6-1-1951

Sulfur in North Dakota Lignite

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Recommended Citation

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SULFUR IN NORTH DAKOTA LIGNITE

A Thesis
Presented To
The Faculty Of The Graduate School
University of North Dakota

In Partial Fulfillment
Of The Requirements For The
Degree Of Master Of Science
In
Chemical Engineering
By
Majduddin Mohammed Jaffer

June, 1951

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Acknowledgement

It is with deep gratitude I would like to give my thanks to the friends on the University Campus. Without their help and cooperation, this work would not have been accomplished.

This thesis on "Sulfur in Lignite" was suggested to me by my professors, Mr. A. M. Cooley and Dr. Alex C. Burr. It owes all to their encouragements, help and advice.

I also owe a great deal to Miss Adelynn Magnusson, analyst of the Bureau of Mines for lending me the necessary equipment, for kindly doing the proximate analysis of the samples, and for her kind and helpful suggestions.

To my friends, Mr. Andrew Rawuka of North Dakota Research Foundation, Mr. C. V. Ratnam of Madras, and to Mr. Jerome Hoeppner, chemist in the United States Bureau of Mines, go my appreciation for their suggestions and help.

I would like to pay my deep respect to the late Dean Harrington, whose presence was always an inspiration.

I must give my thanks to John Rasmussen, studying chemical engineering in the University, for his help and fine company while visiting the North Dakota lignite mines. Furthermore I am indebted to the superintendents of the mines for their cooperation in getting the fresh samples from the mines. The personnel of the United States Geological Survey at the Garrison Dam need my thanks for the trouble they took in taking us across the river and for their help in getting the sample from the lignite beds in the working area and showing us the works in progress at the Garrison Dam.

I am deeply indebted to Dr. Alex C. Burr, Chief of the Fuels Technology Division, United States Bureau of Mines, whose generous help and cooperation enabled me to visit the lignite mines and who made it possible for me to stay here for a longer period for the completion of my thesis. His valuable suggestions and advice have been of so great help to me, that I would have hardly proceeded in my work without them.

The acknowledgement will be incomplete without paying my debt of gratitude to the Government of Hyderabad. I must say that the scholarship which my government paid all these years, has been repaid to them considering the knowledge and wider outlook of life which I have gained in the United States.

Summary

This thesis deals with the sulfur in North Dakota lignite. As the following pages will show, not only the total amount of sulfur has been determined but the resolution of the different forms of sulfur also has been carried out.

The total sulfur has been resolved into the following component parts:

1. Inorganic Sulfur
    a. Sulfate sulfur
    b. Pyritic Sulfur
2. Organic Sulfur
    a. Resinic sulfur
    b. Humic sulfur

Standard methods of analysis were used throughout. Three to six determinations were made on each sample. In the cases of total sulfur, inorganic sulfur and sulfate sulfur, two methods of analysis were used and in each case fair agreement was found. Also the results are in fair agreement with the samples previously analysed from the same mines.

In this work particular emphasis was given to the resolution of organic sulfur into its two component parts, resinic and humic sulfur. With regard to this subdivision of organic sulfur in lignite, there has been no previous work.

In the lignite of North Dakota, the amount of organic sulfur generally runs higher than the inorganic sulfur, but on an average organic sulfur is 0.43 percent and inorganic is 0.401 percent of the lignite. Moreover it is seen that the proportion of humic sulfur is

much smaller when the proportion of pyritic sulfur is high and vice versa. The proportion of resinic sulfur shows far less variation and seems to be independent of the proportion of pyritic sulfur. Another interesting fact is the higher proportion of humic sulfur in the organic sulfur. On an average it is 0.355 while the resinic sulfur is only 0.048.

The samples analysed were taken while on a field trip of the lignite mines last summer and were taken by the standard A.S.T.M. method.

Introduction

Sulfur is one of the most important impurities in coal. It is not only the most harmful of the constituents, but its economic importance also cannot be denied. It is present in amounts ranging from traces to as high as ten per cent. Generally most of the coals rarely contain more than five per cent.

Sulfur is harmful in coal or coke made from it, when they are used for metallurgical purposes. It not only effects the metal badly but the fumes of sulfur dioxide from the industrial areas cause great damage to vegetable and animal life. Damages to the buildings are also caused by the fumes of sulfurous acid. It attacks the building stones, concrete and metal; thus leading to the general weakening of the structures.

On the other hand we have another side to the sulfur in the coal, which adds to the economy of the coal industry. The middle Eocene brown-coals of Alsace, lower Rhine and Bonn were a source of pyrite and alum. Large quantities of iron vitriol and alum were produced.

Occurance of Sulfur in Coal:

Sulfur is present in coal in four different forms.

1. As sulfides (pyrites and marcasite)
2. As part of the coal substance in organic combination
3. As sulfates (gypsum) in weathered coals
4. As elemental sulfur (in some brown-coals)

The great proportion of the sulfur in coal is probably combined with metals, especially with iron. It is then found in the form of pyrite or in the isomeric crystalline form known as marcasite. It is not usual that iron sulfide corresponds to the formula FeS_2. It varies between FeS_2 and $FeS_{1.7}$. Pyrite often occurs in fissures, cleat and crevices in the coal beds. It may occur as horizontal layers; as fillings in the vertical cleat cracks; as nodular masses parallel with or at an angle to the bedding; as fillings in the desiccation cracks, the fusain and resin rodlet cravities more commonly occupied by calcite and kaolinite; as minute aggregates scattered through the various lithologic ingredients of the coal; and as intimate mixtures with the impregnations of certain parts of coal such as fusain. Pyrite is found in coal in particles from microscopic sizes on up to large masses several feet in diameter and in definite widely extending bands in the bed up to a foot in thickness.

The finely disseminated pyrite may form thin filmlike coatings on the joint planes. The large masses are usually found toward the top or the bottom of the bed. It is seen that larger masses of pyrite are contaminated with shale, clay and carbonaceous material.

Pyrite sulfur is extremely variable in its occurance in coals, both in amount and form. The origin of pyrite is a matter of much speculation. Its presence has been attributed to both external and internal sources of sulfur. Hydrogen Sulfide evolving through the organic matter, precipitates iron sulfide by reacting with soluble iron compounds. The ferrous sulfide is later transformed into pyrite.

Donath suggests the formation of pyrites according to the following reactions.

$$Fe_2O_3 + 3H_2S \longrightarrow 2FeS + S + 3H_2O$$

$$Fe\,S + S \longrightarrow FeS_2 \text{ (under pressure and temperature)}$$

Sulfur balls and lenses were formed in the early stages of coal formation since the surrounding coal subsequently became compacted to a smaller thickness than the pyrite mass. The pyrite filling joint cracks and other vertical and horizontal partings is probably of secondary origin and formed largely since the consolidation of the bed to its present thickness. Its secondary origin is attributed to the fact that there is a lack of differential shrinkage between the coal and the pyrite.

Sulfides of other metals are less common. Pyrite is often so finely disseminated in coal that it cannot be seen without the aid of microscope. In contact with the air, it readily oxidizes to iron sulfate. Heat is thereby generated which may lead to the ignition of coal. Iron sulfate frequently blossoms out in strip-mines and is often found as an oxidation product of iron pyrite in mine waters. From these solutions iron sulfate can be changed back again into pyrite by the reducing action of organic material.

