

## OCCURRENCE OF SULFUR IN ILLINOIS COALS

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## Introduction

Sulfur in its several forms is prominent among the species of mineral matter known to occur in coal. Not only is its presence widespread but its effects may be very detrimental, particularly in specialized uses. The many problems associated with the presence of sulfur in coal include those involving air pollution, restrictions on amount of sulfur allowed in metallurgical coke, boiler corrosion and deposits, difficulties in mining, acid drainage from mines and spoil piles, and spontaneous combustion of coal.

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 founding more than 50 years ago. This paper attempts to summarize the pertinent data concerning the occurrence of sulfur in Illinois Coals from this long term study. These data have been acquired by many members of the Survey staff.

Except when specifically stated to the contrary, all data discussed in this paper were obtained from analyses of face channel samples of coal. These samples were taken in the mines by Survey personnel following recommended United States Bureau of Mines methods of sampling, which provide for exclusion of mineral bands over 3/8 inch in thickness (Holmes, 1911).

## Distribution of Sulfur Within Illinois Coals

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,



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

Sulfate Sulfur. Sulfate sulfur is present in minor amounts in nearly all of the samples analysed. The sulfate sulfur values range from a high of 0.57 percent to a low of 0.00 percent. The mean, calculated from sulfate sulfur analyses of 300 face channel samples of Illinois coals is 0.071 percent and the mode, although not calculated, would be lower than the mean.

Organic Sulfur. Organic sulfur values ranged from a low of 0.27 percent to a high of 2.98 percent in Illinois coals sampled to date. The distribution of organic sulfur for all face channel sample analyses of No. 2 Coal, No. 5 Coal, No. 6 Coal and No. 7 Coal are given in the histograms on figure 1. None of the histograms have the shape of a normal distribution. The organic sulfur values of No. 2 Coal and No. 5 Coal are rather evenly distributed and are between 0.4 percent and 2.4 percent. It is probable that these diagrams would show a normal distribution if additional data were included. Too few analyses of samples from No. 7 Coal are available to draw any conclusions from the histogram. Organic sulfur from No. 6 Coal shows a distinct bimodal distribution with one peak between 0.2 and 0.8 percent and the second peak between 1.6 and 2.2 percent.

Pyritic Sulfur. The range in values of pyritic sulfur in face channel samples is even greater than the range in organic sulfur. The range is from a low value of 0.10 percent to normally high values of 4.5 percent to 5.0 percent with a few extreme values approaching 9.0 percent. Histogram depicting the distribution of the pyritic sulfur values for each of four coals are given in figure 2. The histogram of pyritic sulfur values in No. 5 Coal shows the most nearly normal distribution and that for No. 6 Coal shows a bimodal distribution. Again it must be emphasized that these data are obtained from face channel samples and any mineral bands in the coal, including iron sulfides, over 3/8 inch thick were excluded from the sample.

Total Sulfur and Relationship Between Pyritic and Organic Sulfur. Total sulfur in face channel samples ranges from low values of less than 0.5 percent to high values of 5.5 percent with a few extreme cases of nearly 10 percent. Sulfur in these few very-high-sulfur channel samples is predominantly pyritic.

Four graphs showing the relationships between organic and pyritic sulfur for four Illinois coals are given in figure 3. Each point on graphs 3a and 3b (No. 2 Coal and No. 7 Coal) represents sulfur values from a single face channel sample analysis, whereas each point on graphs 3c and 3d (No. 5 Coal and No. 6 Coal) represent average sulfur values for a single mine. Using mine averages rather than individual analyses does not alter the overall picture but does facilitate handling of the data.

Correlation coefficients for the four graphs vary considerably. The correlation is poor for Coal No. 5 (correlation coefficient .24) and non-existent for Coal No. 7 (correlation coefficient -.09). However, coals No. 2 and No. 6 do show a fairly good correlation between pyritic and organic sulfur (.76 for No. 6 Coal and .75 for No. 2 Coal). Both of these latter values demonstrate a high degree of significance, well over the 99.9 percent 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. The one graph showing negative correlation (No. 7 Coal) is not statistically significant because of the small number of analyses.

Differing conclusions have been drawn by various workers as to the relation of pyritic to organic sulfur in coals. A number of researchers have reported such a correlation (Rose and Glenn, 1959; Leighton and Tomlinson, 1960; Wandless, 1959) whereas others have not observed the correlation in their studies (Yancy and Fraser, 1921; Brooks, 1956).

Discounting No. 7 Coal because of lack of sufficient data, the Illinois coals do show a positive correlation between organic and pyritic sulfur. This correlation is much better for No. 2 Coal and No. 6 Coal than for No. 5 Coal.

The fact that a correlation does exist, suggests that in a coal-forming-swamp environment which was relatively high in sulfur, the sulfur contribution to the plants would be high and that sulfur in the environment also would be available for the formation of pyrite during the early stages of peat formation. The correlation exists even though much secondary inorganic pyritic sulfur has been added to the coal as veins and deposits along fractures which occurred subsequent to the peat formation and possibly very late in the history of the coal bed. It is also conceivable that much of the late secondary pyrite may represent a reorganization of the sulfur that was introduced into the environment at a very early stage of coal formation.

The bimodal distribution of both pyritic sulfur and organic sulfur shown in figures 1 and 2 also might suggest a close correlation between the two forms. However, the low sulfur coals in Illinois have been mined extensively and therefore have also been of much interest to the Survey and have been sampled heavily. The low sulfur peaks in the bimodal distribution may simply represent preferential sampling.

