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SULFUR IN ILLINOIS COALS

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Reference to Wanless (1959) — Should be Wandless (1959)

SULFUR IN ILLINOIS COALS

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ABSTRACT

Data concerning the occurrence and distribution of sulfur in Illinois coals have been developed at the Illinois State Geological Survey over a period of many years. These data have been assembled and analyzed, and the following observations and conclusions have resulted.

Sulfur is present within coal as sulfide (pyritic sulfur), as sulfate, and in organic combination (organic sulfur). Sulfide sulfur occurs primarily as pyrite. Sulfate sulfur is usually of little significance, except in weathered coals where ferric and ferrous sulfates may be of importance.

There is a wide range of both pyritic and organic sulfur in face-channel samples of coal in considering Illinois as a whole, although the range is less for organic sulfur than for pyritic sulfur. Generally, there is a positive correlation between pyritic and organic sulfur in these samples.

The pyritic sulfur content is usually greater in the fusain bands than in the clarain and vitrain bands. The organic to pyritic sulfur ratios are higher for both vitrain and clarain, with clarain being the richest in organic sulfur.

Three areas of relatively low-sulfur coal are sufficiently well known to be outlined and mapped. These are an area of Herrin (No. 6) Coal in south-central Illinois (Franklin and several adjacent counties), an area of Herrin (No. 6) Coal in southwestern Illinois (St. Clair and Madison Counties), and an area of Harrisburg (No. 5) Coal in southeastern Illinois (Saline and several adjacent counties).

The organic sulfur content is more uniform throughout a vertical section of a coal seam than is the pyritic sulfur content. Large vertical variations in pyritic sulfur
are commonly observed. When the mineral bands in excess of 3/8-inch thick are disregarded, there is a tendency for pyrite, and therefore total sulfur content, to be greater in the top and/or bottom benches of the coal seam.

INTRODUCTION

Sulfur in its several forms is prominent among the species of mineral matter known to occur in coal. Not only is the occurrence of combined sulfur prevalent in coal, but its effects can be extremely detrimental, and some of the coals with high sulfur content are restricted in the manner in which they may be utilized.

The public has become aware of several of the many problems associated with the presence of sulfur in coal with the recently increased concern for all forms of air and water pollution, including sulfur dioxide (SO₂) emission into the atmosphere from coal-fired boilers and acid drainage into streams from coal mines, spoil piles, and refuse dumps. Other problems associated with the presence of sulfur in coal include possible contribution to spontaneous combustion of coal in mines, in refuse piles, and in stored and stockpiled coal; the formation of boiler deposits and associated corrosion of boiler tubes; difficulties in mining and coal preparation; and the need for low-sulfur coals in the manufacture of metallurgical coke.

Because of the recognition of the importance of sulfur in the utilization of coal, investigations concerning sulfur in coal have been pursued at the Illinois State Geological Survey since its founding more than 60 years ago. One of the objectives of this Circular will be to summarize the pertinent data concerning sulfur in coal, which have been collected, and in many cases published, by members of the Geological Survey staff over that period of time. In addition, recently developed data on the distribution of sulfur in Illinois coals will be discussed. The information from the chemical analyses of the coal samples in which we are interested has been put into a form whereby computer processing is possible, and this enables us to analyze much more completely this large amount of data.

Except where specifically stated to the contrary, all data from chemical analyses discussed in this paper were obtained from analyses of face-channel samples of coal. These samples were taken in the mines by Geological Survey personnel following recommended U. S. Bureau of Mines methods of sampling, which provide for exclusion of mineral bands over 3/8-inch in thickness (Holmes, 1911). The excluded bands may be composed of pyrite or pyrite and other minerals. In some instances, those bands may represent a significant amount of sulfur in comparison to the total sulfur in the resulting face-channel sample.

Acknowledgments

The photomicrographs in figure 1 were taken by the late John A. Harrison of the Illinois State Geological Survey and were given to the authors. Data on sulfur in Illinois coals have been collected at the Illinois State Geological Survey on a continuing basis for over 60 years. Much of this material, collected and in a large part reported by previous workers, is summarized within this report. The research reported in this Circular was supported, in part, by the U.S. Department of Health, Education, and Welfare, Division of Air Pollution, Bureau of State Services, Public Health Service, through Research Grant AP00517.
FORMS OF SULFUR IN COAL

Organic Sulfur

It has long been recognized that sulfur occurs in coal in both inorganic and organic forms. It occurs inorganically as sulfides and sulfates, but the exact mode of occurrence of the organic sulfur is not known. Given and Wyss (1961) state that it is usually assumed that sulfur is in one of the following four forms:

1. mercaptan or thiol, RSH
2. sulfide or thio-ether, RSR'
3. disulfide, RSSR'
4. aromatic systems containing the thiophene ring, \( \text{HC} \begin{array}{c} \text{S} \\ \text{CH} \end{array} \)

They also suggest that sulfur could be present in the \( \gamma \)-thiopyrone system:

Free Sulfur

Free sulfur, or native sulfur, has been reported in coal (Yurovski, 1959; Berteloot, 1947). However, its occurrence is rare and small enough in amount to be disregarded for most purposes. It has not been reported from Illinois coals.

Sulfate Sulfur

The small amount of sulfate sulfur that occurs in nearly every face-channel sample of Illinois coal is contained primarily within the mineral gypsum \((\text{CaSO}_4 \cdot 2\text{H}_2\text{O})\), which occurs as a secondary vein and cleat filling.

