mo		--		--		--
Sr		204		111		
Pb		LD		0.0		LD
Zn		3		4.7		<.5
Cd		<.1		.09		<.1
As		1.1		0.0		.2
Ga		2.3		0.0		.15
Se		1.6		.43		.6
U		.7		.13		.05
Ba		265		218		15
Ce		5.9		3.6		1.2
Hf		.64		.11		.20
La		6.0		1.36		1.3
Lu		.08		.03		.03
Rb		1.20		.34		<1.0
Cs		.11		.0		<.05
Sc		1.3		.50		.42
Sm		.80		.06		.03
Tb		.10		.03		.07
Dy		.65		.39		LD
I		.61				.3
Ta		.10		.01		.LD
Yb		.84		.05		.23
Te		.6				.2
Th		1.4		.00		0.6
W		1.2		.03		.LD
Eu		.15		.03		.05
Sb		.35		.09		.18

ISA

240 m<sup>2</sup>/g

estimated from adjusted washability curves (F/S EXT) and from analysis of the acid-washed mineral-matter-free (MMF) residues. Data are given for an eastern U.S. coal, the Illinois Herrin (No. 6) Coal and a western U.S. coal. Comparison of concentrations for F/S EXT and MMF shows that the majority are in close agreement. Exceptions include Ca, Fe, Be, and B in the eastern coal; Br, V, Be, U, and Sb in the No. 6 Coal; and Ca, Fe, Mg, Na, P, B, Be, Zn, and Ba in the western coal. It is likely that minor elements, i.e., major ash-forming elements such as Ca, Fe, Mg, and perhaps P, are for the most part inorganic but are incompletely removed during float/sink gravity separations. It is also likely that Na and Ba in the western coal; Br in the No. 6 Coal; B and Be in all three coals; and, perhaps, Se in some Illinois coals (not shown) are actually organic, as indicated by float/sink tests, but appear to be inorganic from the acid extraction evidence. That is, these elements may be loosely combined with the organic coal material and easily displaced from it by the acid treatment.

Although these data are still being combined with results from on-going pyrolysis and volatility studies, some preliminary conclusions can be drawn. Table 6 summarizes the means and correlations of the sulfur values determined for the mineral-free material and the values for organic sulfur obtained using the standard ASTM method (D2492) for analysis of raw coal. The means are in close agreement, which indicates that for the 25 coals analyzed in this study, the pyritic sulfur is quantitatively removed by the ASTM procedure.

The correlations between organic sulfur and the other elements determined in the coal samples are listed in Table 7. It is apparent that correlation with organic sulfur is not an indicator of the organic association of other elements. The data show that a significant correlation exists only if those elements were introduced into the coal-forming swamp at or near the same time as the organic sulfur or if the geochemical properties were sufficiently similar to cause deposition under similar conditions.

Table 8 shows the mean and standard deviation of the concentrations of 11 mineral-matter-free Illinois No. 6 Coal samples. Since

some of the deviations equal or exceed the mean concentration, each coal must be evaluated separately in order to make predictions about organic associations and their effect on reactions during processing.

Finally, the data imply that most of the organically associated elements are rather weakly bound, having been deposited after the formation of the coal. Moreover, for the elements studied, no more than a very few parts per million can be considered an inherent part of the organic molecules. Therefore, it can be presumed that pollution or problems in coal combustion, liquefaction, or other processes will for the most part be associated with the inorganic matter in the coal. It is still possible, however, that enhanced volatility of an organically associated trace element could lead to its concentration in a process steam (gas or liquid effluent).