#### Mineralogical Occurrence of Sulfur

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	possibly the hydronium jarosite (carphosiderite) $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_4 \cdot 7\text{H}_2\text{O}$

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 since 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 ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ) in the

laboratory. The dehydration is very rapid; occurring in a few minutes time in the case of melanterite → rozenite.

**Pyritic Sulfur.** Iron disulfide can occur as either pyrite which forms in the isometric crystal system or as marcasite which is orthorhombic. Pyrite is the most commonly reported dimorph although marcasite is often mentioned as occurring in lesser amounts. Marcasite has only rarely been reported in Illinois coals and pyrite is apparently the dominant sulfide.

The macroscopic forms of pyrite in coal were systematically described by Yancy and Fraser (1921). A summary of their description follows: 1) fine pyrite, as small disseminated particles or thin film-like coating on joint planes (cleat) or along the bedding; 2) lenses, from 1 to 2 inches long and a fraction of an inch thick to those 3 or 4 feet thick and hundreds of feet long; 3) nodules, roughly spherical in shape, may also be either inches or several feet in diameter; 4) beds or continuous bands of pyrite, often may include coal or bony coal and/or may be intimately associated with argillaceous sediments.

The finely disseminated pyrite grades downward in size to the microscopic forms of the mineral. Microscopic pyrite is very widespread in coal and has been observed in all coal macerals except massive micrinite. A complete range from euhedral crystals to irregular anhedral aggregates may be observed microscopically in Illinois coals (J. A. Harrison, personal communication). Observations similar to those preceding were made for the Pittsburgh coal by Gray, Schapiro and Coe (1963).

#### Sulfur in the Banded Ingredients of Coal

A study was made by Survey personnel into the distribution of the forms of sulfur in the megascopically distinguishable banded ingredients (Cady, 1935a). The banded ingredients sampled were vitrain, clarain and fusain. Durain or dull splint coal is very rare in Illinois coals and none was sampled. Figure 5 summarizes the sulfur analyses of approximately 100 samples of banded ingredients.

In general the pyritic sulfur content is greater in the fusain than in the other bands, although it does show a wide range in the different fusain samples. This is due to the degree to which the cavities in the fusain are filled with pyrite. Vitrain and clarain have a higher organic to pyritic ratio with ratios generally greater than one. The organic sulfur content of vitrain is usually lower than of clarain from the same coal. The preceding generalizations not withstanding, Cady (1935a) concluded that the variations in organic sulfur content of Illinois coals cannot be ascribed only to variation in relative amounts of banded ingredients.

#### Occurrence of Low-Sulfur Coal in Illinois

There are three known areas in the state where there has been significant production of low-sulfur coal, most of which contain less than 1.5 percent sulfur. These areas, outlined in figure 6, are highly generalized and are subject to appreciable modification.

The largest of the three low-sulfur areas, and the most important on the basis of tonnage of coal produced, is in No. 6 Coal in Franklin County and

adjacent portions of Jefferson County to the north and Williamson County to the south and is similar to the area reported by Cady (1919). The delineation of the low sulfur area has been based on the following information:

- 1) Data from the files of the Illinois State Geological Survey on face channel samples of mines, most of which have been published by Cady (1935b, 1948).
- 2) Evaluation of a few miscellaneous coal samples from mines in the general area and from diamond drill core analyses.
- 3) Interpretation of drill logs based on character of overlying strata.

Utilization of the data in 1) and 2) above is self-explanatory, but 3) should be more fully explained. The interpretation of drill logs is based on the observation that in this general area where No. 6 Coal has a thick gray shale overlying the coal, the sulfur content is relatively low. Conversely, where the black "slaty" shale and 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; Wandless, 1959; Williams and Cawley, 1963).

The low sulfur area in Franklin, Williamson and Jefferson Counties is outlined primarily by analyses of mine samples. However, details of the configuration of the "low-sulfur" line are based on interpretations of drill hole logs of variable quality including electric logs of oil test holes. The presence of more than 20 feet of gray shale immediately above the coal has been used as indicating low sulfur content and less than 10 feet between the coal and the overlying black shale and limestone as indicating higher sulfur area. Intermediate thicknesses of gray shale have been variously interpreted depending in large measure on the geographic relationship of such datum points.

All of the low sulfur lines on the map indicate areas in which the sulfur content is believed to average 2 percent or less. The analytical data within the Franklin-Williamson-Jefferson Counties area indicate that most of the area outlined contains coal with less than 1.5 percent sulfur (as received basis, face channel sample), and a substantial part of the area has included coal, now largely mined, which averaged less than 1 percent sulfur.

In the western part of this low-sulfur area there is a portion mapped as containing "split coal." The split consists of beds of shale and siltstone interbedded between coal benches. It is believed that most of the coal in the "split-coal" area is probably of low-sulfur content. As shown on the map (fig. 6), the low sulfur area extends locally a relatively short distance west of the "split coal" area.

A second important area of low-sulfur coal occurs in the Harrisburg (No. 5) Coal in Saline County. Coal with less than 1 percent sulfur has been mined in this area and there is a substantial area in which the coal probably averages less than 2.5 percent sulfur as shown in Figure 7. This area is much less well defined than the previously described low-sulfur area of No. 6 Coal because much less data concerning it are available.

A third substantial area of low-sulfur No. 6 Coal lies in parts of Madison and St. Clair Counties in the vicinity of Troy, Illinois, and is shown

in figure 6. Although less is known of this area than the areas described previously, there is perhaps up to 70 square miles of coal with a sulfur content less than 1.5 percent. Analyses of face channel samples from one mine which operated in this low-sulfur area, reported by Cady (1948), showed the coal to average less than 1 percent sulfur.