The amount of sulfate sulfur increases rapidly upon weathering of the coal as the oxidation of pyrite \((\text{FeS}_2)\) gives rise to ferrous and ferric sulfates. The following minerals have been identified from samples collected in deep mines, from old mined-out areas, and from samples of coal, which have weathered from exposure at the surface either in outcrop, mine dumps, or in the laboratory:

- Rozenite \( \text{FeSO}_4 \cdot 4\text{H}_2\text{O} \)
- Melanterite \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \)
- Coquimbite \( \text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O} \)
- Roemerite \( \text{FeSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O} \)
- Jarosite usually a sodium jarosite \((\text{Na,K}) \text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 \)

More than one of these phases often occur in a single sample. It is also difficult to know exactly which phases occur in the mines, as melanterite \((\text{FeSO}_4 \cdot 7\text{H}_2\text{O})\) dehydrates to rozenite \((\text{FeSO}_4 \cdot 4\text{H}_2\text{O})\) and then to szomolnokite \((\text{FeSO}_4 \cdot 2\text{H}_2\text{O})\) in the laboratory. The dehydration is very rapid, occurring in just a few minutes, as in the case of melanterite to rozenite.
Pyritic Sulfur

The term pyritic sulfur refers to either of two dimorphs of ferrous disulfide (FeS$_2$)—pyrite or marcasite. The two minerals have identical chemical compositions but different crystalline forms. Pyrite is isometric (cubic) and marcasite is orthorhombic. They can be distinguished only by their crystalline structure, which is usually determined by X-ray analyses. Pyrite is the most commonly reported dimorph, although marcasite is often mentioned as occurring in lesser amounts. Marcasite has not as yet been substantiated as occurring in Illinois coals, and pyrite is the dominant sulfide.

The modes of occurrence of pyrite in coals of the world have been described by many workers including Thiessen (1945), Sprunk and O'Donnell (1942), Chapman and Rhys Jones (1955), and Whelan (1954). Yancy and Fraser (1921), Cady (1935a), and Ball (1935) described specifically pyrite occurrences in Illinois coals. Macroscopic pyrite occurs in coal in the following predominant forms: (1) veins that are usually thin and filmlike along the vertical joints (cleats), but may be up to several inches wide and contain large pyrite crystals with well developed crystal faces; (2) lenses that are extremely variable in shape and size but usually flattened and elongate in cross section, ranging in size from a fraction of an inch thick by several inches in diameter to several inches thick and hundreds of feet in lateral extent (the latter, perhaps, are more properly referred to as beds than lenses); (3) nodules or balls, roughly spherical in shape and from inches to several feet in diameter (these sulfur balls usually are not pure pyrite but include one or more of the following: calcite, siderite, clay minerals, and organic matter); and (4) disseminated crystals and irregular aggregates that are extremely variable in size with little or no apparent relationship to veins, fractures, or other structural features.

In addition to the macroscopic pyrite in coal, much of the iron disulfide is present in forms visible only with the aid of a microscope. Microscopic pyrite has been described as occurring as small globules and blebs, fine veinlets, dendrites, small euhedral crystals, cell fillings, and replacement of plant material (Chapman and Rhys Jones, 1955; Gray, Shapiro, and Coe, 1963; Thiessen, 1920; and Neavel, 1966). Figure 1 is composed of photomicrographs, taken in reflected light, of polished samples of coals that contain pyrite generally visible only under a microscope. Photomicrograph 1A shows a common occurrence of finely disseminated discrete pyrite grains (bright grains) in vitrinite, which are from 1 to 2 microns (.002 mm, or .00012 inch) in diameter. Photomicrograph 1B depicts pyrite filling the cell cavities in fusain. Crystalline "fiber-bundles" in vitrinite are shown in 1C, and small crystalline aggregates of pyrite in vitrinite are shown in 1D.

DISTRIBUTION OF SULFUR IN ILLINOIS COALS

The discussion that follows is based on the interpretation of 474 chemical analyses of coal for which varieties of sulfur (sulfate sulfur, sulfide sulfur, and organic sulfur) were determined. These were either face-channel samples or diamond drill-core samples. All of the data were put on punch cards to enable automatic data processing to be utilized.
Figure 1 - Microscopic pyrite in coal. All photomicrographs are of samples of No. 6 Coal taken in reflected light:

a. Discrete grains in vitrinite.
b. Cavity fillings in fusinite.
c. Crystalline "fiber-bundles" in vitrinite.
d. Crystalline aggregates in vitrinite.
Sulfate Sulfur

Sulfate sulfur is present in minor amounts in nearly all of the samples analyzed. The sulfate sulfur values, as shown on figure 2, range from a low of 0.00 percent to a high of 0.88 percent. Values over 0.20 percent are relatively rare, and the mean of 361 sulfate sulfur analyses on face-channel and drill-core samples of Illinois coals is 0.08 percent. The mode is between 0.02 and 0.04 percent.

Organic Sulfur

Organic sulfur values range from a low of 0.27 percent to a high of 2.98 percent in Illinois coals that have been sampled to date. The mean value for organic sulfur of all coals is 1.46 percent. The distribution of organic sulfur for all face-channel and drill-core samples is given in a histogram in figure 3. These data are then reanalyzed, based on the coals sampled, and histograms showing the distribution of organic sulfur in the Colchester (No. 2), Harrisburg and Springfield (No. 5), and Herrin (No. 6) Coal Members comprise figure 4.