Organic sulfur is next to the pyritic sulfur. The variation of the organic content of a coal bed from top to bottom is usually low. As regards the horizontal distribution, this may vary considerably with coals containing a high percentage of organic sulfur, but taken as a whole the variation is not to be compared with that of the pyritic sulfur. In low-sulfur coals variation in the horizontal distribution of organic sulfur is small and the amount may be nearly uniform over a considerable area. Due to the large variation in the amount of pyritic sulfur, there is no relationship between the quantities of organic and pyritic sulfur present in the coal. Coal cleaning processes do not remove the organic sulfur as it is homogeneously combined with the coal material. Generally it is seen that low sulfur coals have a greater percentage of organic sulfur. In destructive distillation of coal, a part of sulfur comes off as hydrogen sulfide and various thiophene compounds but this furnishes little information as to the exact nature of the sulfur compounds in the coal itself.

It is not known whether the sulfur-containing organic compounds are simple or complex in nature. According to Wheeler, all natural ulmins contain sulfur as confirmed in the extract of coal. He also said that the organic sulfur compounds are part of the fundamental constitution of coal and are uniformly distributed. Postovsky and Harlampovich detected the presence of thio-ether linkages in coal by the methyl iodide reaction and such linkages were estimated by them to account for 18-32 per cent of the total sulfur content of the coal. Another theory suggests that as the organic solvents do not dissolve the organic sulfur compounds of the coal; so the sulfur is supposed to be associated with carbon in a solid product of complex nature.

Powell and Parr divided the organic sulfur in the coal into two kinds, the phenol soluble or resinic sulfur and the phenol insoluble or humic sulfur. According to Petraschek, higher organic sulfur content accompanies better coking properties in the coal. Effects of oxidation on the sulfur in coal have been discussed by Horton and Randall. About $\frac{1}{2}$ or more of the total original sulfur is oxidized to sulfate. A certain proportion of organic sulfur is capable of easy oxidation to sulfate; the remainder oxidizes more slowly, but can ultimately be converted to sulfate to the extent of over ninety per cent.

The origin of organic sulfur is most probably due to the sulfur in the coal forming plants. Sulfur is one of the essential elements of present day plants, and presumably also of all coal-forming plants. Dieulafait found that modern members of the Equisetacease family, a family of important coal-forming plants, and found greater amounts of sulfur in their ashes than in the ashes of other plants; he concluded that, as these plants contained more sulfur than other plants, their palaezoic ancestors did also.

Sulfur occurs in plants as a constituent of proteins and of certain waste and protective substances, especially in seeds. During the decay of the plants, protein sulfur compounds are quickly destroyed and much sulfur is released as Hydrogen Sulfide. Part of this escapes to the atmosphere and part dissolves in the bog water, where it may combine with dissolved iron compounds or be washed away or absorbed by the organic coal-forming materials. It also has been suggested that part of the organic sulfur in coal may be derived from the residues of animal life which lived in the decaying peat bog. Such residues are rare and of minor account; in any event they would be similar in nature to organic sulfur from plants.

Sulfate sulfur exists as calcium sulfate and in weathered coal it exists as iron sulfate. Larger amounts of sulfate sulfur indicate that the coal has been weathered. Freshly mined coal from beds which have never been uncovered or subjected to the action of oxygen bearing percolating waters are practically free from sulfates. Most of the sulfur remains in the ash after the combustion of the coal, but a small amount may be decomposed to CaO and SO_3, and some may be reduced to Calcium Sulfite, and Calcium sulfide, which are less stable and may give rise to Sulfur di-oxide.

Pure sulfur is very unimportant, although it occurs as a decomposition product of pyrite. Atmospheric weathering of the coals developed free sulfur in Indian coals where no free sulfur existed in the fresh sample. Organic sulfur and sulfate sulfur do not alter but pyrite sulfur oxidizes to give sulfates, sulfuric acid and free sulfur.

Description of Samples

In order that the lignite be free from any contaminations and that it should not have undergone any aging or weathering, in the older samples, fresh samples were collected during my field trip to the lignite mines of North Dakota. The following eight mines were visited, and the samples were taken from the working pits.

	Mine	County	Company
1.	Noonan	Divide	Noonan Baukol
2.	Columbus	Burke	Kincaid
3.	Velva	Ward	Traxx-Traer
4.	Custer	McLean	Traxx-Traer
5.	Garrison Dam	McLean	United States Army
6.	Hazen	Mercer	Dakota Star
7.	Beulah	Mercer	Knife River
8.	Zap	Mercer	Dakota Colleries

In addition to these mines, we visited the Lehigh mine at Dickinson but were not able to get any samples from the mine, because the work was not in progress.

All these mines are strip mines except at Beulah. In Noonan and Columbus the work was not being done, as they had been cleaning their mines due to the recent rains. But it was possible to take fresh samples from these mines. As the samples gathered, were too much wet, they all were dried before analyzing. The fresh samples were kept in air tight bottles to minimize the effects of weathering in the presence of oxygen. The samples after being dried enough were pulverized, so that the bulk of the material could pass through a sixty mesh screen.

The proximate analysis of these samples shows that they are in close agreement with the previous data available for these mines. Except in the case of Noonan sample, where the sulfur content is not in agreement, all the other samples are representative within the limits of sampling error.

Table I

Proximate Analysis of Samples

(Air Dried)

No.	Mine	County	Moisture	Ash	Volatile Matter	Fixed Carbon	BTU	Total Sulfur
1	Noonan	Divide	13.5	9.2	36.1	41.2	9662	1.340
2	Columbus	Burke	16.1	12.3	35.8	35.8	8657	0.470
3	Velva	Ward	20.8	7.5	34.0	37.7	8392	0.528
4	Custer	McLean	20.2	5.0	35.9	38.9	8728	0.470
5	Garrison	McLean	16.5	7.5	39.5	36.5	8999	0.726
6	Hazen	Mercer	20.0	5.4	33.8	40.8	8670	0.250
7	Beulah	Mercer	22.6	5.5	33.3	38.6	8574	0.689
8	Zap	Mercer	17.3	10.5	34.8	37.4	8689	0.905

Table II

Proximate Analysis of Samples

(Moisture Free)

o.	Mine	County	Moisture	Ash	Volatile Matter	Fixed Carbon	BTU	Total Sulfur
1	Noonan	Divide	--	10.6	41.7	47.7	11170	1.552
2	Columbus	Burke	--	14.7	42.7	42.7	10318	0.563
3	Velva	Ward	--	9.5	42.9	47.6	10596	0.666
4	Custer	McLean	--	6.3	45.0	48.7	10937	0.590
5	Garrison	McLean	--	9.0	47.3	43.7	10777	0.861
6	Hazen	Mercer	--	6.8	42.3	50.9	10838	0.313
7	Beulah	Mercer	--	7.1	43.0	49.9	11077	0.792
8	Zap	Mercer	--	12.7	42.1	45.2	10507	1.096

Methods and Precision of Analysis

Many efforts have been made to resolve the total sulfur content of solid fuels into component parts, and to explain the origin and behavior of each form thus differentiated. Three methods of classification are frequently used are:

A. Depending upon reaction during carbonization
    1. Fixed Sulfur--that remaining in the coke or char after carbonization
    2. Volatile Sulfur--that eliminated during carbonization

B. Depending upon reaction during combustion
    1. Non-combustible Sulfur--that remaining in the coal ash after combustion
    2. Combustible Sulfur--that eliminated during combustion.

C. Depending upon reaction during analysis
    1. Inorganic Sulfur
        a. Sulfate Sulfur
        b. Pyritic Sulfur
    2. Organic Sulfur
        a. Resinic Sulfur
        b. Humic Sulfur

In this work the third classification has been used. It discusses the nature and forms of this important coal constituent, sulfur, and throws light on the behavior of these different forms of sulfur when analysed by different methods and by different solvents.