#### Vertical and Lateral Distribution of Varieties of Sulfur

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 1 and 2. There have been, however, differences of opinion as to the amount of local variation which exists in the organic sulfur content. There are no such differences of opinion concerning the pyritic sulfur distribution inasmuch as extremely localized concentrations of secondary pyrite are common.

Cady (1935a, p. 30, 31) observed, "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 extensively the variations in varieties of sulfur both vertically and laterally within a single mine in southern Illinois. Concerning the lateral variation in organic sulfur they concluded that uniformity in organic sulfur distribution is confined to very limited areas in the coal seam (Yancy and Fraser, 1921). They found this variation to be large within a single mine, although not as large as variations in pyritic sulfur. Within the mine studied, the organic sulfur in the face channel samples (No. 6 Coal) ranged from .69 to 1.90 percent and the pyritic sulfur from .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 on the margin of the area of low sulfur coal in Franklin County.

Yancy and Fraser (1921) also analyzed individual benches of face channel samples for varieties of sulfur. They took 12 face channel samples from a mine in southern Illinois, six samples from a mine in west Kentucky in No. 7 Coal, and two samples from a mine in Kentucky No. 8 Coal. The organic sulfur content was relatively uniform between benches of the individual face channel samples. The greatest variation in any single section was a minimum of 0.57 percent and 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 percent to 5.54 percent and from 0.02 percent 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, were 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 Kentucky No. 7 Coal. The two samples of the Kentucky No. 8 Coal had the highest pyritic sulfur in the lowest benches but the uppermost benches were relatively low in sulfur. Wandless (1959) in a general discussion of the occurrence of sulfur in British coals reached conclusions which 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, Wandless' (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).

Further studies on the varieties of sulfur and their vertical and lateral variation are in progress. Preliminary results suggest that a concentration of pyritic sulfur at the top and bottom of the coal tends to occur in No. 6 Coal samples obtained from southern Illinois, and that the vertical distribution of organic sulfur within these coals is relatively uniform. Further data will allow more definite conclusions to be drawn concerning the local variation laterally in organic sulfur.

Wandless (1959) in a review article on sulfur in British coals stated an admonition with which we heartily concur. Concerning conclusions drawn from chemical analyses of sulfur in coal he wrote, (Wandless, 1959, p. 259) "Unfortunately the number of exceptions to these generalizations is sufficient to render them non-specific in individual cases. Here, as elsewhere, the examination of very large numbers of samples provides a graveyard for promising generalizations; nevertheless, the trends noted are interesting and can, with proper caution, prove useful on occasion."

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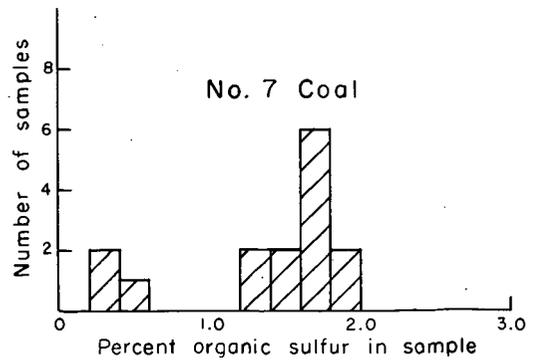
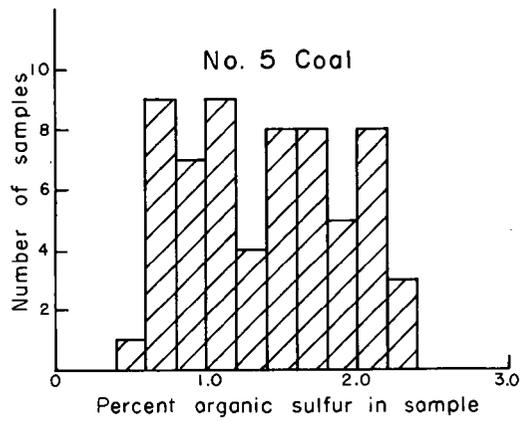
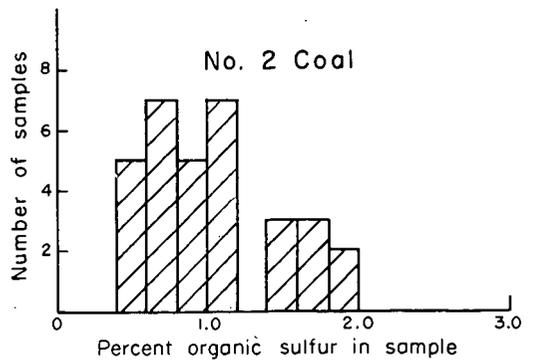
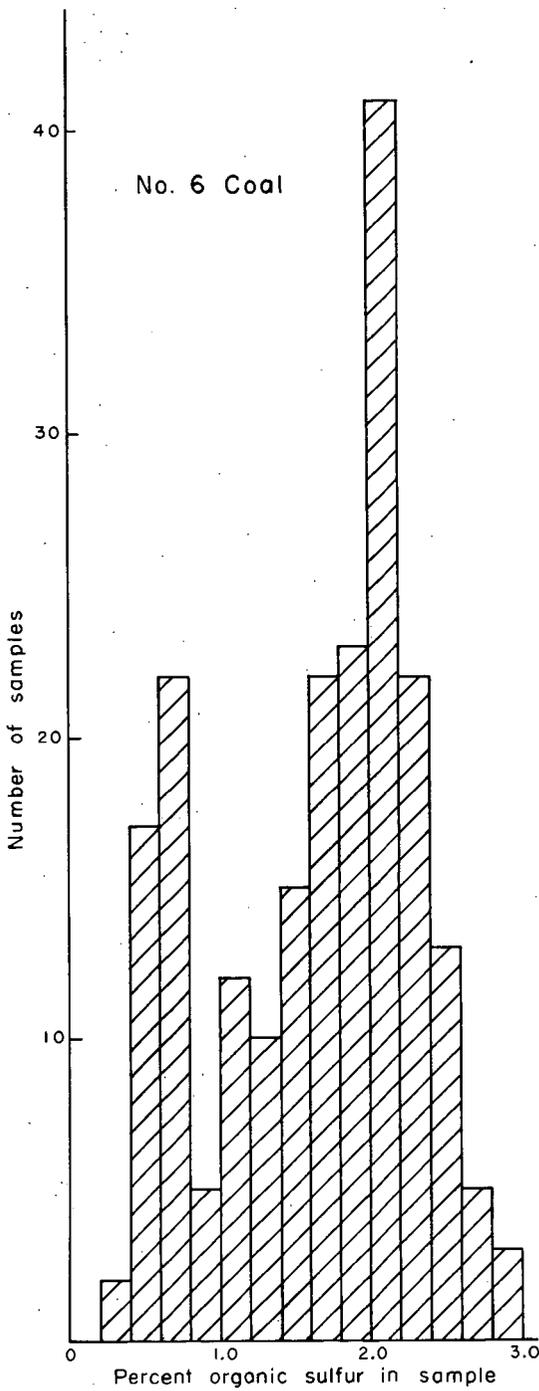