Organic sulfur ranges from 0.4 percent to nearly 3.0 percent in No. 2 Coal, from 0.4 percent to 2.6 percent in No. 5 Coal, and from 0.4 percent to 3.0 percent in No. 6 Coal. Organic sulfur distribution is not plotted in the case of the Danville

![Figure 2 - Sulfate sulfur distribution in 361 face-channel and drill-core samples of Illinois coals.](image-url)
SULFUR IN ILLINOIS COALS

(No. 7) Coal Member, but all of the 17 analyses in hand show the organic sulfur content to be from 1.0 to 2.0 percent. The organic sulfur distribution in the No. 6 Coal suggests a bimodal distribution with a peak at 0.6 to 0.8 percent and another at about 2.0 percent. A similar bimodal distribution is seen in the histogram of pyritic sulfur distribution of No. 6 Coal and also in the histogram of organic sulfur distribution of No. 5 Coal. This probably represents a preferential sampling of the very heavily mined, low-sulfur coals in southern Illinois. These coals have been of much interest in the state and have been sampled frequently by the Illinois State Geological Survey for use in a variety of investigations.

Pyritic Sulfur

The range in values of pyritic sulfur in face-channel and drill-core samples is greater than the range in organic sulfur. The range is from a low value of 0.00 percent to normally high values of 4.0 to 5.0 percent, with a few extreme values as high as 7.5 to 9.0 percent (fig. 5). The mean value of all the analyses shown on figure 5 is 2.06 percent. Histograms depicting the distribution of the pyritic sulfur values for No. 2, No. 5, and No. 6 Coals are given in figure 6. The histogram of pyritic sulfur values in No. 5 Coal shows the most nearly normal distribution, and that for No. 6 Coal shows the bimodal distribution mentioned previously. Pyritic sulfur distribution in No. 7 Coal is not shown graphically. The range in pyritic sulfur for No. 7 Coal is from 1.30 percent to 4.88 percent.

Total Sulfur

Total sulfur in face-channel samples of Illinois coals ranges from a low of less than 0.50 percent to normally high values of 5.0 to 6.0 percent, with a few extreme cases approaching 10 percent and one sample exceeding 10 percent. The sulfur in these extremely high-sulfur coal samples is primarily pyritic sulfur. The mean total sulfur content for all 473 face-channel samples is 3.57 percent.

Relationship Between Pyritic and Organic Sulfur

The ratio of pyritic sulfur to organic sulfur in face-channel samples of Illinois coals ranges from 0 (three face-channel samples of one coal for which chemical analysis showed no pyritic sulfur) to 13.67. The correlation coefficient for this relationship is 0.31, and the mean value for the ratio of pyritic sulfur to organic
sulfur is 1.56. There is, on the average, approximately one and one-half times as much pyritic sulfur in a sample as there is organic sulfur.

Three graphs showing the relationship between organic and pyritic sulfur for three Illinois coals are given in figure 7. Each point on the graphs represents sulfur values from a single face-channel sample analysis. Correlation coefficients for the three graphs vary considerably. The correlation is relatively poor in the case of No. 5 Coal (correlation coefficient 0.21), although it exceeds the 95 percent confidence level. No. 2 and No. 6 Coals show a better degree of correlation with correlation coefficients of 0.44 and 0.55, respectively. Both of these latter values demonstrate a high degree of significance, well over the 99 percent confidence level. The rate of increase of pyritic sulfur with an increase in organic sulfur is much greater for No. 6 Coal than for No. 2 Coal. A similar statistical analysis of data from only 17 face-channel samples of No. 7 Coal shows no real correlation between organic sulfur and pyritic sulfur.

Differing conclusions have been drawn by various workers as to the relation of pyritic sulfur to organic sulfur in coals. A number of researchers have reported such a correlation: Cady (1935a), Horton and Randall (1947), Rose and Glenn (1959), Wanless (1959), Leighton and Tomlinson (1960), and Neavel (1966). Yancy and Fraser (1921) and Brooks (1956) have not observed such a correlation in their studies. Neavel (1966) observed a poor correlation between organic sulfur and pyritic sulfur in 4- to 10-inch blocks of coal from the Redstone Seam in West Virginia. However, when entire columns of the same coal were considered, the correlation between organic and pyritic sulfur was quite good (correlation coefficient +0.87; Neavel, 1966, p. 149).

With the exception of Illinois No. 7 Coal, which may be discounted because of lack of sufficient data, the Illinois coals do show a statistically signifi-
cant, positive correlation between organic and pyritic sulfur. This correlation is best in the case of No. 6 Coal and poorest in the case of No. 5 Coal.

The chemical analytical methods for determining varieties of sulfur could possibly contribute, in part, to the observed correlation between organic and pyritic sulfur. The coal is analyzed directly for total sulfur, sulfate sulfur, and pyritic sulfur. Organic sulfur is then determined by difference, and a consistent error in any of the direct determinations will affect the organic sulfur value. However, a sufficient number of comparison analyses have been done both between different laboratories and by different analytical techniques within a single laboratory to demonstrate that the influence of the methods of analyses on the observed correlation is not great.

The fact that a correlation between organic and pyritic sulfur is often observed suggests that the two forms of sulfur are related with regard to their modes of formation. It does not necessarily follow that the organic and pyritic sulfur had the same genesis or time of genesis. However, the presence of such a correlation does suggest that in a coal-swamp environment that was high in sulfur, there would also be sulfur available for the formation of pyrite, coincidental to the time of formation of the organic sulfur compounds, or at some later time.

FORMS OF SULFUR IN BANDED INGREDIENTS OF COAL

Cady (1935a) investigated the distribution of the forms of sulfur (organic and pyritic) in the three megascopically distinguishable banded ingredients comprising the
Figure 6 - Pyritic sulfur distribution in No. 2, No. 5, and No. 6 Coals.
Figure 7 - Pyritic sulfur-organic sulfur relationship in face-channel and drill-core samples of Illinois coals.
coal: vitrain, clarain, and fusain. The fourth banded ingredient, durain, which is found in coals in many parts of the world, is very rare, if present at all in Illinois coals, and none was sampled. The data obtained from the chemical analyses of a wide variety of coals from throughout Illinois are shown in figure 8, which has been modified slightly from Cady (1935a).

