

## DATA ON THE DISTRIBUTION OF ORGANIC SULFUR FUNCTIONAL GROUPS IN COAL

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### 1.0 Introduction

Coals contain inorganic sulfur compounds, like iron pyrite and gypsum and organic sulfur, which is bound to the organic matrix. Detailed reviews of sulfur functional groups in coal were recently published by Attar (1977)(1) and Attar and Corcoran (1977)(2). The chemistry, the kinetics and the thermodynamics of reactions of the sulfur were described by Attar (1978) and therefore will not be reviewed here in detail.

This work had two objectives:

1. to identify and quantify the organic sulfur group functionalities in different coals, and
2. to examine the implications of these functionalities on potential desulfurization processes.

The main results are:

1. The majority of the organic sulfur in high ranked coals, i.e., LVB is thiophenic while in low ranked coals, i.e. lignites, most of the organic sulfur is thiolic or sulfidic.
2. 18-25% of the organic sulfur is in the form of aliphatic sulfides in all coals.
3. Part of the organic thiols are present in the form of ionic thiolates, presumably of calcium.
4. Coals containing mainly thiolic groups can be easily desulfurized.

### 2.0 Principle of the Method of Analysis

Detailed description of the principle of the method of analysis was published by Attar and Dupuis (1978)(4). Therefore only the main points will be described here.

1. All the organic sulfur functional groups can be reduced to  $H_2S$  if a sufficiently strong reducing agent is used.
2. Each sulfur group is reduced at a rate which can be characterized by a unique activation energy and a frequency constant.
3. If a sample which contains many sulfur groups is reduced and the temperature is gradually increased, each sulfur group will release  $H_2S$  at a different temperature given by:

$$\frac{A_i RT_i^2}{\alpha E_i} = c \frac{E_i}{RT_i} \quad (1)$$

where  $T_{mi}$  is the temperature of the maximum  $E_i$  and  $A_i$  are the activation energy and the frequency factor, and  $\alpha$  is the linear rate of temperature increase. The rate of evolution of  $H_2S$  from the reduction of the  $i$ -th group can be described by:

$$\frac{d[H_2S]_i}{dt} = \frac{A_i}{\alpha} [H_2S]_{i0} \exp\left[-\frac{E_i}{RT} - \frac{A_i RT}{E_i} - c \frac{E_i}{RT}\right] \quad (2)$$

where  $[H_2S]_{i0}$  is the total amount of  $H_2S$  that reduction of the  $i$ -th group would release. The detailed derivation of the previous equations was done by Jüntgen (1964)(5), and Jüntgen and Van Heek (1968)(6).

4. The value of  $T_{mi}$  is a characteristic unique to the sulfur functionality reduced and the area of each peak is proportional to the quantity of sulfur present in the form of the group reduced.

The implication of these discussions is that the area of the peak whose maximum is at  $T_{mi}$  is proportional to the concentration of sulfur present in the sample in the form of the  $i$ -th group. Therefore, quantitative determinations of the  $i$ -th sulfur group can be accomplished by determining the area of each peak.

### 3.0 Experimental

The experimental system consists of six parts:

1. a reduction cell,
2. a gas feed and monitoring system,
3. a hydrogen sulfide detector,
4. a recorder,
5. an integrator, and
6. a temperature programmer.

Figure 1 is a schematic diagram of the experimental system. The coal sample is placed in the reduction cell with a mixture of solvents catalyst and a reducing agent. The gas flow rate is then adjusted and the temperature is programmed up. The rate of evolution of  $H_2S$  is recorded vs. the cell temperature and the signal of each peak is integrated using the integrator. A more detailed description of this system was recently published by Attar and Dupuis (1978)(4).

The data described in this paper were derived using an improved version of the same experimental system. The following modifications were made:

1. stronger reducing conditions were used in order to obtain more complete reductions of the organic sulfur,
2. the sensitivity of the detector was improved, and
3. the cell design was changed and now it is possible to obtain detailed analysis on a routine basis.