Fig. 1- Organic Sulfur - Distribution in Illinois Coals

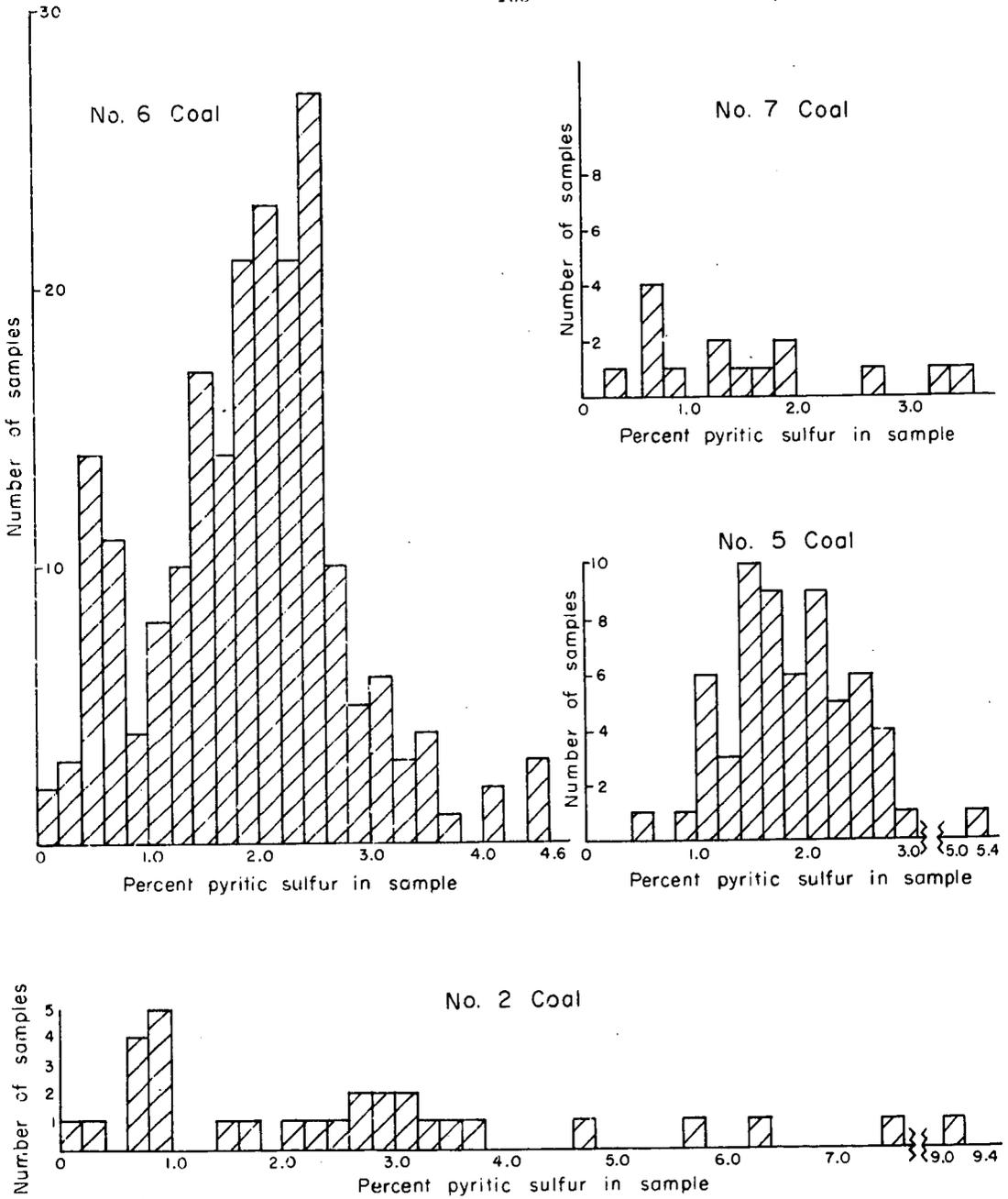


Fig. 2 - Pyritic Sulfur - Distribution in Illinois Coals

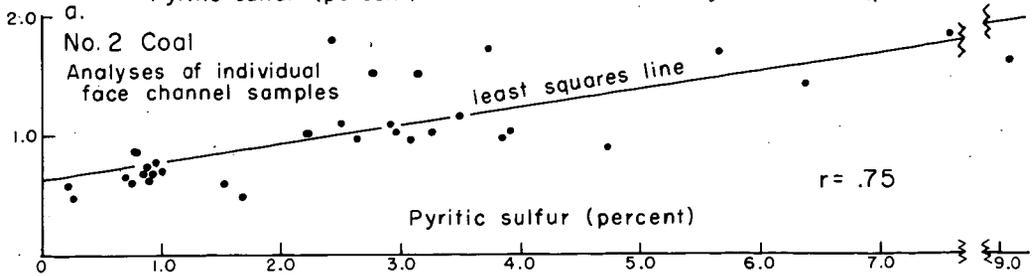