Standard methods of analysis were used throughout. Three to six determinations were made on each sample.

A. Total Sulfur

Total Sulfur was determined directly by both the Eschka and Turbidimeter methods. Except at very low and very high concentrations of sulfur, the agreement was good. The reason is that the turbidimeter works in a restricted range. If the sulfur is too low or too high the indicator is out of the range. The only way to find a solution for low sulfur was to take at least two fusions in the peroxide bomb and mix both the contents into one and then take a reading on the turbidimeter. In the case of too high a sulfur content the mixture was diluted and a reading of the dilute solution was taken and then corrected for the original amount.

In the Eschka method no trouble of this kind is encountered. A one gram sample of 60 mesh coal is mixed with 3 gram of Eschka mixture (2 part MgO and 1 part Na_2CO_3)in a nickel or porcelain crucible and with 1 gram of this mixture on top of it. It is slowly heated to a temperature of about 1500°F in an hour and then this temperature is maintained for another 1½ hour. Afterwards the crucible is removed and (if no black particles are present) the contents are mixed with hot water, and heated for 30 minutes. The filterate contains the sulfur in the form of alkali sulfates and is precipitated with the addition of $BaCl_2$. The precipitated $BaSO_4$ is dried, ignited and weighed and then the sulfur content is calculated. Thus the Eschka method involves at least 2 days until the final result is obtained; but the accuracy of this method cannot be denied.

On the other hand the Turbidimeter method though not very precise as the Eschka method, is still very useful as it not only gives fair agreement but it needs only half an hour to get the final result. In other words it could be said that the Turbidimeter method is an effective short-cut around some of the time consuming steps common to gravimetric procedures in the analysis of sulfur in coal. In this method, the mass of an insoluble compound is suspended in a fluid form, thus avoiding the customary filtration, washing, drying and weighing operations. The principle of this method is to indicate the relative turbidity of an unknown solution as compared with the turbidity of a similar solution in which the amount of the precipitate is known.

First of all the lignite sample is treated in a Parr sodium peroxide combustion bomb. After mixing all the ingredients, which include sodium peroxide, an accelerator potassium chlorate, and a combustion aid benzoic acid, and all of which must be completely dry, the charge is ignited in the bomb by an electric ignition circuit. The material, inside the bomb, melts and intense heat is generated which is removed by circulating cold water. After cooling of the bomb takes place, the charge is mixed with distilled water, heated, neutralized with hydrochloric acid, and filtered. To this filterate, $BaCl_2$ is added, which precipitates the sulfur in the form of $BaSO_4$ and the turbidity of this solution as observed in the turbidimeter gives the measure of the sulfur content.

Sulfate Sulfur or Sulfur soluble in Hydrochloric Acid

Sulfate sulfur was determined directly by the Powell and Parr, (P.P.), and by the British coke research Association method (B.C.R.A.) and fair agreement was found.

In the P.P. method 5 grams of 100 mesh coal is digested with 300 cc of 3 percent hydrochloric acid for 40 hours. The solution is filtered and $BaSO_4$ is precipitated, and sulfur is calculated as usual.

In the B.C.R.A. method the time of 40 hours is shortened to only ½ an hour, but a higher concentration (5N) is used with only 50 cc of the acid. In this method the mixture is boiled to hasten the reaction. The sulfur is precipitated as usual with the filtrate.

It is seen that where the inorganic sulfur is high the results disagree, probably due to the attack of the acid in the boiling condition on other forms of sulfur.

Inorganic Sulfur or Sulfur soluble in Nitric Acid

Inorganic sulfur was determined directly by the P.P. and B.C.R.A. methods and fair agreement was found. In this case the B.C.R. A. method agrees very well even where there is high pyritic sulfur.

In the P.P. method 1 gm of coal is placed with 80 cc of (1:3) nitric acid for 24 hours at room temperature. The residue is discarded after filtration and $BaSO_4$ is precipitated.

In the B.C.R.A. method the time of 24 hours is shortened to only ½ an hour. The strength of the nitric acid used is 2N and the solution is boiled for half an hour.

The pyritic sulfur is determined by difference, subtracting the directly determined sulfate sulfur from the directly determined inorganic sulfur.

Organic Sulfur

Organic sulfur is determined by differences by subtracting the directly determined inorganic sulfur from the total sulfur.

1. Resinic sulfur is determined indirectly by subtracting from the total sulfur the sulfur remaining in the residue of the sample extracted with phenol. To find out this amount of phenol insoluble sulfur, 0.5 gm of lignite is digested with 25 cc of phenol at 140°C. for 20 hours. This mixture is filtered. The filtrate is discarded

which does not leave anything when burned, showing that only sulfur of organic nature is dissolved in the phenol. The residue is washed with alcohol and ether. From this residue sulfur is determined by the Eschka method.

2. <u>Humic sulfur</u>

a. The amount of humic sulfur is determined by subtracting the amount of resinic sulfur from the total organic sulfur.

b. Another method recommended by Powell and Parr is by dissolving the sulfur after the nitric acid extraction has been taken out. The result obtained is not very well in agreement. Powell and Parr had the same trouble with the Illinois coals.

Results of Analysis

The following tables present the averaged data obtained upon the analysis of the samples studied in the investigation. Detailed analytical results are found in tables XIII to XVII in the appendix.

Table III

Forms of Sulfur in North Dakota Lignite

Per cent of Weight of Sample--dry basis

Sample	Sulfate Sulfur	Pyritic Sulfur	Inorganic Sulfur	Resinic Sulfur	Humic Sulfur	Organic Sulfur	Total Sulfur
1. Noonan	0.054	1.333	1.387	0.082	0.083	0.165	1.552
2. Columbus	0.030	0.053	0.083	0.005	0.475	0.480	0.563
3. Velva	0.047	0.174	0.221	0.061	0.384	0.445	0.666
4. Custer	0.022	0.082	0.104	0.048	0.438	0.486	0.590
5. Garrison Dam	0.057	0.190	0.247	0.132	0.482	0.614	0.861
6. Hazen	0.039	0.075	0.114	0.005	0.194	0.199	0.313
7. Beulah	0.046	0.133	0.179	0.013	0.601	0.613	0.792
8. Zap	0.092	0.784	0.876	0.035	0.185	0.220	1.096
AVERAGE	0.048	0.353	0.401	0.048	0.355	0.403	0.804

Table IV

Forms of Sulfur in North Dakota Lignite

Per cent of total Sulfur -- Dry Basis

Sample	Sulfate Sulfur	Pyritic Sulfur	Inorganic Sulfur	Resinic Sulfur	Humic Sulfur	Organic Sulfur	Total Sulfur
1. Noonan	3.5	85.8	89.3	5.3	5.4	10.7	100.0 100.0
2. Columbus	5.3	9.4	14.7	1.0	84.3	85.3	100.0
3. Velva	6.9	26.0	32.9	9.8	57.3	67.1	100.0
4. Custer	3.7	13.9	17.6	8.3	74.2	82.5	100.1
5. Garrison Dam	6.7	22.0	28.7	15.4	56.0	71.4	100.1
6. Hazen	12.5	24.0	36.5	1.5	62.0	63.5	100.0
7. Beulah	5.8	16.9	22.7	1.6	75.8	77.4	100.1
8. Zap	8.4	71.5	79.9	3.2	16.9	20.1	100.0
AVERAGE	6.6	33.7	40.1	5.8	54.1	59.9	--

Discussion of Results and Conclusion

A. 1. Tables V and VI show the distribution of total sulfur in North Dakota lignites according to previous work. Comparing these with the eight samples examined in this investigation, the results are in harmony. Generally the North Dakota lignites are low in sulfur content.