Figure 2 shows a typical kinetogram.

### 4.0 Results and Discussion

The distributions of sulfur functional groups (USFG) in four types of solids are described:

1. sulfur containing polymers with well characterized sulfur functional groups,
2. raw coals,
3. treated coals, and
4. iron pyrite.

The analysis of the DSFG consists of two parts:

1. the qualitative assignment of a peak of a kinetogram to a given chemical structure, and
2. the determination of the quantity of each sulfur group in the (coal) sample.

#### 4.1 Qualitative Identification of the Sulfur Groups

Tests of polymers with a known structure were used to identify the temperature at which each sulfur group releases its sulfur. Four polymers were tested:

1. polyphenylene sulfide (7) as a representative of aromatic sulfides,
2. polythiophene as a representative of thiophenic sulfur,
3. a copolymer produced from cyclohexene and 1,2 ethylene dithiol (7), as a representative of aliphatic and alicyclic sulfides, and
4. vulcanized natural rubber as a representative of aliphatic sulfides and disulfides.

All the polymers contained some thiolic sulfur.

The use of sulfur containing polymers can be used to identify the temperature region where each sulfur group is reduced only if two conditions are fulfilled:

1. the rate of the chemical reaction controls the rate of release of  $H_2S$  when both coal samples and polymer samples are examined,
2. the rate of the reduction of each sulfur functional group depends only on the hydrocarbon structure in its immediate vicinity.

Table 1 shows the results of tests of the various polymers and the maximum temperature for each group.

#### 4.2 Quantitative Analysis of the Concentrations of Sulfur Groups

##### 4.2.1 Recovery of Organic Sulfur

Quantitative analysis can be accomplished provided that all the sulfur present in the form of each group is reduced to  $H_2S$ . It is also assumed that the distribution does not change during the analysis and that all the  $H_2S$  released is detected and determined.

Each mole of sulfur, when reduced, produces one mole of  $H_2S$ . Therefore, the number of moles of  $H_2S$  formed during the reduction of each group is proportional or equal to the number of moles sulfur present in the sample in that form.

The recovery of sulfur from model compounds containing aliphatic thiols, thiophenes and aryl sulfides was 94-99%.

Table 2 shows the results of the quantitation of the kinetogram of three samples of Illinois #6 coal with different particle sizes. The two most important conclusions from these tests are that the recovery of thiophenes and aromatic sulfides depends on the coal particle size used and that to a first order approximation, the recovery of other groups is independent of the coal particle size. 17

is conceivable that during the analysis, in the interior of large coal particles, the sulfur groups can condense and form (graphitized) compounds which are less amenable to reduction. The strong reducing agent used can penetrate into smaller coal particles and inhibit the rate of condensation. While aliphatic thiols and sulfides are reduced at low temperature, before condensation commences, the reduction of thiophenes occur simultaneously with the condensation and therefore in a large particle thiophenic group could form condensed thiophenes which are less amenable to reduction.

#### 4.2.2 Recovery of Pyritic Sulfur

Table 3 shows that a very small fraction of the pyritic sulfur is recoverable when pure crystalline iron pyrite is tested. In all the cases tested, the recovery never exceeded 1-2%. Somewhat larger recovery is obtained when slow heating rates or reducing agents with smaller reducing potential are used. When strong reducing agents are used, a layer of metallic iron is believed to be formed on the surface of the iron sulfide which prevents diffusion of the reducing species.

Small iron pyrite particles, of the order of 1-10 microns are often reduced more effectively than larger particles because they are less crystalline and often contain more impurities than larger particles.