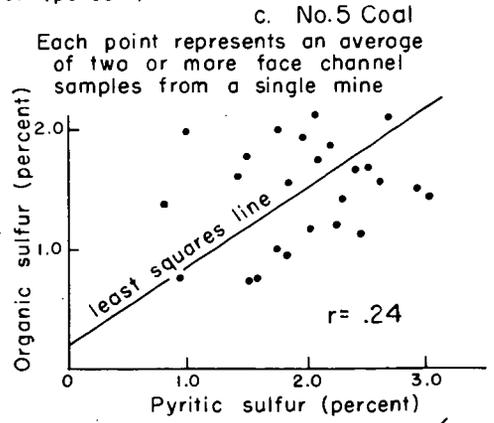
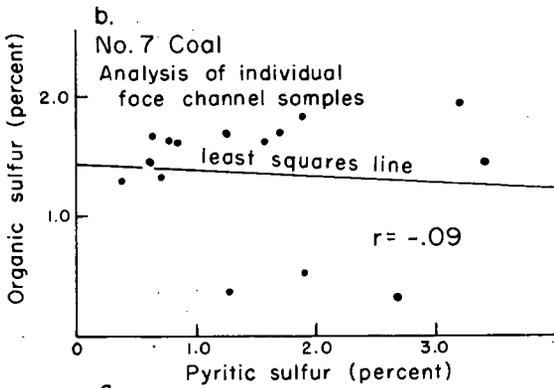
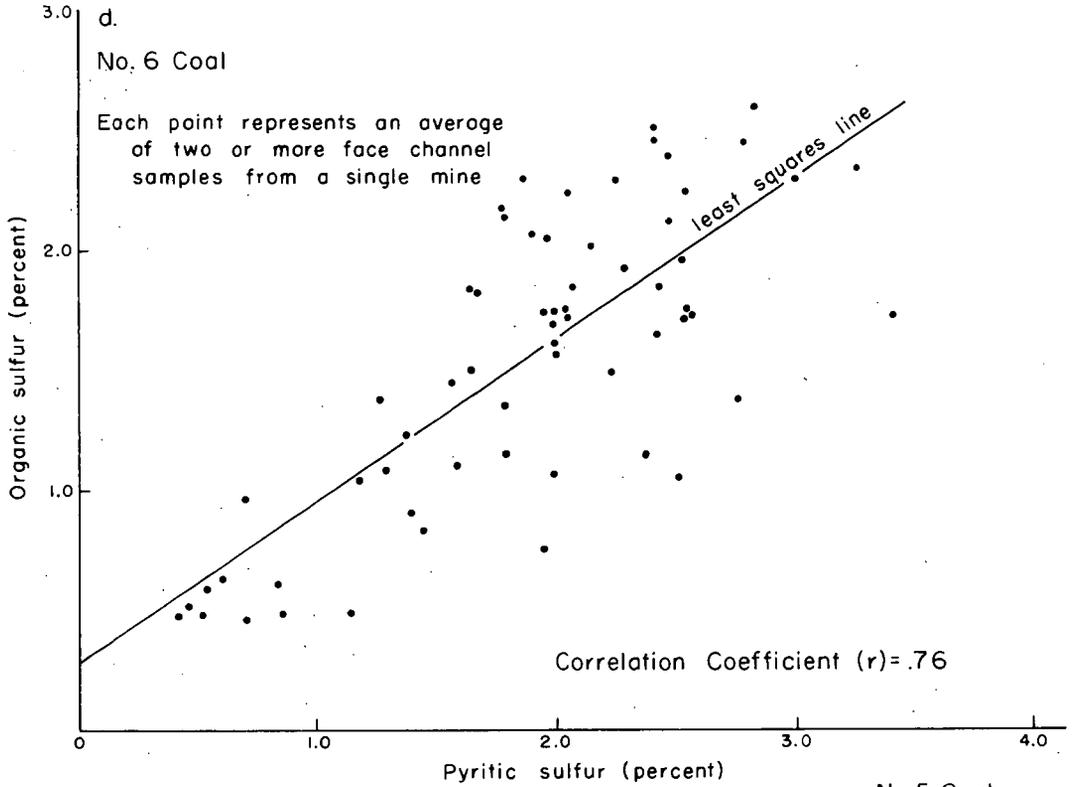
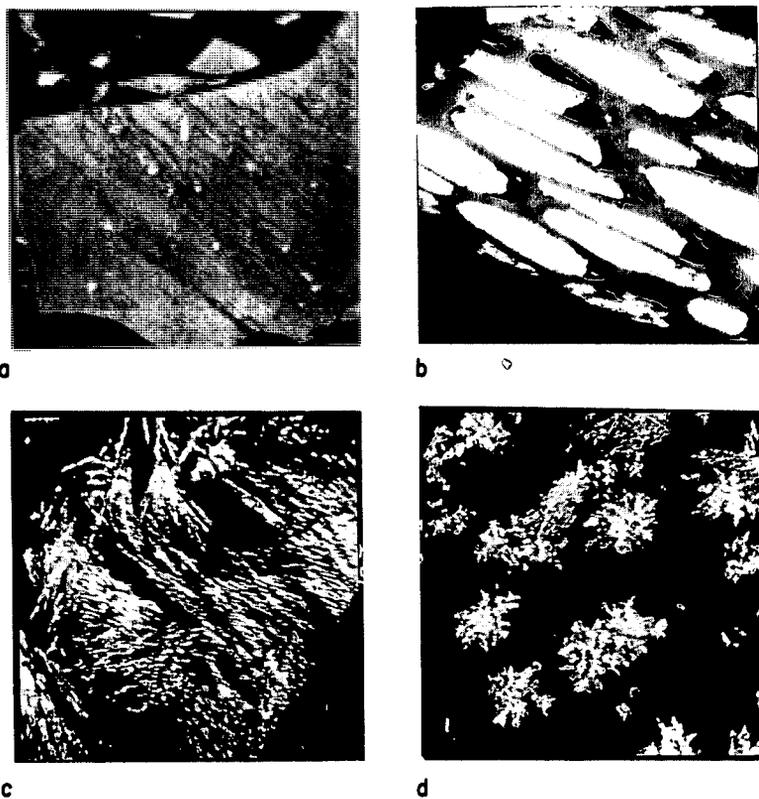