2. Tables III, IV and VII show the distribution of sulfur in the lignite samples. Table VII is the previous data and agrees well with the work in Table III. Generally it is seen that organic sulfur is higher than the inorganic sulfur, showing the lesser amounts of pyritic and sulfate sulfur, with an indication that the decay has not gone very much as compared to some other coals (see Table IX).

a. The Tables III and IV sho that the proportion of sulfur occuring in inorganic sulfur is in accord with the previous data (Table VII).

b. The proportion of sulfate sulfur occuring in the sulfate form, probably as $CaSO_4$, is in accord with previous results. The proportion of sulfate sulfur in North Dakota lignite is very low, indicating very well that it has not come into contact with oxygen.

c. The proportion of pyritic sulfur is also in agreement with the previous work. Though in some samples it seems to be of a higher proportion, it is generally lower than the organic sulfur.

d. In view of the conclusions reached in a,b, and c it is true that the proportion of organic sulfur is in accord with previous data.

On the basis of the foregoing conclusions, it can be said that within the error of sampling, these eight samples are representative,

Table V

Mean Total Sulfur content in North Dakota Lignite[8]

County	No. of Samples	Mean
Adams	36	2.4
Billings	5	7.5
Bowman	23	1.5
Burke	60	0.7
Burleigh	37	1.4
Divide	27	0.8
Dunn	7	1.5
Golden Valley	7	2.1
Grant	26	1.7
Hettinger	39	2.4
McKenzie	14	1.3
McLean	70	0.8
Mercer	134	1.2
Morton	52	1.4
Mountrail	39	1.6
Oliver	4	1.3
Slope	6	2.5
Stark	67	1.3
Ward	235	0.4
Williams	101	1.0
Sioux	3	1.3
Renville	6	1.5
STATE	1017	1.0

Table VI

Total Sulfur in North Dakota Lignite

(Previous Results)*

Mine	County	Sample Number	Air Dried	Moisture Free
1. Noonan	Divide	16641	0.5	0.8
		B79123	0.7	1.1
2. Columbus	Burke	5960	0.4	0.6
		D-8106	0.4	0.5
3. Velva	Ward	A-45986	0.4	0.6
		13634-4	0.44	0.69
4. Custer	McLean	16644	0.4	0.6
		16307	0.3	0.5
5. Garrison Dam	McLean	15817	0.6	0.8
		P72	0.5	0.8
6. Hazen	Mercer	D-33375	0.4	0.6
		16134	0.3	0.46
7. Beulah	Mercer	8309	0.4	0.6
		5757	0.6	0.9
8. Zap	Mercer	10129	0.8	1.2
		76	0.6	0.9

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* Bureau of Mines Data, card catalogue

Table VII

SULFUR IN NORTH DKOTA LIGNITE

Distribution by Forms[2]

(Moisture-free Basis)

No.	County	Mine	Total Sulfur	Organic Sulfur	%	Inorganic Sulfur	%	Sulfate Sulfur	Pyritic Sulfur
%									
1.	Burke	Kincaid	0.49	0.41	84	0.08	16	0.02	0.06
2.	Burke	Kincaid (dried)	0.54	0.41	76	0.13	24	0.01	0.12
3.	Divide	Baukol Noonan	0.76	0.46	61	0.30	39	0.05	0.25
4.	Divide	Baukol Noonan	0.59	0.44	75	0.15	25	0.04	0.11
5.	McLean	Garrison	0.54	0.49	91	0.05	9	0.01	0.04
6.	McLean	Garrison	0.59	0.42	71	0.17	29	0.05	0.12
7.	McLean	Damsite	1.62	1.16	72	0.46	28	-	-
8.	McLean	Damsite	0.75	0.63	84	0.12	16	-	-
9.	McLean	Damsite	0.76	0.51	67	0.25	33	-	-
10.	Mercer	Hazen	0.73	0.28	38	0.45	62	0.04	0.41
11.	Mercer	Hazen	1.27	0.23	18	1.04	82	0.07	0.97
12.	Stark	Lehigh	1.32	0.50	38	0.82	62	0.11	0.71
13.	Ward	Quality	0.52	0.40	77	0.12	23	0.02	0.10
14.	Ward	Quality	0.40	0.29	73	0.11	27	0.02	0.09
15.	Ward	Velva	0.56	0.27	48	0.29	52	0.04	0.25
16.	Ward	Velva	0.35	0.23	66	0.12	34	0.01	0.11
17.	Ward	Velva	0.30	0.25	83	0.05	17	0.03	0.02

at least as for as sulfur is concerned.

B. The purpose of this investigation has been to resolve the organic sulfur into two fractions, the resinic and the humic forms. Table VIII shows this resolution for the samples analysed, on the total amount of organic sulfur. The ratio of humic sulfur to resinic varies from 1 to 82.3 and on an average it is 9.3.

Table III shows the analysis of humic and resinic forms on the sample basis and Table IV is based on percentage of total sulfur. As these Tables, III and IV, show the proportion of the humic sulfur has some relation with the pyritic sulfur in the lignite. When the humic sulfur is much smaller, the proportion of pyritic sulfur is high and vice versa.

The proportion of the resinic sulfur shows far less variation when compared with the variation in humic sulfur, and moveover it seems to be independent of the proportion of the pyritic sulfur.

The figure summerizes these results. The prooportion of pyritic sulfur has been plotted as against the proportions of the humic and resinic sulfur. The resinic sulfur points on the graph are almost all concentrated in one place in a haphazard fashion and does not show relation with pyritic sulfur. But the humic sulfur data falls in a definite patter, following a negative exponential curve .

C. No similar data are available on the other American lignites. However, comparison may be made with other American coals, with Indian coals, including a few samples of lignite and with Chinese coals.

In general, the sulfur content of Illinois coal is considerably higher than than that in North Dakota lignite. More significant is the much higher proportion of pyritic sulfur in the Illinois coal