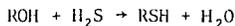
#### 4.3 Resolution

The evolution of  $H_2S$  from aliphatic sulfides and from iron pyrites coincides to the extent that it is almost impossible to resolve the two peaks. However, since iron pyrite can be determined independently using ASTM D3131, it was possible to estimate the relative contribution of pyritic sulfur and sulfidic sulfur to the unresolved peaks. Somewhat better resolution was obtainable at slow rates of heating, however in these cases the overall recovery and the signal to noise ratio were reduced.

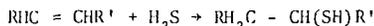
#### 4.4 The Sulfur Distribution in Raw Coals

Table 4 shows the distribution of the various classes of sulfur in five coals and table 5 shows the distribution of the organic sulfur groups in the same five coals. The results shows that the content of thiols is substantially larger in lignites and HVB coals than in LVB coals. The fraction of aliphatic sulfides is approximately the same in coals with different ranks and vary around 20% of the organic sulfur. If it is accepted that all the unrecovered organic sulfur is due to thiophenes (and aromatic sulfides), then the data indicate clearly that larger fractions of the organic sulfur is present as thiophenic sulfur in higher ranked coals than in lower ranked coals. The accepted theory on the hydrocarbon structure of coal is that higher ranked coals are more condensed than lower ranked coals. It should not, therefore, be surprising that the sulfur groups are also more condensed, more thiophenic, in higher ranked coals than in lower ranked coals.

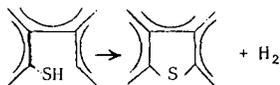
The data on the relative amounts of -SH, R-S-R and thiophenic sulfur can be explained as follows: suppose that most of the organic sulfur is initially trapped by the organic matrix in the form of thiolic sulfur. Typical "trapping reactions" are:



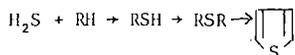
and



During the coalification, thiols can condense to form sulfides and eventually aromatic sulfides and thiophenes:



The sequence of the condensation reactions is therefore:



In other words, the sulfides are an intermediate form which the sulfur may have before it is converted to the thiophenic form. Thus, it should not be surprising that the fractions of sulfidic sulfur is approximately constant since during the coalification, sulfidic groups are formed from thiolic groups and are consumed to produce thiophenes. These processes are condensation processes which are believed to occur in the structure of coal during coalification.

#### 4.5 The Sulfur Distribution in Treated Coals

Various treatments are known to be selective to specific sulfur groups. It was therefore interesting to examine the kinetogram of treated coals. Three treatments are described:

1. oxidation with  $H_2O$  or  $HNO_3$ ,
2. removal of the alkaline minerals with  $HCl$ , and
3. methylation of the coal with methyl iodide.

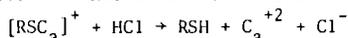
##### 4.5.1 Oxidation

Mild oxidation of coal with acidic solutions of hydrogen peroxide or nitric acid dissolves the iron pyrite and converts the thiols to sulfonic acids. Some organic functional groups oxidize to the corresponding sulfides and sulfones (8). However, in general, the latter process requires strong oxidizing conditions. From the analytical point of view one might think that it is not important whether the organic sulfur groups are oxidized or not, since the reducing agent used converts them back very rapidly to the non-oxidized form. Therefore, the results of the analysis will not differentiate between the reduced and the oxidized form of a sulfur group. In other words, oxidation could have been used to remove the interference from pyrite without much effect on the determination of the other sulfur groups. However, oxidation appears to increase the resistance to mass transport and thus to reduce the resolution. Figure 3 shows the kinetograms of two coal samples analyzed for the U.S. Department of Energy. The first is the original coal, the second is an oxidized sample. The results show that the oxidation did

not remove any organic sulfur although the pyritic sulfur was removed. The signals are however much less resolved in the oxidized sample than in the raw coal. Since the oxidation was conducted in an acidic inorganic solution, and because it is known that sulfonic acids can be hydrolyzed to hydrocarbons and sulfuric acid, some of the thiols seem to disappear as a result of the oxidation.