Fig. 3- Pyritic Sulfur-Organic Sulfur Relationships in Face Channel Samples of Illinois Coals



Scale  
0.2 mm

Figure 4. 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

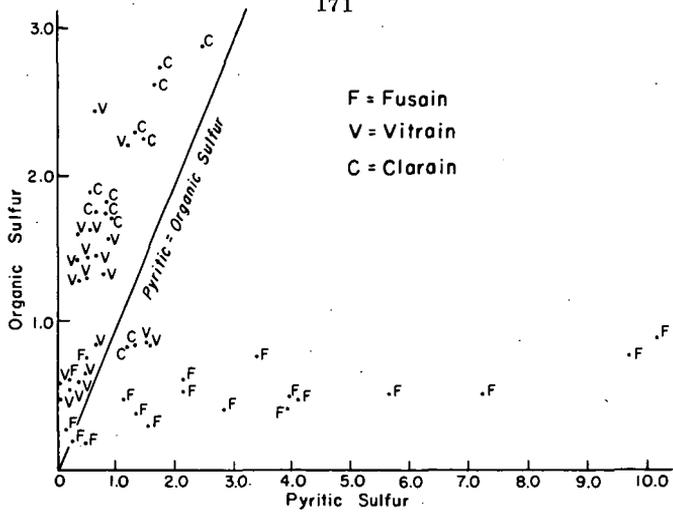
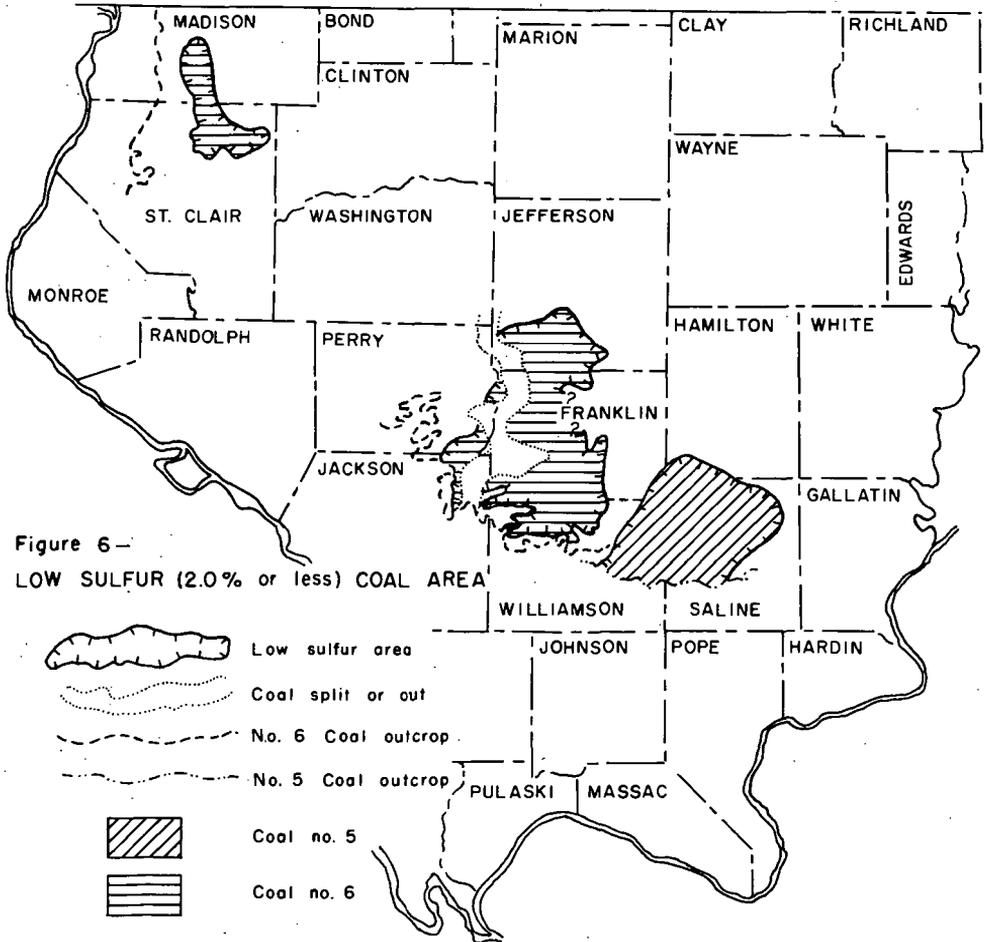