#### VOLATILE PRODUCTS FROM PYROLYSIS OF COAL

Volatilized constituents—organic and inorganic—from coal can be obtained by means of devolatilization of coal at low ( $\leq 250^\circ\text{C}$ ) and medium ( $250^\circ\text{C}$  to  $650^\circ\text{C}$ ) temperatures. Determination of these constituents and their relation to variations in the physical and chemical characteristics of different coals should yield information concerning the structure of coal as related to carbonization, gasification, and liquefaction. For this purpose, we have used several pyrolysis systems; Figure 2 shows the system as recently modified. Chars were prepared from 12 different coals by heating at temperatures ranging between  $200^\circ\text{C}$  and  $900^\circ\text{C}$  in  $50^\circ\text{C}$ -to- $100^\circ\text{C}$  steps. Analyses of the char and comparison with analysis of the whole coal yielded the following results:

1. Most coals exhibited similar behavior. For example, the Herrin (No. 6) Coal from Illinois, heated in steps to  $700^\circ\text{C}$ , showed a reduction of sulfur from 4.5 percent in the raw coal to 1.5 percent in the char, a 66 percent loss of sulfur on a whole-coal basis. Most of the sulfur was lost while the coal was heated between  $300^\circ\text{C}$  and  $400^\circ\text{C}$ .

**TABLE 6**  
**CONCENTRATIONS OF SULFUR IN 25 COAL SAMPLES**

Type of coal	Number of samples	Mean percentage of organic sulfur in whole coal	Mean percentage of sulfur in MMF coal	Correlation coefficient
Eastern	5	.99	.95	1.00
Western	5	.43	.42	.96
Illinois No. 6	11	1.70	1.71	.98
Illinois No. 5 to No. 2	4	1.26	1.26	.99

NOTE: Values have been normalized to the same weight basis.

**TABLE 7**  
**CORRELATION BETWEEN ORGANIC SULFUR AND OTHER ELEMENTS**

Element	Correlation coefficient	Element	Correlation coefficient	Element	Correlation coefficient
Al	-.16	B	.33	Ce	.10
Br	-.22	Cu	.24	Hf	-.14
Ca	.26	Co	-.35	Te	-.06
Fe	-.14	Ni	-.28	La	-.14
P	-.12	Be	-.18	Lu	-.35
K	.03	Cr	-.04	Eu	-.10
Si	-.21	Mo	.07	Cs	-.50
Ti	-.21	Sr	.12	Sc	-.27
V	-.16	Zn	.12	Sm	-.01
Mg	.14	As	-.13	Dy	-.45
Mn	.08	Ga	.44	I	-.21
Na	.01	U	.00	Th	.12
Sn	.06	Ba	.04	Sb	.07

**TABLE 8**  
**CONCENTRATIONS OF ELEMENTS IN 11 MMF ILLINOIS NO. 6 COALS**

Element	Mean (ppm)	Standard Deviation	Element	Mean (ppm)	Standard Deviation
Al	60	14	Cu	3.5	1.6
Br	3.9	2.4	Co	.4	.2
Ca	42		Ni	5.7	5.4
Fe	63	28	Be	.04	.03
P	4.3	3.5	Cr	6.4	2.2
K	8.4	15	Mo	.8	.5
Si	56	20	Sr	4.2	3.3
Ti	30	15	Pb	1.8	3.2
V	7.1	4.4	Zn	1.7	1.3
Mg	28	9.8	Cd	.5	.5
Mn	.4	.2	As	.15	.07
Na	6.4	3.8	Ga	.6	.1
S	1.70	.48%	Se	.4	.2
Sn	.9	1.0	U	.2	.1
B	7.6	1.4			