In general, the pyritic sulfur content is greater in fusain than in the other banded ingredients, although pyritic sulfur exhibits a wide range in the different fusain samples. This is due to the degree to which the cell cavities in fusain are filled with pyrite. The organic sulfur content of fusain is in all cases less than one percent. Vitrain and clarain have higher organic sulfur to pyritic sulfur ratios than does fusain, and this ratio generally has a numerical value greater than one (more organic than pyritic sulfur). The amount of organic sulfur contained in vitrain is usually lower than that contained in clarain from the same coal.

Cady (1935a, p. 35) concluded, "Increase in the relative amount of clarain in a coal would probably result in an increase in the organic sulfur content, but the variations in the organic sulfur content of Illinois coals cannot be ascribed simply to variations in the relative proportions of the banded ingredients..." This conclusion follows from the observation that vitrain in No. 6 Coal in one part of the state may very well contain more organic sulfur than does clarain in the same coal in another part of the state.

VERTICAL AND LATERAL DISTRIBUTION OF VARIETIES OF SULFUR

Previous Work

The variations in both pyritic and organic sulfur in the individual coal seams are very large when considering the state as a whole, as can be seen from figures 3, 4, 5, and 6. However, there have been differences of opinion as to the amount of local variation that exists in the organic sulfur content. There are no such differences of opinion concerning the pyritic sulfur distribution, inasmuch as extremely localized concentrations of authigenic pyrite are common.

Cady (1935a, p. 30, 31) observed that "local variation in organic sulfur is rarely more than 1 percent...and generally not more than 0.5 percent irrespective of the locality" and "the organic sulfur is the best index of the sulfur content and the organic sulfur content is regionally consistent for each coal bed." Yancy and Fraser (1921) studied in detail the distribution of varieties of sulfur both vertically and laterally within a single mine in southern Illinois. They found the organic sulfur content to be rather uniform vertically within the seam, but also found that the lateral variation in organic sulfur could be considerable, even within a single mine. This variation was not as large as the lateral variation in pyritic sulfur (Yancy and
Fraser, 1921. p. 64). Within the mine studied, the organic sulfur in the face-channel samples (No. 6 Coal) ranged from 0.69 to 1.90 percent and the pyritic sulfur from 0.66 to 3.17 percent. It has been suggested (Cady, 1935a, p. 31) that the wide range in organic sulfur observed by Yancy and Fraser (1921) may be attributable in some way to the location of the sampled mine. It was on the eastern margin of the area of low-sulfur coal in Franklin County and included samples from both within and outside the low-sulfur coal area.

Yancy and Fraser (1921) also analyzed individual benches of face-channel samples for varieties of sulfur. They took 12 face-channel samples of Herrin (No. 6) Coal from a mine in southern Illinois, 6 samples from a mine in western Kentucky in No. 12 Coal (Jamestown Coal Member of Illinois), and 2 samples from a mine in No. 9 Coal of Kentucky (No. 5 Coal of Illinois). The entire coal seam was sampled in all instances except the "blue band," a shale bed up to 2 or 3 inches thick sometimes including pyrite, which was excluded from all 12 face-channel samples of Herrin (No. 6) Coal. The organic sulfur content was relatively uniform between benches of the individual face-channel samples. The greatest variation in any single section was from a minimum of 0.57 to a maximum of 1.25 percent. Most of the benches in a single face channel had an organic sulfur content within 25 percent of each other. The vertical variation in pyritic sulfur was found to be very large between different benches in the same face-channel sample, ranging, in two instances, from 0.81 to 5.54 percent and from 0.02 to 2.09 percent. Yancy and Fraser (1921) reported that in nearly every section (face-channel sample), the pyritic sulfur, and thereby also the total sulfur, was much higher in uppermost and lowermost benches. This conclusion was found to be true for their samples of Illinois No. 6 Coal and for the No. 12 Coal of Kentucky. The two samples of the No. 9 Coal of Kentucky had the highest pyritic sulfur in the lowest benches, but the uppermost benches were relatively low in sulfur. Wanless (1959), in a general discussion of the occurrence of sulfur in British coals, reached conclusions that support Yancy and Fraser in recognizing the concentration of pyrite at the top and bottom of the coal and also in the rather uniform organic sulfur composition in a single section. However, Wanless' (1959) observation that organic sulfur is uniform over a wide area in a single seam is in better agreement with the similar observation for Illinois coals by Cady (1935a).

From a recent study of the Redstone coal seam in a single mine in West Virginia, Neavel (1966, p. 293, 294) concluded that "organic sulfur is relatively constant in any column except for higher amounts toward the base and toward the top," and that "the same factors that control organic sulfur also exert a control on pyrite formation."

Recent Studies

Recently, it has been possible to obtain carefully controlled benched samples in order to observe the vertical distribution of the varieties of sulfur within a single coal seam and the lateral distribution along the seam for narrowly limited distances. Three groups of such samples for which analytical data are available will be discussed. The coals represented are Herrin (No. 6) Coal in central Illinois, and both the Herrin (No. 6) and the Harrisburg (No. 5) Coals in southern Illinois.