Table VIII

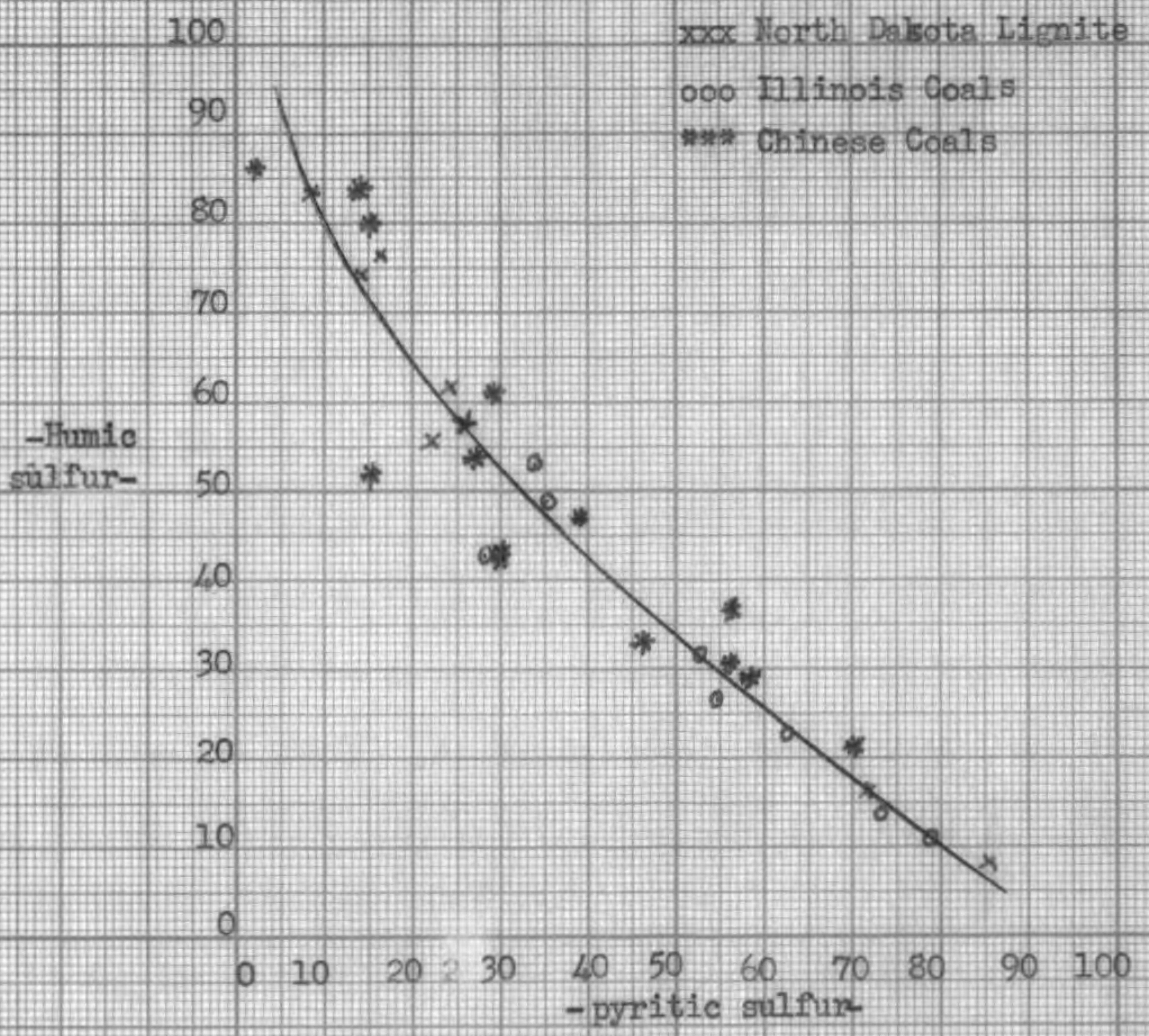
Humic and Resinic Sulfur
Per cent of Total Organic Sulfur

(Dry Basis)

Sample	Resinic	Humic	Ratio H/R
1. Noonan	49.5	50.5	1.0
2. Columbus	1.2	98.8	82.3
3. Velva	14.6	85.4	55.9
4. Custer	10.0	90.0	9.0
5. Garrison Dam	21.6	78.4	3.6
6. Hazen	2.4	97.6	40.7
7. Beulah	2.1	97.9	46.0
8. Zap	15.9	84.1	5.3
AVERAGE	9.7	90.3	9.3

FIG. I

pyritic vs. humic sulfur



as compared with lignite. The proportion of sulfate sulfur averages approximately the same in Table IV and IX and is extremely variable in both. A much higher fraction of the total sulfur occurs in the organic form in the lignite than in the Illinois coals. In both sets of data the proportion os sulfur in the humic form is distinctly higher than that in the resinic form, the ratio being 2.0 for Illinois coal and 9.3 for North Dakota lignite.

Majumdar has reported data on a number of Indian coals, including three lignites. A representative selection of his data is presented in Table X.

The total sulfur in Indian coals and lignite is also higher than that in North Dakota lignite; however, the fraction in the inorganic form is about the same. Therefore, the fraction occurring in the organic form is about the same. The pyritic sulfur is distinctly lower in the Indian coals, and the sulfate sulfur distinctly higher than in North Dakota lignite.

Young has reported data on Chinese coals, Table XI allows a comparison with North Dakota lignite.

Again, the total sulfur in Chinese coals is higher than in the North Dakota lignite. The fraction of the sulfur occurring in the inorganic form is slightly less in the Chinese coal than in our lignites. The proportions occurring in the sulfate and pyritic forms are similar. The proportion of Humic to Resinic sulfur is 5.2 in Chinese coals and 9.3 in the lignite. A summary of these is given in Table XIII.

Table IX

Sulfur in Illinois Coal

(Per cent of total Sulfur -- Dry Basis)

Calculated from Data of Powell and Parr[10]

No. of Sample	Percent Sulfur	Distribution of Sulfur					
		Sulfate Sulfur	Pyritic Sulfur	Inorganic Sulfur	Resinic Sulfur	Humic Sulfur	Organic Sulfur
1	2.68	1.5	52.0	53.5	15.6	31.0	46.6
2	2.18	7.8	72.5	80.3	6.9	12.8	19.7
3	0.64	0.0	26.6	26.6	31.3	42.1	73.4
4	2.14	2.3	33.6	35.9	15.9	48.5	64.4
5	5.00	26.2	40.5	66.7	15.5	17.8	33.3
6	3.31	0.3	62.3	62.6	15.1	22.3	37.4
7	1.02	1.0	78.2	79.2	9.9	10.8	20.7
8	1.40	0.0	53.5	53.5	15.0	31.4	46.4
9	0.94	2.1	33.0	35.1	12.8	52.1	64.9
10	1.20	20.8	33.3	54.1	12.3	32.5	45.8
AVERAGE	2.05	6.2	48.6	54.8	15.1	30.1	45.3

Humic Sulfur/Resinic Sulfur = 2.0

Table X

Sulfur Forms in Indian Coals and Lignites

Data of Majundar[2]

No.	Sample	Percent		Dist. of	Sulfur	
		Sulfur	Sulfate	Pyritic	Inorganic	Organic
1.	Palana Lignite Bikaner Rajputana	3.02	8.7	14.9	26.7	77.3
2.	"" "" ""	9.09	46.4	40.1	86.5	13.5
3.	Cashmere Lignite	0.54	11.1	24.1	35.2	64.8
4.	Dishergarh Raniganj	0.29	3.5	24.5	28.0	72.0
5.	Baraker Jharia	0.62	1.6	6.4	8.0	92.0
6.	Makerwal	5.10	23.7	14.0	37.7	62.3
7.	Naga Hills	2.78	29.1	17.6	46.7	53.3
8.	"" "" ""	4.80	54.5	7.9	62.4	37.6
	AVERAGE	3.28	22.3	18.3	41.4	59.1

Table XI

Sulfur Forms in Chinese Coals
(Percent of Total Sulfur--dry basis)
Based on Data of Young[16]

No. Sample	Percent Sulfur	Distribution of Sulfur					
		Sulfate	Pyritic	Inorganic	Resinic	Humic	Organic
1. Shantung	2.86	8.8	38.8	47.6	4.9	47.5	52.4
2. Hopei	0.65	3.2	14.9	18.1	1.6	80.1	81.7
3. Hopei	1.43	5.6	56.3	61.9	0.8	37.3	38.1
4. Chahar	0.76	7.8	55.8	63.6	6.5	30.0	36.5
5. Hopei	0.78	2.5	28.7	31.2	7.5	61.3	68.8
6. Honan	0.84	9.6	26.5	36.1	9.6	54.3	63.9
7. Shantung	0.78	28.8	2.5	31.3	25.0	43.8	68.8
8. Hopei	0.97	12.5	14.6	27.1	20.8	52.0	72.8
9. Hopei	1.39	12.1	29.3	41.4	17.1	41.5	58.6
10. Anhwei	5.47	0.9	70.4	71.3	8.0	20.8	28.8
11. Anhwei	1.66	4.2	58.1	62.3	8.5	29.1	37.6
12. Shansi	0.57	0.0	14.3	14.3	1.7	84.0	85.7
13. Hunan	0.65	0.0	1.5	1.5	12.3	86.1	98.4
14. Chekiang	3.35	6.6	45.5	52.1	14.7	33.3	48.0

Table XI Cont'd.