Revised Pyrolysis Unit

Retort modification June 24, 767-48

Furnace modification June 28, 767-58

Collection modification July 1, 767-71

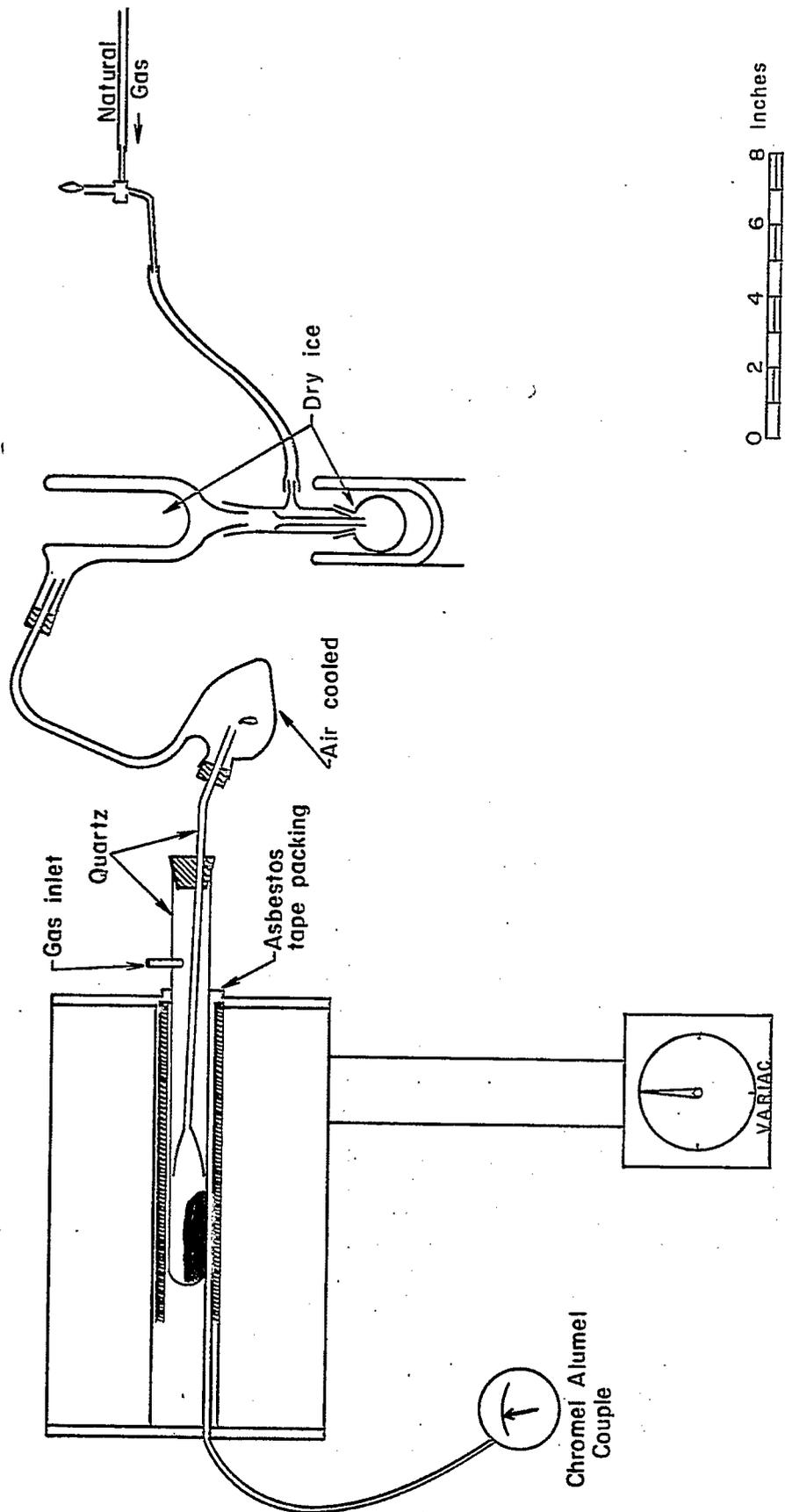


Figure 2

2. Only a small amount of sulfur was lost while the char was heated to 700°C. The greatest rate of sulfur loss occurred over the same temperature range (300° C to 400° C) at which the coal char exhibited maximum Gieseler fluidity and minimum internal surface area (ISA).
3. The internal surface area of pyrolysis residues increased slightly when a coal was heated to about 300°C; ISA then exhibited a rapid decrease, reaching a minimum at 350° C to 400° C. As the coal was further heated to about 700° C to 750° C, the ISA increased to approximately its original level. Heating above 750°C completely destroyed the original coal structure, and the ISA decreased. Thus, we may conclude that a coal changes continually as it is heated to higher temperatures in an inert atmosphere (nitrogen); the greatest change occurs as the coal passes through the 350°C-to-450°C range, at which it reaches maximum Gieseler fluidity, minimum surface area, greatest rate of sulfur loss, and release of the majority of volatile organics.

Because of the typical pyrolysis pattern observed, it has been concluded that for our studies the two most important temperatures for which volatility data need to be obtained are 450°C and 700°C. At 450°C reactivity is highest and most volatile products are released; at 700°C all volatile products are released but the coal structure (ISA) is still intact.