The two sets of data from the southern Illinois samples are derived from chemical analyses of specially selected diamond drill cores. The coal cores were wrapped tightly in plastic immediately upon removal from the core barrel. Within the following 24 to 48 hours they were described in detail, benched, crushed, and
sealed in plastic bags. Chemical analyses followed within a matter of days. In order that these data would be directly correlative with analyses of face-channel samples, all mineral bands over 3/8-inch thick were omitted from the bench samples. In some instances, the exclusion of mineral bands in excess of 3/8-inch resulted in an appreciable reduction in pyritic sulfur. In other instances, the bands excluded were composed entirely of shale with little or no pyrite content, and removing these bands resulted in a relative increase in the pyrite content of the coal core. It is recognized that pyrite lenses, stringers, and nodules may occur at any position within the coal seam, and the discussion that follows is concerned only with the finer pyrite bands (less than 3/8-inch thick) and the pyrite more intimately associated with the coal. Chemical analyses of varieties of sulfur were made on each bench described. The results of these analyses are shown in figures 9 and 10.

Herrin (No. 6) Coal - Southern Illinois

Each of the six bar diagrams in figure 9 represents the coal from a single drill core. All of the drill holes are in a 9-square-mile area, the two most distant being 3 1/4 miles apart. The length of the bar is the total sulfur content of that particular bench, and the bar is divided into pyritic and organic sulfur portions. Sulfate sulfur is not shown, inasmuch as it occurs in negligible amounts in all benches. The vertical scale represents the full thickness of the seam, as evidenced by the diamond drill core. The general pattern is one of fairly uniform organic sulfur content and a wide variation in pyritic sulfur content. The maximum variation in organic sulfur content within a single drill-core sample (between benches) is 212 percent. That is, the highest organic sulfur content is slightly more than twice the lowest value. The maximum variation in pyritic sulfur content between benches of a single core is much greater: the highest pyritic sulfur content is nearly 15 times the lowest value for a variation of 1486 percent.

The organic sulfur content varies little between benches of a single drill-core sample and exhibits a greater variation between different drill cores. That is, the lateral variation in organic sulfur within the seam was greater than the vertical variation.

The higher concentrations of pyritic sulfur, and therefore of total sulfur, occur in the top and/or bottom benches with only one exception. Drill-core sample B has the bench with the highest pyritic sulfur and total sulfur content in the middle part of the seam. The bottom bench of this sample contains the next highest amount.

Harrisburg (No. 5) Coal - Southern Illinois

In four of the six drill holes discussed above, it was possible to obtain samples of cores of No. 5 as well as No. 6 Coals. Bar diagrams depicting the distribution of pyritic and organic sulfur in these four cores are shown in figure 10. As was the case with the cores of No. 6 Coal, the organic sulfur content is more uniform vertically throughout the seam than is the pyritic sulfur content.

The uppermost benches contain the largest amount of pyritic sulfur in three of the four sets of analyses. The only exception is that designated by the letter "G." This core was only benched into three units because of the rather badly broken condition of the coal core. It is possible that if the upper bench of this core had been subdivided, the uppermost portion might then have been the highest in total sulfur as a result.
Figure 9 - Organic and pyritic sulfur distribution in vertical sections (drill cores) of Herrin No. 6 Coal in southern Illinois.
No. 5 COAL

Figure 10 - Organic and pyritic sulfur distribution in vertical sections (drill cores) of Harrisburg (No. 5) Coal in southern Illinois.

Herrin (No. 6) Coal - Central Illinois

Four face-channel samples of Herrin (No. 6) Coal were collected from one mine in central Illinois. The coal face was carefully described, and individual benches were removed for analyses. The results of chemical analyses for varieties of sulfur on these benches are graphically shown in figure 11. Channel samples 2 and 3 are
Figure 11 - Organic and pyritic sulfur distribution in vertical sections (face-column samples) of Herrin (No. 6) Coal in central Illinois.
within approximately 500 feet of each other, and the maximum distance between samples (from site of sample 3 to site of sample 4) is nearly 3 miles.

As was the case with the benched drill-core samples from southern Illinois, the organic sulfur content is more uniformly distributed vertically within the seam than is the pyritic sulfur. The maximum variation in organic sulfur between benches of a single channel is 161 percent, whereas pyritic sulfur in the same channel has a maximum variation of 822 percent. That is, the maximum organic sulfur content in a bench of a face-channel sample is only 1.61 times as large as the lowest organic sulfur content, but a similar ratio for pyritic sulfur is 8.22.

The uppermost benches of channel samples 2 and 3 do have the highest total sulfur within those channel samples. However, the general pattern of pyrite, and therefore total sulfur, being concentrated in the upper and/or lower benches does not otherwise emerge from this set of analyses.

In general, the data shown in figures 9, 10, and 11 support previous observations by Cady (1935a), Wanless (1959), and Neavel (1966), as well as a portion of the observations made by Yancy and Fraser (1921). The organic sulfur content is relatively uniform vertically within the coal seams studied and also varies less widely over short distances laterally than does the pyritic sulfur. Large vertical variations in pyritic sulfur were commonly observed in all of these studies.

Most of the workers mentioned above (Yancy and Fraser, 1921; Wanless, 1959; and Neavel, 1966) noted a tendency for total sulfur (and therefore pyrite) to be concentrated near the upper and lower margins of the seam. This was generally, but not universally, the case in the samples described in this report. Recently several mechanisms were suggested whereby this pattern could arise. Neavel (1966, p. 295) concluded that "organic sulfur is relatively constant in any column except for higher amounts toward the base and toward the top," and that "organic sulfur concentration is apparently controlled by two factors, (1) the availability of sulfate sulfur to the local environment and (2) the rate of sulfate reduction to the sulfide state." He also observed (p. 293) that generally the pyrite concentration was correlative with the organic sulfur concentration. This correlation is attributed to the necessity for sulfate to be available for either pyritic or organic sulfur to be concentrated. The pyritic sulfur varies to a greater extent than does the organic because, in addition to the availability of sulfate, it is also necessary to have sulfate-reducing bacterial colonies present and sufficient amounts of iron available. Neavel (1966) suggested that the iron was probably transported adsorbed on the clays, and therefore coal immediately below the clay-containing roof would be a reasonable site for above-normal amounts of pyrite to form.