#### 4.5.2 HCl Treatment

Dilute HCl dissolves the organic and carbonate salts of calcium, magnesium and iron. Since some H<sub>2</sub>S can react with basic calcium and iron salts, it was desired to examine the effect of HCl treatment on the kinetogram. Figure 4 shows the kinetograms of raw coal and HCl extracted coal. The most important difference between the kinetograms is that the second peak due to thiophenols disappeared and the thiols peak is increased. It is plausible that some of the sulfur which is determined as thiophenolic is indeed thiolic. Thiols can react with calcium to form calcium thiolates, reduction of which may require larger activation energy than thiols. HCl treatment replaces the calcium with hydrogen and converts the thiolates into thiols:



#### 4.5.3 Treatment with Methyl Iodide

Samples of Illinois #6 were treated with methyl iodide, CH<sub>3</sub>I, and the products were analyzed using two methods: The method of Postovski and Harlampovich (9) for thiols and aliphatic sulfides, and using our thermokinetic method. The results of the analysis are described in table 6. The results show that only a very small fraction of the organic sulfur is indeed accounted for by the CH<sub>3</sub>I method and therefore the value of this method as an analytical tool is questionable.

The kinetograms of an untreated but demineralized sample and that of a demineralized sample treated with CH<sub>3</sub>I are shown in figure 5. The data show that the methyl iodide treatment results in lower recovery of organic sulfur and in a change in its distribution. In particular, some of the sulfur which is originally detected as aromatic thiol is apparently alkylated and becomes aromatic sulfide. However, the alkylation must also reduce the rate of mass transport since the thiophenes and aromatic sulfides are not visible in the kinetogram of the treated coal.

#### 5.0 Implications to Coal Desulfurization

It is widely recognized today that coal desulfurization efficiency depends on the distribution of sulfur in the original coal to pyritic and organic sulfur. Pyritic sulfur can be removed relatively easily while it is more difficult to remove organic sulfur.

Preliminary data show that part of the organic sulfur can be easily desulfurized. In particular, it seems that the thiolic sulfur and part of the sulfidic sulfur can be easily removed. Therefore, the authors suggest coals may be classified into two groups: coals which can be easily desulfurized, (most

of their organic sulfur is thiolic) and coals which can not be easily desulfurized (most sulfur is non-thiolic). Thus, thermokinetic tests can be used to screen coals and to infer which are best used as feeds for precombustion desulfurization.

#### References

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Table 2: The Effect of Particle Size on the Analysis of Sulfur Functional Groups

Run #	Coal	Mesh Size	Sample weight mg	-SH mg g coal	$\phi$ -SH mg g coal	R-S-R FeS <sub>2</sub> mg/g coal	$\phi$ -S- $\phi$ mg g coal	 mg g coal	Total mg g coal	Recovery %
S-111	Illinois #6	-100+120	32.7	1.33	1.44	4.15	1.17	*	8.07	19
S-112	"	-200+270	32.3	1.11	1.58	3.48	*	*	6.16	14.7
S-113	"	-325	32.2	1.69	1.80	3.11	*	67	7.26	17.1

\* Not detected

Table 3: The Effect of Pyrite Particle Size on the Recovery of Sulfur

Particle Size	% Recovered
mesh	
microns	
-60+100	0.9
149-250	
-100+120	1.9
125-149	
-120+170	1.6
88-125	
-170+200	1.5
77-88	
-200+270	1.5
53-74	
-270+325	0.9
44-53	
-325	2.1
< 44	

\* The estimated error is  $\pm$  0.4%.