From iron-sulfide-phase equilibria studies, it is known that pyrite breaks down to pyrrhotite and sulfur at 743°C; however it appears that the pyrite contained in coal is converted to pyrrhotite at 450°C or lower in a nitrogen atmosphere. This is shown by X-ray diffraction analysis and scanning electron microscopy with energy-dispersive X-ray analysis of the mineral matter from the raw coals and of the chars produced by pyrolysis. Chemical analyses also indicate a greater loss of sulfur from the pyrite than organic sulfur at low

temperatures, whereas the reverse is true at high temperatures (> 450°C).

Determinations of trace elements for the whole coals and the resulting chars indicate that certain trace elements are lost through heating. The importance of assessing the levels and fate of trace elements volatilized during coal utilization is of concern from both economic and environmental standpoints. Highly volatile species may be lost from some conventional power plant emission control devices. The extent to which volatile species will create new hazards in coal conversion is unknown, and the effect of trace elements on conversion catalysts is still uncertain.

Six coals (Table 9) are currently being studied for trace-element volatility during pyrolysis under an inert gas (N<sub>2</sub>) flow at 450°C (and later at 700°C) in order to simulate conditions in gasification and liquefaction. The percentage weight loss during pyrolysis is given in Table 10. Table 9 lists preliminary results of energy-dispersive X-ray fluorescence (XES) analyses of both the raw coals and the char residues. (Char values have been corrected for apparent concentrating effects from losses of volatile matter.) Indium, Sn, and Sb are volatilized and lost during pyrolysis, and Cd and Zn appear to be volatilized to a lesser degree. Support for this comes from atomic absorption analyses that indicate very small amounts of Cd are present in the trapped volatile fraction. Results based on instrumental neutron activation analysis (INAA) and wavelength-dispersive X-ray fluorescence (XRF) analysis indicate that As, Cl, Br, S, and Se are also lost in varying degrees while most other elements remain in the residue or are lost in amounts too small to be detected.

Direct analysis of the condensed volatiles from the pyrolysis system has proved to be difficult. The condensate is a tarlike material that is difficult to process without risk of contamination or loss. The quantities of trace elements are so low that lack of sensitivity is a problem in the determination of some elements by XRF methods. Such a material can also present a problem for INAA during irradiation in a nuclear reactor. Charcoal traps have been used to collect volatile species; however, with this

TABLE 9  
PRELIMINARY XES DATA FOR PYROLYSIS OF SIX COALS

Element	C-18440		C-18571		C-18571-F		C-18847		C-18857		C-18185	
	Raw Coal	450°C	Raw Coal	450°C <sup>a</sup>	Raw Coal	450°C	Raw Coal	450°C	Raw Coal	450°C	Raw Coal	450°C
Cd	2.3	2.3	3.3	1.6	1.8	0.8	1.4	0.9	1.9	0.75	7.0	7.0
In	2.6	0.72	1.7	0.10	1.9	<0.1	2.0	<0.1	0.9	<0.1	0.8	<0.1
Sn	5.0	1.0	6.9	0.18	5.1	0.8	3.9	<0.1	2.2	.68	1.4	<0.1
Sb	5.6	2.0	5.2	0.07	5.8	1.0	5.0	<0.1	1.9	<0.1	3.3	<0.1
Te	1.3	4.4	0.7	0.56	0.9	0.3	1.5	1.4	0.8	1.1	0.5	1.8
I	3.9	8.5	2.7	1.4	1.4	0.8	3.2	3.0	1.8	1.4	2.5	2.8
Cs	9.2	26.9 <sup>b</sup>	2.7	3.8	2.9	2.0	8.6	8.4	3.3	3.3	2.4	8.9 <sup>b</sup>
Ba	337	1205	44	48.5	34.3	35.1	202	241	51	53.8	40	302
La	8.1	10.7	8.8		6.3	4.9	13.5	13.9	10.8	8.9	4.9	8.1
Ce	8.7	13.6	9.2		9.7	7.0	20.4	24.7	10.0	11.5	8.9	12.3
Zn	3.7	14.3	84.5	48.3	21.8	18.3	13.7	12.1	35.3	45.7	323	246
Br	2.3	2.8	7.2	10.0	10.1	7.1	2.7	1.9	9.1	5.7	4.4	5.0
Rb	4.9	6.4	12.1	11.1	10.3	8.6	14.0	10.9	12.3	10.0	9.2	9.4
Sr	241.	245.1	27.5	30.4	21.7	19.6	68.2	59.3	29.8	26.4	22.0	27.5

NOTE: All values expressed as  $\mu\text{gr}/\text{gr}$ .