Figure 5 — Pyritic and Organic Sulfur content of Banded Ingredients modified from Cady (1935a, p.34)



## SCANDIUM IN AUSTRALIAN COALS AND RELATED MATERIALS

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## INTRODUCTION

There is a continued interest in the general chemistry of scandium and in special properties of the metal and its compounds. For example, ferrites containing a small amount of scandium have been used as solid state devices in electronics, and the properties of alloy systems of scandium are being investigated in various laboratories. The metal has a high melting point and a low density. The atomic radius of  $\text{Sc}^{3+}$  is smaller than that of yttrium and the lanthanide ions, which means that it is not commonly associated with the lanthanide elements, but rather with elements such as iron (as  $\text{Fe}^{2+}$ ). Scandium forms complexes readily.

Despite its widespread occurrence in rocks and minerals, only two definite minerals of scandium have been reported, namely thortveitite  $(\text{Sc},\text{Y})_2\cdot 2\text{SiO}_2$  and sterrettite  $\text{ScPO}_4\cdot 2\text{H}_2\text{O}$ . The scarcity of these and other minerals containing more than 0.1-0.5% Sc has led to interest in sources of scandium, amongst which coal ash, with its wide variety of inorganic constituents, often enriched relative to common rocks and sediments, would seem to be a possibility. The first determinations of scandium in coal were probably those carried out by Goldschmidt and Peters (1), who found 3-300 p.p.m. Sc in 14 samples of ash from bituminous and brown coals (0.1-8 p.p.m. on a coal basis). Deul and Anell (2) found <1 to 100-1000 p.p.m. Sc, with most values between 10 and 100 p.p.m., in 319 samples of low-rank coals from the U.S.A. As part of a general survey of diverse possible sources of scandium in the U.S.A., Ross and Rosenbaum (3) analysed 13 coal-ash samples; these contained 10-30 p.p.m. Sc. The present paper gives the results of an extensive survey of Australian coals and related materials for scandium.

## SCANDIUM IN COALS AND VITRAINS

General information on the coal samples is given in Table 1, and the geographical locations of the coalfields are shown in Fig. 1. Details of the emission spectrographic method of analysis are given in the Appendix. It is clear from the results for coals from the Sydney Basin (Table 1) that the overall assessment of the scandium status given by clean-coal composites differs little from that given by whole-seam composites or subsection samples. Hence, later determinations were usually carried out on clean-coal composites. These results showed that there was a fairly constant concentration (mean 2-4 p.p.m.) in the N.S.W. and Queensland Permian coals. However, slightly higher values were found for the Rosewood-Walloon coals (mean 7 p.p.m.) and the highest values were found for the West Moreton coals (mean 15 p.p.m.). These trends were also apparent in the vitrains (Table 2) which had been separated by flotation, usually at a specific gravity of about 1.3, from samples of most of the seams referred to in Table 1.

Most of the coal ashes had scandium contents close to the Clarke (i.e. the mean abundance of scandium in the earth's crust), which has recently been reassessed (4) as 30 p.p.m. Sc, the main exceptions being some of the Queensland coals. However, apart from the Latrobe Valley brown coals, in which scandium was not detected, the concentrations in most of the coal ashes exceeded the mean content of 10 p.p.m. Sc in sedimentary

rocks (5) and that of 8 p.p.m. Sc for subsoils (6). Shale bands associated with coals in the Sydney Basin had < 3-16, with a mean of 7 p.p.m. Sc. The ashes of the vitrains generally showed distinct enrichment relative to the earth's crust or sedimentary rocks, and the enrichment factors for the former (i.e. the ratio of mean content to the Clarke) varied from about 1.5 to 10. The maximum content of 600 p.p.m. Sc (i.e. 0.09%  $\text{Sc}_2\text{O}_3$ ), which was found in samples from three seams in the West Moreton coalfield, exceeded the highest reported value in coal ash of 300 p.p.m. Sc (1).

#### MODE OF OCCURRENCE OF SCANDIUM

The fact that there is a fairly high concentration of scandium in the vitrains, which contain only traces of clay and other minerals present in the bulk coal, suggests that part of the scandium in the coal is organically bound. Experiments were carried out on six samples of coals from the Sydney Basin in order to ascertain the extent and variability of this association with the coal substance. Each sample was demineralized by treatment with acids to reduce the ash yield to about 1% or less (7). Scandium was determined in the coal before and after demineralization and calculations showed that between 40 and 95% of the scandium in the original coal was organically bound to the coal substance.