Table 4: Sulfur Class Distribution in Five Coals

Coal	Denote	Total s (wt.%)	Pyritic s (wt.%)	Sulfatic s (wt.%)	Organic s (wt.%)
Illinois	A	4.5	1.23	0.06	3.2
Kentucky	B	6.6	5.05	0.135	1.43
Martinka	C	2.20	1.48	0.12	0.60
Westland	D	2.60	1.05	0.07	1.48
Texas lignite	E	1.20	0.4	—	0.80

Table 5: Distribution of Organic Sulfur Groups in Five Coals

Coal	% Organic s Accounted	Thiolic	Thiophenolic	Alip Sulfide	Aryl Sulfide	Thiophenes*
A	44	7	15	18	2	58
B	46.5	18	6	17	4	55
C	81	10	25	25	8.5	21.5
D	97.5	30	30	25.5	—	14.5
E	99.7	6.5	21	17	24	31.5

\* Corrected for "unaccounted for" sulfur

\* C and E are calculated on total sulfur content

Table 6: Analysis of Illinois #6 Coal by the CH<sub>3</sub>I Method by Thermokinetics

	LECO % mg/gm	ASTM % mg/gm	DSFG % mg/gm	CH <sub>3</sub> I method % mg/gm	DSG on CH <sub>3</sub> I treated coal (S-105) % mg/gm	
Total Sulfur	4.5	45				
Sulfate Sulfur		0.04	0.4			
Pyritic Sulfur		1.23	12.3	4.81	0.6	
Organic Sulfur $\left. \begin{array}{l} \text{-SH} \\ \phi\text{-SH} \\ \text{R-S.R.} \\ \text{A-S.A.} \end{array} \right\}$ 			6.1	1.36	8.6	
				8.5		3.45
				8.6	0.96	8.0
Total Organic Recovered		3.23	32.3	85.1	27.5	
				7.2	62.1	
				2.32	20.05	

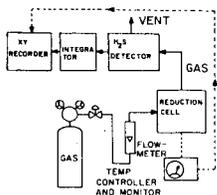


FIGURE 1 SCHEMATIC DIAGRAM OF EXPERIMENTAL SYSTEM

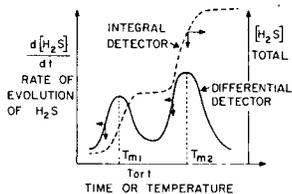


FIGURE 2 ANALYSIS OF A MIXTURE CONTAINING TWO GROUPS USING A DIFFERENTIAL AND AN INTEGRAL DETECTORS

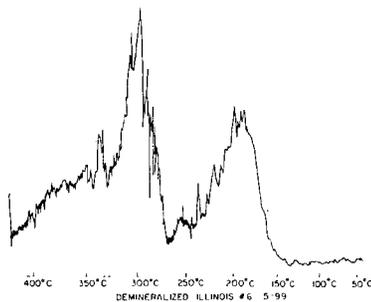
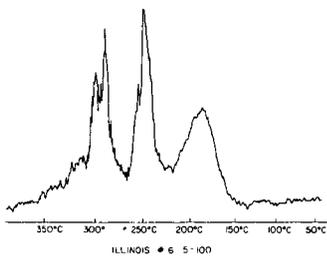


Figure 3

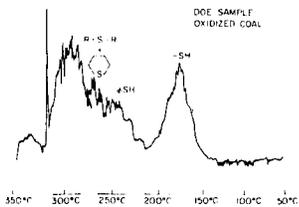
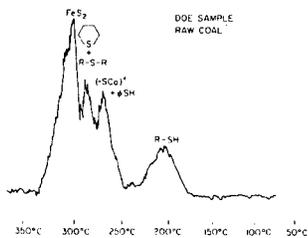


Figure 4

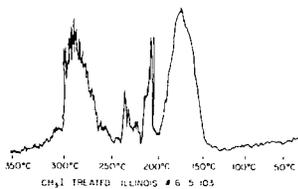
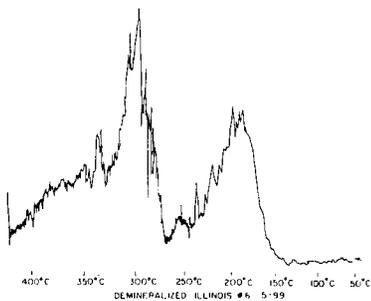


Figure 5