<sup>a</sup>Average of two determinations

<sup>b</sup>Interference from Ba

TABLE 10  
PERCENTAGE VOLATILE MATTER LOST DURING PYROLYSIS

Sample number	Seam and state	Percentage weight loss at 450°C
C-18857	No. 6 Illinois	32.2
C-18571	No. 6 Illinois	27.5
C-18571F	No. 6 Illinois	30.3
C-18440	Lignite North Dakota	33.9
C-18185	No. 5 Illinois	27.0
C-18847	Blue Creek Alaska	8.4

approach total entrapment is never certain, and the blank levels in the charcoal itself are often high and variable.

Consequently, work is progressing on a new laboratory trapping system of greater capacity. The system consists chiefly of a Parr reactor vessel; a water-jacketed, large-bore glass column packed with small pieces of plastic tubing to slow the gas stream and decrease the size of the bubbles; and the associated cold traps ( $-30^{\circ}\text{C}$  and  $-80^{\circ}\text{C}$ ). The column through which the volatile gases are bubbled contains acetone and methanol to dissolve organics and dimethoxypropane to react with any water in the system to form acetone and methanol. A resin for adsorbing organics has been used, but no trace elements were detected in it. With this system, when high volatile "A" coals were pyrolyzed, thick condensed tars have tended to collect and plug the gas inlet from the Parr reactor. In addition, some gas is still lost from the final cold trap when it is warmed to room temperature.

Attempts are being made to concentrate the volatile trace elements, if any, by burning the trapped organic material and then retrapping the released trace elements in a scrubber from which they can be precipitated. For some very volatile gases, it may be possible or even necessary to pass them directly from the pyrolysis unit to a combustion unit for trapping the trace elements. The volatile organic material given off contains innumerable compounds. Efforts are being made to identify those that contain sulfur by subjecting the sample of volatile organics to an acid-base-neutral compound separation. The three fractions thus obtained are then analyzed for the relative distribution of sulfur compounds by means of a gas liquid chromatograph equipped with a

sulfur-specific flame-photometric detector. As expected, the major portion of the sulfur-containing compounds are in the neutral fraction. A few are in the basic fraction and fewer still in the acid fraction. An attempt is being made to identify the more clearly separated compounds by gas chromatography-mass spectroscopy.

Because the concentrations of some volatile trace elements are very low, a continuous-feed pyrolysis furnace is under construction. This unit will allow the pyrolysis of coal in sufficient amounts that concentrations of traces of additional volatile components can be detected and quantified.

#### BENEFICIATION OF CHAR

Three coal samples have undergone various pyrolytic treatments in a preliminary study to determine the effect of heat on the composition of the char produced and on subsequent beneficiation of the charred residues. The first of these, a Herrin (No. 6) Coal sample from Illinois, was heated under nitrogen in a Parr pressure reactor at  $600^{\circ}\text{C}$  for 48 hours, and the residue was separated into magnetic and nonmagnetic fractions (coal A, Table 11). The second sample, also from the Herrin (No. 6) Coal Member, was heated in the Parr pressure reactor at  $650^{\circ}\text{C}$  for 20 hours and again separated into magnetic and nonmagnetic fractions. (In addition, samples of this char are currently being subjected to Mossbauer, electron probe, and scanning electron microscope analyses to determine various mineral phases.)