An organic sulfur concentration at the top and/or bottom of the seam was not evidenced by the three sets of data on varieties of sulfur in benches of full seam samples of Illinois coals discussed above. The general tendency for total sulfur to be higher at the top and bottom in these samples is due to the increased pyritic sulfur content.

Neavel (1966) and Reidenouer, Williams, and Dutcher (1967) assume that the pyrite and total sulfur content of the coal was determined early within the peat stage. However, authigenic pyrite, which formed later, does occur in coal. The large pyrite-filled cleats or nearly vertical joints are of later origin. If these fractures had been filled during the peat stage, they would necessarily show the effects of further compaction of the coal. If secondary pyrite can be shown to enter the coal in this manner, then perhaps other occurrences of pyrite could be explained similarly. In any case, the coal-underclay, coal-shale, or earlier peat-clay bound-
ary is an interface across which geochemical conditions would be expected to change and would provide a reasonable location for precipitation of ferrous disulfide. Stated most simply, if at least some portion of the components necessary for iron disulfide formation were supplied from outside the coal, then they would have to encounter the vertical limits of the bed before any other portion, except perhaps for fractures within the bed. The concentration of sulfur (pyrite) at the top and/or bottom of the seam and along fractures is then to be expected.

LOW-SULFUR COAL IN ILLINOIS

Methods Used in Compilation of Data on Low- and Medium-Sulfur Coal in Illinois

Data used in this discussion of low-sulfur coal in Illinois come from chemical analyses of face-channel samples of coal from mines and from chemical analyses of diamond drill cores of coal. In addition, data obtained from the interpretation of drill-hole records of various types have also been utilized. Data obtained from interpretation of drill logs are based on the observation that in two areas of No. 6 Coal and in one area of No. 5 Coal, all in southern Illinois, the sulfur content of the coals is relatively low in those regions in which the coal is overlain by a thick gray shale. Conversely, where the black "slaty" shale and/or marine limestone lie close to the top of the coal, the sulfur content is substantially higher. This association of high-sulfur coal and overlying marine beds has also been reported for Russian and British coals (Yurovski, Mangubi, and Zyman, 1940; Wanless, 1959; Williams and Cawley, 1963). There are areas in Illinois, however, where the coal is overlain by a thick gray shale, and where the coal is relatively high in sulfur. In such instances, the gray shale is thought to represent a unit that occurs above the normal position of the marine limestone in the cyclic sequence of sediments that characterize the coal-bearing rocks. The gray shale, which lies below the position of the limestone and which is associated with low-sulfur coal, is absent, as are the marine black shale and marine limestone. When the sequence is relatively complete, and when there is 20 feet or more of gray shale between the coal and the black shale or limestone, the coal is generally accurately classified as "low sulfur."

All of the analytical and interpreted data were plotted on base maps (1:62,000, or approximately 1 inch to the mile), and the approximate boundaries of relatively low-sulfur coal areas were delineated. These data, in conjunction with previously determined information concerning coal thickness (from coal reserve studies), enabled the estimating of reserves of low-sulfur coals. This estimate was arrived at by first measuring the areas underlain by coal of various average thicknesses within each low-sulfur region with a planimeter. Using an estimate of 1800 tons per acre foot of coal, reserves were calculated for each planimetered area and totals combined for each coal seam and each county. Estimates were for total coal remaining in the ground. In order to bring these figures up to date, inasmuch as the base maps of mined-out coal areas were made in 1959, a figure for total production of coal from each of these areas from 1959 through 1966 was calculated (assumption of 50 percent recovery) and subtracted from the total reserves.

Reserve data presented herein is a geologic report on total coal in the ground updated to the beginning of 1967. Although similar studies that we have made include coal to a minimum thickness of 28 inches, 42 inches of coal was the minimum
thickness estimated in any of the areas treated in the present statement. Mining conditions, the actual coal thicknesses, the availability of the land containing the coal, and numerous other economic factors were not taken into consideration when low-sulfur coal reserves were calculated. Therefore, reserve figures presented herein may differ significantly from a commercial evaluation of low-sulfur coal reserves in Illinois.

Low-Sulfur Coal Reserve Areas

Although low- and relatively low-sulfur coal areas are known throughout the state, only three are sufficiently well known to attempt to delineate the areas and to estimate remaining reserves (fig. 12). Two additional areas (Murphysboro and northeastern Illinois), which produced low-sulfur coal and in which the low-sulfur coal has been essentially worked out by mining, are mentioned at the end of this section. By relatively low-sulfur coal, the writers refer to coal that appears to be of the order of 2.5 percent sulfur and less, which is significantly less than the normal range of 3 to 5 percent.

Some of the known but unmapped occurrences of low-sulfur coal may prove to have significant reserves of relatively low-sulfur coal, but data in hand are insufficient to outline such areas or make reserve estimates. It is probable that additional occurrences not now recognized may also prove to have relatively low-

![Figure 12 - Principal "low-sulfur" reserve areas in southern Illinois.](image-url)
SULFUR IN ILLINOIS COALS

sulfur coal reserves. We believe, however, that there is a sufficiently large amount of data on Illinois coals, and that even though relatively large additional areas of low-sulfur coal will be delineated in the future, the total percentage of low-sulfur coal in the state will remain quite small relative to total reserves.

The three best known low-sulfur areas that have been mapped in detail are discussed below and shown in figure 12.