NO.	Sample	Sulfur Percent	Distribution of Sulfur Sulfate	Pyritic	Inorganic	Resinic	Humic	Organic
15	Kiangsi	0.54	0.0	14.8	14.8	11.1	74.0	85.1
Average		1.51	6.8	31.5	38.3	10.0	51.7	61.7

Humic Sulfur/Resinic Sulfur = 5.2

Table XII

Sulfur Distribution in Various Coals

	N. Dak. Lignite	Illinois Coal	Indian Coal	Chinese Coal
Total S	0.804	2.05	3.28	1.51
Sulfur Distribution				
1. Sulfate	6.6	6.2	22.3	6.8
2. Pyritic	33.7	48.6	18.3	31.5
3. Inorganic	40.3	54.8	41.4	38.3
4. Humic	54.0	30.1	--	51.7
5. Resinic	5.8	15.1	--	10.0
6. Organic	59.9	45.3	59.1	61.7
7. Humic/Resinic	9.3	2.0	--	5.2

Conclusion

From this comparison, it is seen that one outstanding characteristic of North Dakota lignite is the high ratio of humic to resinic sulfur. This fact may be related to the relative youth, in a geologic sense, of these lignites and to the absence of reactions due to great pressure during the coalification process.

APPENDIX

Methods of Analysis:-

A. Total Sulfur

1. Eschka Method:-

A sample of 60 mesh coal weighing about 1 gram is throughly mixed in a 30 cc porcelain crucible with about 3 g of Eschka mixture, (2 parts of MgO & 1 part of Na_2CO_3), and about 1 g of the mixture is spread over the top to form a cover. The crucible with its contents is placed in the furnace, and the temperature is slowly raised to 800-25°C (1472-77°F) in about one hour. Slow heating during the preliminary period is essential to avoid rapid expulsion of volatile matter, which tends to prevent complete absorption of the products of combustion of the sulfur. The maximum temperature of 800-25°C is maintained for about 1½ hours.

When the crucible is removed from the muffle, the contents are throughly stirred. If any black particles remain, the crucible is returned to the muffle and heated until all black particles are burned out, a condition which indicates that the process is complete. The crucible and the contents are then allowed to cool, and the contents are transferred to a beaker and digested with 100 cc of hot filtered water for at least 30 minutes. Filteration into a beaker follows; the insoluble residue is washed twice with hot water by decantation, and after being transferred to the filter paper is washed with small quantities of hot water until the volume of solution in the beaker is about 250cc. About 4 cc of saturated Br-water and enough dilute (2:1) HCl to make the solution slightly acid are needed. The solution is next boiled to expel the liberated bromine, and the sulfur is precipitated as $BaSO_4$ by adding slowly 10-20 cc of hot 10% solution of $BaCl_2.2H_2O$. The solution containing the precipitate is allowed to stand for at least 2 hours or preferably overnight, at a temperature just below boiling.

The solution is filtered through an ashless paper and washed with hot distilled water until a $AgNO_3$ solution shows no precipitate with a drop of the filtrate. The test for excess $BaCl_2$ is made by adding a few drops of the filtrate to a dilute solution of H_2SO_4. The precipitate is then ignited and the paper being folded over the precipitate only loosely to prevent spattering. The paper should be smoked off very gradually at first, and the paper is burned off completely; the heating is continued for a few minutes, then the crucible is cooled and weighed. The weight in grams of $BaSO_4$ after deducing the weight of $BaSO_4$ found in a blank determination using the same reagents, multiplied by 13.75 and divided by the weight of the sample taken.

A_2. Turbidimeter Method:-

The turbidimeter method is an effective short-cut around some of the time consuming steps common to the gravimetric procedures in the analysis of sulfur in coal. By this method, the mass of an insoluble compound can be determined while suspended in a fluid, thus avoiding the customary filtration, washing, drying and weighing operations. For this purpose Parr turbidimeter is used, whose principle is to indicate the relative turbidity of an unknown solution as compared with the turbidity of a similar solution in which the amount of precipitate is known.

By treating a sulfate solution with barium chloride it is possible to precipitate all of the sulfur as barium sulfate, and the turbidity of the resulting solution as observed in the turbidimeter can be taken as a measure of the sulfur content.

There are certain limitations encountered in the turbidimeter method. Parr turbidimeter requires 200 ml of test solution in which turbidimeter measurements are made in terms of the depth of turbid solution which will obscure the image of an electric lamp filament when viewed through the solution. The depth readings are taken in millimeters, as indicated by a scale mounted on the front of the instrument. This is a visual extinction method, hence there is a limit of low turbidity and one of high turbidity between which the readings must fall in order to come within the working range. If the whole sample produces a dense turbidity outside of the work-range, it must be brought within bounds by taking from it a test portion which, in turn, must be diluted to 200 ml for the turbidity test. On the other hand, in the case of samples which produce very low turbidities it may be necessary to concentrate larger samples in order to come within the working range. For sulfur determination a 200 ml test solution should contain not less than 3.8 milligrams and not more than 7.0 milligrams of sulfur. This is clearly shown in the calibration curve for sulfur.

To meet the required minimum sulfur content of 3.8 mg a 0.5 gram sample tested in peroxide bomb should contain not less than 0.76% sulfur by weight. In case of very lean samples it is possible to combine the washings from two combustions in order to secure enough sulfur to meet the minimum requirement. If a sample is rich in sulfur, then a test portion is taken from the solution; this test portion will have a sulfur content within the 3.8 to 7.0 mg. limits.

Before making a sulfate solution, it is necessary to treat the sample in a Parr sodium peroxide combustion bomb. The precedure for preparing the charge for the bomb is described below.

All of the ingredients in a bomb charge, excepting the peroxide, should be weighed on an analytical balance, and the amounts used should not exceed those mentioned. The sample itself must be properly dried and ground and the other ingredients must be carefully selected for use. The fusion cup should be clean and throughly dry before putting in the charge. It is well to dry the cup in an oven to be sure that all moisture has been eliminated, though, of course, it should be at room temperature for charging.

Weigh exactly about 1.0 gram potassium perchlorate accelerator and place it in the fusion cup. Weigh exactly about 0.50 gram sample and add to the accelerator in the cup. A small amount, about .3g of benzoic acid powder is added to the mixture and mixed well with a stirring rod. One dipper (holding 15 gms) of sodium peroxide is added and immediately mixed throughly by stirring or shaking, or both. The bomb is assembled. For firing the bomb, a single length of wire 7 cm long from the card and attached to the electrodes on the bomb head. This fuse loop is not made too long. It is better to have it just touching the surface of the charge. The fuse wire should not touch the wall of the fusion cup. To assemble the electric ignition bomb, the floating bottom is placed in the foot of the bell body. The small holes around the side of the bell body are inspected to be sure that they are all open. Then the fusion cup is inserted and it is covered at once with the bomb head. The bomb is sealed by turning down the screw cap, which is tightened firmly. The necessary hose connections are made; the bath is filled with water until the bomb is submerged. A continuous stream of cold water is passed through the bath during the ignition and cooling period. After all the connections are made, the charge is ignited by pressing the switch button on the ignition unit and holding the switch closed until the pilot light stops glowing. The light should not be on for more than two seconds. If the pilot light fails to go out disregard the light and open the circuit within five seconds after firing. Allow the bomb to cool in the water for at least five minutes.