Differences in the composition of the magnetic and nonmagnetic fractions of these two coals, as determined by X-ray fluorescence, are shown in Table 11. Per-

TABLE 11  
PERCENTAGE IRON CONCENTRATION IN MAGNETICALLY  
SEPARATED, HEATED COALS

	Coal A (%)	Coal B (%)	Coal C (%)
Original char	1.19	1.05	2.07
Nonmagnetic fraction	.61	.63	1.28
Magnetic fraction	1.28	1.50	3.06

TABLE 12

## PYROLYTIC CONVERSION OF PYRITE TO PYRRHOTITE

Treatment (°C/hr)	Wt. Loss (%)	Total S (%)	Pyritic S (%)	SO <sub>4</sub> Sulfur (%)	N (%)	Ash (%)
175/6	0.5	4.27	1.82	.36	--	15.0
(Whole Coal)	--	4.37	1.86	.37	--	15.3
650/48	33.0	2.39	0.08	--	0.94	20.6
(Char)	--	3.04	0.10	--	1.19	--
650/48	33.0	1.03	0.04	0.01	1.00	12.6
(HCl- extracted Char)	--	1.21	0.05	0.01	1.18	--

NOTE: Upper values determined on analyzed basis; lower values on moisture-free and ash-free basis.

tag recoveries are not given and differences in elemental concentrations cannot be directly compared. Nevertheless, the results show a significant quantity of magnetic iron resulting from conversion of pyrite (nonmagnetic) to pyrrhotite (magnetic) during heat treatment.

Table 12 shows the nearly total disappearance of pyritic sulfur in the two partially pyrolyzed coals (chars) and the reduction of total sulfur (from 3.04 to 1.21 percent) in the HCl-extracted char. Hydrochloric acid usually removes little sulfur from coal (only the sulfate sulfur and low concentrations of sulfides other than pyrite are soluble in HCl). In this case, however, pyritic sulfur has been extracted from the char by means of conversion to pyrrhotite, which is soluble in HCl. Future tests with the continuous-feed pyrolysis furnace should indicate the potential for producing cleaner chars by controlling parameters that will allow more efficient beneficiation of the products of pyrolysis systems.

#### MOSSBAUER SPECTROSCOPY STUDIES

Through a cooperative effort of Southern Illinois University with the Illinois State Geological Survey, a study of the kinds of iron in pyrolyzed coal residues has been made using Mossbauer spectroscopy. Samples of whole coal, coal pyrolyzed at 175°C for 6 hours, at 405°C for 48 hours, and at 550°C for 48 hours were supplied by the Survey to G. V.

Smith, Professor of Chemistry at Southern Illinois University, for the Mossbauer study. In addition, a sample of unpyrolyzed vitrain and fusain were supplied. All samples were from the Herrin (No. 6) Coal Member.

Because of the high sensitivity and noninterference of Mossbauer effects, the presence of several iron species were demonstrated in whole coal and in its pyrolyzed residues. Differences in isomer shifts and quadrupole splitting between pure pyrite and pyrite in coal indicate that there may be an interaction between the pyrite and the organic coal matrix (Smith, 1977). Recent investigations by A. Volborth (1977) support this conclusion, which may well have been first postulated by G. Cady (1935). The association appears to break down when the coal is heated to temperatures even as low as 175°C. Any amorphous iron sulfide present (isomer shifts indicate this possibility) in the whole coal is converted to pyrite at low temperatures. Further, advances in instrumentation and data reduction techniques have made it possible to identify four Fe<sup>+2</sup> species in heat-treated coal samples. Previously, two types of iron were recognized in whole coal samples.

For our samples, the total quantity of iron species in different coal lithotypes are about the same, but have different distributions. The single fusain sample had the least amount of Fe<sup>+2</sup> when compared to the vitrain or whole coal sample used. Two types of pyrrhotite have

been identified in the heat-treated samples. One is unstable and contains dissolved sulfur, which is apparently liberated as the temperature is increased. The heat treatment in an inert atmosphere tends to produce little change in  $\text{Fe}^{+2}$  species. It has been observed, however, that when a coal has been evacuated for the determination of these Fe species, then subsequently reexposed to air, and finally reevacuated, the types of iron change dramatically. This phenomenon may result from the removal of protective gases from the pores in the coal; the significance of this event in relation to spontaneous combustion is being investigated further.

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