Franklin, Jefferson, Williamson, Perry, and Jackson Counties

The best known and the most intensively mined low-sulfur coal area in Illinois is from the region that has been termed the "Quality Circle" in parts of Franklin and adjacent counties, shown on figure 12 and detailed on figure 13. Most of the past mining in Franklin and Jefferson Counties has been from the low-sulfur coal area. These reserves are in the Herrin (No. 6) Coal and have been previously reported by Cady (1919, 1922, and 1935a).

More data are available for delineation of this area than any other, and although subject to some modification as more information becomes available, no significant change in the total reserves is expected.

Within this area, coal with sulfur content as low as 0.5 percent has been reported, but the area with such coal was mined out some years ago. The remaining area is believed to contain coal that will range from 1 to 2.5 percent sulfur and average about 1.5 percent, as determined by face-channel sample analyses. Generally, there is very little gradual transition from low to high sulfur content in this general area, the change being relatively abrupt in crossing the low-sulfur line shown on figure 13.

The areas of unmined low-sulfur coal shown in figure 13 are based on mining as of July 1, 1959. In arriving at figures for remaining reserves as of the end of December 1966, production from mines totally within the remaining reserves area was doubled (based on assumed 50 percent recovery) and subtracted from the total estimated from the map. Five relatively large mines, which have

Figure 13 - Low-sulfur No. 6 Coal, Franklin and adjacent counties.
been producing coal from the northern portion of the area or which are currently under construction, are indicated on the figure by the letters A through E. In the southern part of the area, some mining has occurred in some of the isolated pieces shown, but a similar adjustment was not practical. Because some of the isolated remaining pieces are surrounded by mined-out areas and cannot be recovered, and some of the areas have been mined since 1959, the assumption was made that 60 percent of these isolated areas represent coal reserves.

The "split coal" area shown on figure 13 is an area in which the coal seam is split into two or more benches by up to many feet of siltstone and shale. Although it is believed that the coal may be low in sulfur content in the area, mining has been limited by the split coal, as can be seen by mined-out areas that bound this area. The coals are much thinner in each bench and are variable in thickness and persistence; mining conditions have become relatively poor where mining has continued into the split, until conditions finally become prohibitive. The "cut-out" area indicates very approximately where the positions of the coal and shale are occupied by a sandstone-filled channel.

The estimated low-sulfur No. 6 Coal reserves for the area shown in figure 13 are given below.

<table>
<thead>
<tr>
<th>County</th>
<th>Estimated Reserves (million tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jefferson</td>
<td>579.69</td>
</tr>
<tr>
<td>Franklin</td>
<td>306.80</td>
</tr>
<tr>
<td>Williamson</td>
<td>59.31</td>
</tr>
<tr>
<td>Jackson</td>
<td>37.25</td>
</tr>
<tr>
<td>Perry</td>
<td>34.65</td>
</tr>
<tr>
<td>Total</td>
<td>1,017.70</td>
</tr>
</tbody>
</table>

St. Clair, Madison, and Clinton Counties

The low-sulfur coal area within St. Clair, Madison, and Clinton Counties (fig. 14) is less well known than that of the Franklin County area because of the lesser amount of test drilling and because there has been much less mining in this area. Reserves in this area are also in the Herrin (No. 6) Coal. The westward side of this area is fairly well defined, but the eastward side is less well defined. Coal analyses from within this area indicate a sulfur range from 1 to 2.5 percent, with an estimated average of 1.5 percent. The average sulfur estimate is based on somewhat fewer data than were available in the Franklin County area.

No mines are currently operating within the low-sulfur coal area of these two counties, and most mining was done a number of years ago. One recent mining operation, now abandoned, that had operated to the west in areas of normal (higher) sulfur content, did extend their work a little into the low-sulfur coal area. The coal thins markedly eastward and may average only 48 to 54 inches in the eastern part of the area shown.

This coal has been found to be less suitable for blending for production of metallurgical coke than coal from the low-sulfur area in Franklin and adjacent counties. This coal is classed as high volatile C-rank coal and is somewhat lower in rank than the Franklin County area coal.
ESTIMATED LOW-SULFUR NO. 6 COAL RESERVES BY COUNTY
(Estimated reserves in place; range 1 to 2,5 percent sulfur - estimated average 1,5 percent)

<table>
<thead>
<tr>
<th>County</th>
<th>Reserves (million tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. Clair</td>
<td>380.94</td>
</tr>
<tr>
<td>Madison</td>
<td>244.75</td>
</tr>
<tr>
<td>Clinton</td>
<td>23.49</td>
</tr>
<tr>
<td>Total</td>
<td>649.18</td>
</tr>
</tbody>
</table>

Saline, Hamilton, Williamson, and Franklin Counties

The extent of the medium-sulfur Harrisburg (No. 5) Coal area in Saline County and parts of adjacent Hamilton, Williamson, and Franklin Counties (fig. 15) is less well defined than either of the two areas previously discussed. Although one mine in the area is now producing entirely low-sulfur coal, data indicate that most of the coal in this area has a higher sulfur content than the No. 6 Coal discussed above. No. 5 Coal is generally thinner than No. 6 Coal in southern Illinois. At least one-third of this medium-sulfur area is in the 42- to 54-inch class.

Available data suggest a range of 1 to 3 percent sulfur in the coal in this area. The average sulfur content is roughly estimated at about 2.25 percent. It is believed that much of the coal in the lower ranges cited above has been mined out. The map in figure 15 shows mined-out areas to July 1, 1959. A correction was made to reserve estimates by deducting a value equal to twice the pro-
duction within the area (from 1959 through 1966). This assumes a 50 percent recovery in mining of the coal. There is some uncertainty as to the nature of the northern and eastern boundaries of this low-sulfur area, as shown in figure 15.