After ignition and cooling, dismantle the bomb, remove the head and dip it into a 600 ml beaker containing about 100 ml distilled water previously heated almost to boiling. This dissolves any of the melt adhering to the underside of the head. It is then washed with a fine jet of distilled water, catching the washings in the beaker. With a pair of tongs, the fusion cup is laid down on its side in the same beaker of hot water, covering the beaker immediately with a watch glass. After the melt has dissolved, the cup is removed and washed thoroughly with a fine jet of hot distilled water. All the washings are retained in the beaker.

The solution is colled and neutralized with concentrated HCl, care is taken that the spattering does not occur.

At this point it is advisable to show the reactions taking place in the bomb.

$C - 2Na_2O_2$ ---- $CO_2 - 2Na_2O$ ---- $Na_2CO_3 - Na_2O$

$H_2 - Na_2O_2$ ---- $H_2O - Na_2O$ ---- $2NaOH$

$CH_4 - 4Na_2O_2$ ---- $CO_2 - 2H_2O - 4Na_2O$ ---- $Na_2CO_3 - 4NaOH - Na_2O$

$S - 3Na_2O_2$ ---- $SO_2 - Na_2O_2 - 2Na_2O$ ---- $Na_2SO_4 - 2Na_2O$

At approximately the neutral point, a small piece of litmus paper is placed and the acid is added until the indicator changes color. The solution is made slightly acid. The solution is filtered to remove any ash or suspended matter, it is washed with hot distilled water. The filterate is transferred to a 200 ml volumetric flash and made up to volume; this will be referred to as the "whole sample".

If the total sulfur content of the original sample does not exceed 7.0 mgs, the entire 200 ml of whole sample may be transferred to the 300 ml Erlenmeyer flask for treatment with barium chloride. If the total sulfur content is expected to exceed 7.0 mgs, it will be necessary to take from the whole sample a test portion which will contain an amount of sulfur within the working range of the turbidimeter. The curve determines the size of the test portion which must be taken from a 200 ml whole sample.

Now to this solution in the Erlenmeyer flask, one dipper of barium chloride is added. The flask is shaken vigorously for one minute. Without further delay, the turbid solution is transferred to the solution tube and the instrument lamp is adjusted to 3.0 volts and the turbidity reading is taken.

The sulfur content is computed as follows:

$$\frac{(\text{mg S in test solution})\text{X}(\text{vol\_of whole sample(i.e. 200 ml)})}{(\text{Wt. of original sample-gm})\text{X}(\text{test portion})(10)}$$

B. Sulfate Sulfur:-

Crush the dry coal so that it will pass completely through a 100 mesh screen. Weigh an amount of 5 grams sample and place it in a 500 cc beaker. Cover this carefully with 300 cc of 3% HCl, stir throughly, and place a watch glass on the beaker. Put this beaker on top of a water bath or some other warm place where it can digest at about 60°C.

At the end of 40 hours filter the contents of the beaker, dissolving the coal material left on the filter. Add 2 cc of bromine water and heat almost to boiling. Pour this acid solution into an excess of ammonia and stir to coagulate the $Fe(OH)_3$. Filter off this Fe precipitate, retaining it for the iron determination, if necessary. Make the filterate barely acid with HCl, heat to boiling and add slowly, with stirring, 10 cc of 10% $BaCl_2$. Allow this to stand for several hours, then filter it. Ignite the filter paper and weigh the precipitate of $BaSO_4$, in grams multiplied by 2.75 represents the percent of sulfur, combined as sulfate in the coal.

C. <u>Sulfur soluble in nitric acid</u> (pyritic & sulfate sulfur): Weigh out a 1 gram sample of the coal and place it in a 150 cc beaker. Cover it with 80 cc of dil HNO_3 (1 part HNO_3, sp.gr. 1.42, to 3 parts H_2O). Allow this to stand for 24 hours, with occasional stirring, and filter. Discard the coal residue on the filter. Add 2 cc of conc. HCl to the filterate and evaporate to dryness on water bath. Dissolve the residue in 25 cc of H_2O and 5 cc of conc. HCl. Pour this acid solution into an excess of hot, dilute NH_3. From this point the analysis is the same as that for the HCl soluble sulfur. The weight of $BaSO_4$ in grams, multiplied by 13.75, represents the percentage of sulfur, both pyritic and sulfate, in the coal.

The amount of pyritic sulfur (in percent) is found out by subtracting from the percent of sulfur obtained from the nitric acid method, the percent of sulfur obtained from the HCl soluble method.

The total amount of organic sulfur is calculated by adding the percentages of sulfate and pyritic sulfur and subtracting this from the percent of total sulfur in the coal.

D. Resinic Sulfur:-

The phenol soluble (resinic sulfur) is determined in the following way. An amount of ½ gram of coal is taken into an Erlenmeyer flask, 50 cc and 25 cc of phenol is poured over it. The flask is fitted with a long glass tube that extends 2 ft above to act as a condenser for the phenol vapors. The flask is kept in an oil bath, which is maintained at a temperature of 140°C, the extraction is continued for 20 hrs., when the contents of the flask are filtered through a Gooch crucible while still hot. Every particle of residue is rinsed out of the flask by means of alcohol and ether. The residue in the Gooch crucible is dried, mixed with Eschka mixture, and ignited in a porcelain crucible, at a temperature of 800_25°C, for about 1½ hrs.

When the crucible is removed from the muffle, the contents are throughly stirred. If any black particles remain, the crucible is returned to the muffle and heated until all black particles are burned out. The crucible and contents are then allowed to cool, and the contents are transferred to a beaker and digested with 100 cc of hot water for half an hour. Filteration into a beaker follows; the insoluble residue is washed twice with hot water by decantation, and after being transferred to the filter paper is washed with small quantities of hot water until the wolume of solution in the beaker is about 250 cc. About 4 cc of saturated bromine water and enough dilute (2:1) HCl is added to make the solution slightly acid. The solution is next boiled to expel the liberated bromine and the sulfur is precipitated as $BaSO_4$ by adding slowly 10-20 cc of hot 10% solution of $BaCl_2.2H_2O$. The solution containing the precipitate is allowed to stand for at least 2 hrs or preferably overnight, at a temperature just below boiling.

The solution is filtered through an ashless filter paper and washed with hot distilled water until a $AgNO_3$ solution shows no precipitate with a drop of the filterate. The test for excess $BaCl_2$ is made by adding a few drops of H_2SO_4 to the filterate. The precipitate is then ignited and the paper being carefully. The paper is smoked off very gradually at first, and then it is burned off completely; the heating is continued for a few minutes, when the crucible is cooled and weighed. The weight of $BaSO_4$ multiplied by 13.75 and divided by the weight of the sample taken.

E. <u>Humic</u> <u>Sulfur</u>:-

1. The amount of humic sulfur is found by subtracting the percent of resinic sulfur from the percent of total organic sulfur.

2. The addition of the tree forms of sulfur (i.e. sulfate, pyritic and phenol soluble) does not compare with the total amount of sulfur. This unaccounted sulfur is taken as humus sulfur. A direct estimation of this amount is given.

The residue from the nitric acid extraction for pyritic sulfur is taken. It is mixed with a 25 cc of ammonium hydroxide (sp. gr. 0.90). This mixture is allowed to stand for several hours (3 to 4 hrs), it is then diluted, passed through a filter. (It is very difficult to filter this material, so it was done under vacuum). The filterate is dark brown in color. It is evaporated to dryness. The dry mass is mixed with Eschka mixture, ignited and sulfur determined in the usual manner.