The No. 5 Coal in Saline County and adjacent areas is slightly higher in rank than the No. 6 Coal in Franklin County, and coal produced from the low-sulfur coal mines in this area has been and is being used in blends to produce metallurgical coke. The coal is high-volatile B rank.

ESTIMATED MEDIUM-SULFUR NO. 5 COAL RESERVES BY COUNTY

(Total reserves in place; range 1 to 3 percent sulfur - estimated average 2.25 percent)

<table>
<thead>
<tr>
<th>County</th>
<th>Reserves</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saline</td>
<td>581.84 million tons</td>
</tr>
<tr>
<td>Franklin</td>
<td>249.10</td>
</tr>
<tr>
<td>Williamson</td>
<td>130.21</td>
</tr>
<tr>
<td>Hamilton</td>
<td>93.22</td>
</tr>
<tr>
<td>Total</td>
<td>1,054.37 million tons</td>
</tr>
</tbody>
</table>

In addition to the three major low-sulfur areas described above, there are several other areas that merit mention although they are lower in rank.

Southeastern Illinois (Edwards, Hamilton, Saline, Wabash, and White Counties) - Harrisburg (No. 5) Coal.—An investigation of the Harrisburg (No. 5) Coal in southeastern Illinois has been recently completed by M. E. Hopkins. The results of this study have been published as Circular 431 of the Illinois State Geological Survey. The character of the roof material overlying No. 5 Coal and the thickness of the coal has been mapped in Edwards, Hamilton, Saline, Wabash, and White Counties, and also within parts of most adjacent counties. This area, which is northeast and an extension of the low-sulfur No. 5 Coal area in Saline and adjacent counties (shown on fig. 15), is postulated to contain relatively low-sulfur No. 5 Coal. This is based primarily on the interpretation of electric logs. Within the known area of low-sulfur coal in Saline and adjacent counties, there is generally 20 feet or more of gray shale between the coal and the overlying lime-

Figure 15 - Medium-sulfur No. 5 Coal, Saline and adjacent counties.
stone. The same relationships are believed to be present in the region that extends to the northeast.

Southeastern Macoupin County - Herrin (No. 6) Coal, —Spotti (1941) mapped the Herrin (No. 6) Coal and the various strata overlying the coal in northern Madison and southeastern Macoupin Counties. The northeastern part of the area mapped (T. 8 N., R. 6 W.) is shown as having gray shale in the roof material and, in addition, from 20 to 40 feet of strata between the coal and the first thick limestone overlying the coal (Spotti, 1941, pl. V). Figure 16 extends to the north and to the east of the area of the thick gray shale as mapped by Spotti. This map is based on electric logs and drillers' logs of rather widely spaced drill holes. The relationship between thick gray shale overlying No. 6 Coal and the low sulfur content of the coal has been discussed with regard to other areas in southern Illinois, and it is inferred that the Herrin (No. 6) Coal has a relatively low sulfur content in the general area where thick shale was first mapped by Spotti (1941) and which has been extended as shown in figure 16. No chemical analyses of coal are available from within the mapped area.

Vermilion County - Herrin (No. 6) Coal, —In published analyses of face-channel samples from No. 6 Coal (formerly called Grape Creek Coal) in Vermilion County, only one mine was reported with an average sulfur content of less than 2 percent, and several mines have been reported with averages only slightly exceeding 2 percent. Several individual analyses also reported values under 2 percent. The county average for 6 mines reported in Illinois State Geological Survey Bulletin 62 (Cady, 1935b) was 2.7 percent (dry basis), which is below the general average for No. 6 Coal in Illinois. The coal extends southward into Edgar County, but data on quality are not available.

Northeastern Illinois (Will and part of adjacent Grundy Counties) - Colchester (No. 2) Coal, —Fourteen face-channel samples from the northeastern Illinois field indicated an average sulfur content of 1.9 percent with a number of the samples indicating about 1.5 percent sulfur (dry basis). Although mining is continuing in the general area, sulfur content appears to run higher, and no remaining reserves with sulfur content as low as 1.5 percent are known.
Woodford County - Colchester (No. 2) Coal.—Five face-channel samples from the W. G. Sutton Mine at Minonk, Illinois, are reported to have had an average of 1.2 percent sulfur (dry basis). The only other mine reported in this coal in Woodford County reported an average of 3.3 percent sulfur. This is the order of magnitude of sulfur content of other mines in this general region. Available data do not permit a determination of possible extent of the low-sulfur coal area. This coal is relatively thin (average 36 inches) and is high-volatile bituminous C rank. Mining was suspended in this area over 15 years ago.

Jackson County - Murphysboro Coal.—Mining operations of more than 100 years duration and dating back to the early 1800's were carried on in the vicinity of Murphysboro, Illinois. Fifteen face-channel samples from five mines in the Murphysboro coal in this area have been reported to have had an average sulfur content of 1.4 percent (dry basis). Some individual analyses indicated less than 1 percent sulfur content. The relatively thick, low-sulfur coal area in the Murphysboro Coal is believed to be essentially all mined out, and no remaining low-sulfur reserves have been estimated.

SUMMARY OF LOW-SULFUR COAL RESERVES

Approximately 2 percent of the total estimated coal reserves in Illinois are included in the three major low- and medium-sulfur areas discussed, most of which are believed to contain less than 2.5 percent total sulfur (dry basis). Coal with an average of 1.5 percent sulfur is estimated to constitute slightly more than 1 percent of the total coal reserves. Although additional relatively low-sulfur coal areas will probably be delineated in the future, it is not practical to make any estimate of such additional reserves, and such additions, it is believed, will constitute only a small percentage of total reserves.
REFERENCES