B. C. R. A. METHODS FOR SULPHATE, PYRITIC SULFUR IN COAL

Principle of method:-

The sulphate sulfur is extracted with dilute hydrochloric acid under conditions which do not attack the pyritic sulphur, and is precipitated and weighed as barium sulphate.

Sulphate sulfur:-

Boil 5 g. of coal ground to pass 72 B.S. mesh test sieve with 50 ml. of 5_N hydrochloric acid for 30 min. in a 250 ml. conical flask with an Arnold bubbler (or a boiling tube) through which a slow stream of water passes to form a 'cold-finger' condenser, i.e. the Arnold bubbler rests, without further support, in the neck of the flask. Filter the mixture, wash six times with dilute hydrochloric acid (1 in 20) using about 20 ml. acid in all. Add 1ml. of bromine water, boil and precipitate the iron with ammonium hydroxide, filter and wash. Determine the sulfate sulfur in the filtrate as stated above.

Pyritic Sulfur:-

Boil 1 g. of coal, ground to pass 72 B.S. mesh test sieve, with 50 ml. of 2_N nitric acid in a similar reflux apparatus as that used above for 30 min. Filter and wash six times with 2_N nitric acid. Heat the filtrate to boiling point, and precipitate $BaSO_4$.

Table XIII

Basic Data

Total Sulfur-

Sample	Air Dried		Moisture Free	
	Eschka	Turbidimeter	Eschka	Turbidimeter
Noonan	1.282	1.75	1.482	2.02
	1.417	1.67	1.638	1.93
	1.366	1.72	1.580	1.99
	1.347	-	1.557	-
	1.300	-	1.503	-
Columbus	0.467	0.48	0.556	0.57
	0.462	0.50	0.550	0.60
	0.470	0.44	0.560	0.52
Velva	0.510	0.52	0.644	0.66
	0.537	0.54	0.678	0.68
	0.520	-	0.657	-
	0.512	-	0.646	-
Custer	0.481	0.49	0.604	0.61
	0.446	0.45	0.559	0.57
	0.473	-	0.594	-
	0.480	-	0.602	-
Garrison Dam	0.687	0.79	0.822	0.95
	0.670	0.76	0.802	0.91
	0.693	0.76	0.830	0.91
	0.760	-	0.910	-
Hazen	0.245	0.23	0.306	0.29
	0.258	0.28	0.323	0.35
	0.252	0.24	0.315	0.30
Beulah	0.611	0.552	0.790	0.714
	0.642	0.592	0.829	0.765
	0.621	0.660	0.803	0.854
Zap	0.923	0.92	1.010	1.115
	0.817	0.90	1.110	1.110
	0.960	-	1.118	-

Table XIV

Basic Data

HCl Soluble or Sulfate Sulfur

No.	Sample	Air Dried		Moisture Free	
		Powell & Parr	BCRA Method	Powell & Parr	BCRA Method
1.	Noonan	0.0424	0.129	0.0490	0.1490
		0.0510	0.123	0.0590	0.1435
		0.0458	0.120	0.0458	0.1398
2.	Columbus	0.029	0.028	0.0346	0.0340
		0.018	0.035	0.0215	0.0417
		0.019	0.020	0.0227	0.0238
3.	Velva	0.035	0.044	0.0442	0.0556
		0.033	0.034	0.0416	0.0430
		0.032	0.047	0.0392	0.0594
4.	Custer	0.0173	0.0179	0.0217	0.0214
		0.0160	0.0198	0.0201	0.0248
		0.0166	0.0169	0.0208	0.0212
5.	Garrison Dam	0.0464	0.0495	0.0556	0.0593
		0.0324	0.0400	0.0388	0.0480
		0.0420	0.0586	0.0503	0.0703
6.	Hazen	0.0314	0.0400	0.0393	0.0500
		0.0324	0.0288	0.0406	0.0360
		------	0.0238	------	0.0298
7.	Beulah	0.0253	0.0452	0.0328	0.0585
		0.0398	0.0371	0.0515	0.0480
		0.0308	------	0.0398	------
8.	Zap	0.0678	0.0992	0.0820	0.012
		0.0728	0.0661	0.0880	0.080
		0.0686	------	0.0830	------

Table XV

Basic Data

Nitric Acid Soluble Sulfur

No.	Sample	Air Dried		Moisture Free	
		Powell & Parr	BCRA Method	Powell & Parr	BCRA Method
1.	Noonan	1.241	1.205	1.435	1.393
		1.200	1.160	1.385	1.342
		1.211	1.185	1.400	1.370
2.	Columbus	0.0730	0.062	0.087	0.0738
		0.0650	0.075	0.0774	0.0894
		0.0721	0.0703	0.0860	0.0837
3.	Velva	0.176	0.180	0.222	0.227
		0.176	0.164	0.222	0.207
		-----	0.172	-----	0.218
4.	Custer	0.0852	0.0753	0.1070	0.0944
		0.0743	0.0927	0.0932	0.1162
		0.0848	------	0.1063	------
5.	Garrison Dam	0.199	0.218	0.238	0.261
		0.213	0.211	0.255	0.253
		0.204	-----	0.244	-----
6.	Hazen	0.090	0.100	0.1125	0.1250
		0.090	0.085	0.1125	0.1062
7.	Beulah	0.1280	0.1470	0.1660	0.190
		0.1575	0.1385	0.2040	0.179
		0.1358	------	0.1755	-----
8.	Zap	0.748	0.818	0.905	0.990
		0.662	0.654	0.800	0.790
		0.727	-----	0.880	-----

Table XVI

Basic Data

Phenol Insoluble Sulfur

No.	Sample	Air Dried	Moisture Free
1.	Noonan	1.230	1.420
		1.305	1.510
		1.290	1.490
2.	Columbus	0.465	0.554
		0.465	0.554
		-----	-----
3.	Velva	0.484	0.611
		0.507	0.640
		0.442	0.658
4.	Custer	0.428	0.537
		0.436	0.547
		0.431	0.540
5.	Garrison Dam	0.595	0.714
		0.625	0.750
		0.601	0.720
6.	Hazen	0.253	0.316
		0.238	0.298
		0.250	0.313
7.	Beulah	0.606	0.784
		0.623	0.806
		0.612	0.792
8.	Zap	0.910	1.100
		0.822	0.995
		0.900	1.089

Table XVII

Basic Data

Ammonia Soluble Sulfur

No.	Sample	Air Dried	Moisture Free
1.	Noonan	0.157	0.182
		0.184	0.213
		0.138	0.159
2.	Columbus	0.455	0.542
		0.420	0.500
		0.471	0.561
3.	Velva	0.303	0.383
		0.280	0.354
		0.321	0.406
4.	Custer	0.435	0.545
		0.414	0.518
		0.424	0.532
5.	Garrison Dam	0.455	0.545
		0.575	0.689
		0.479	0.574
6.	Hazen	0.201	0.251
		0.165	0.200
		0.188	0.235
7.	Beulah	0.371	0.480
		0.324	0.418
		0.362	0.468
8.	Zap	0.1035	0.125
		0.0910	0.110
		0.0735	0.089

Table XVIII
Humic Sulfur

Dry Basis

No.	Sample	By Difference	By Ammonia Sol. Method
1	Noonan	0.038	0.185
2	Columbus	0.475	0.534
3	Velva	0.384	0.381
4	Custer	0.438	0.531
5	Garrison Dam	0.482	0.603
6	Hazen	0.194	0.229
7	Beulah	0.601	0.455
8	Zap	0.185	0.108

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