As there was also some scandium associated with the mineral matter in the coals, it was decided to ascertain the scandium content of minerals or mineral-rich materials which had been separated from certain coal seams. As will be seen from Table 3, scandium was detected in some siderites, kaolinites and calcites, albeit in low concentrations. On the basis of its atomic radius (0.8Å) scandium may be expected to be able to replace several cations - for example,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Sn}^{4+}$ . The most common host minerals for  $\text{Sc}^{3+}$  are those high in  $\text{Fe}^{2+}$  - for example, pyroxenes and biotite - although it is not clear how the substitution is effected, depending as it does on a secondary replacement or rearrangement to balance the otherwise excess positive charge. The presence of scandium in some of the siderites may be the result of a  $\text{Sc}^{3+}$ - $\text{Fe}^{2+}$  replacement. The association of scandium with a limestone, possibly replacing  $\text{Ca}^{2+}$  (8), may be relevant to the detection of scandium in some of the calcites, where a similar replacement may have occurred. As scandium is unlikely to be substituted in lattice positions or interstitially in kaolinite, its presence in the latter is probably due to adsorption. So far, it has not been possible to separate an apatite from Australian coals, but a subsection sample of a Burrum coal, known to be high in phosphorus present as fluorapatite, contained a lower concentration of scandium than the clean-coal composite of which it was a part. Hence in this case there was no enrichment of scandium as phosphate.

#### SCANDIUM IN COKE, BOILER DEPOSITS AND FLY-ASH

The results in Table 4 show that scandium, unlike several other trace elements in Australian coals, is not enriched in boiler deposits (9). The concentrations in coke and fly-ash are much the same as in coal ash. As expected, the Queensland cokes had higher scandium contents than those made from N.S.W. coals.

#### DISCUSSION

The results for scandium in Australian coals indicated a trend from the Latrobe Valley brown coals, in which this element was not detected (i.e. < 0.5 p.p.m.), to the West Moreton bituminous coals with a mean content of 15 p.p.m. Although the latter coals are Triassic, so is Callide coal, which is low in scandium, and, if the one vitrain sample is a guide, then Leigh Creek coals, which are also Triassic, will have similar scandium contents to the N.S.W. and Queensland Permian coals (mean 2-4 p.p.m.). Hence, age is probably not the factor relevant to increase in scandium concentration. It is more likely that the high scandium contents in the West Moreton coals were brought about by adsorption from solutions emanating from source rocks, especially those of

igneous origin, which were able to supply a higher concentration of scandium than was available in other areas. The trivalent scandium ion is readily adsorbed and its small radius and high charge should favour the formation of stable organic complexes, effecting the removal of  $\text{Sc}^{3+}$  from percolating solutions and its fixation in the coal substance. Although the relative amounts of organically bound scandium vary, there are no minerals associated with Australian coals that are greatly enriched. Some siderites, kaolinites and, to a lesser extent, calcites, showed low scandium contents, and these are the constituents of the mineral matter in coal which contribute scandium. As in the earth's crust, scandium is ubiquitous in Australian coals.

Results for a range of boiler deposits formed during the burning of bituminous and hard brown coals either by grate or pulverized-fuel firing, showed that no enrichment of scandium had occurred. From the point of view of possible use as a source of scandium, the ash from certain coals and vitrains from the West Moreton coalfield merits some consideration. It is difficult to ascertain the present price of scandium, but in 1962 it was quoted as \$2700 per pound of 99% pure  $\text{Sc}_2\text{O}_3$  (3). However, the desirability of further production of scandium, either from a low-grade, by-product source by solvent extraction (10) or from a higher-grade material, rests on the value assigned to its compounds and alloys in modern technology.

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#### APPENDIX. METHOD OF ANALYSIS

Gravimetric and spectrophotometric methods, often after separation of a scandium-rich fraction by solvent extraction, cation exchange or paper chromatography, have been reported frequently in the recent literature from the U.S.A., Japan and Russia. However, since satisfactory chemical methods for scandium are usually long and involved, more direct methods, such as neutron activation, X-ray spectrography and emission spectrography, are preferable. For a survey of diverse materials varying widely in scandium content, emission spectrography is well suited, and was used in this investigation.

Samples which were mainly carbonaceous, for example coals and vitrains, were ashed at 800°C prior to analysis, while low-carbon materials, such as boiler deposits and fly-ash, were not ashed. Samples should be about 100 B.S. mesh or less. Two spectrographic techniques were used, brief details of each being as follows:

- (1) When sufficient sample was available, 20 mg, for example, of coal ash was mixed with 20 mg of graphite powder in a small vibratory ball mill, and the mixture was filled into a graphite electrode of the type undercut below the cup to increase the temperature

and thereby assist volatilization. Anode excitation was used in a 9-amp. d.c. arc, with a 4.5-mm arc gap and an exposure time of 2.5-3 min (total burn). A Hilger Automatic Large Quartz (E492) spectrograph was used and the spectra were photographed on Ilford N.50 (Thin Film Half Tone) plates. The final semi-quantitative estimations were made by visual comparison with standard spectrograms. Standards were prepared in a synthetic matrix of similar major-element composition to the samples. The analysis lines used were the ion line at  $2552.36\text{\AA}$  and the atom line at  $3269.90\text{\AA}$ . The former line is singularly free from interference, apart from platinum which is rarely found, and the latter line can be used in the presence of up to 20% iron and/or 1% zirconium without interference. Each of these lines had a detectability of 10 p.p.m. Sc. The synthetic standards were checked by using them to determine scandium in the synthetic rock sample W-1 (U.S. Geological Survey). The value of 40 p.p.m. Sc obtained is close to most of the values reported; of the 20 values listed by Fryklund and Fleischer (4), 17 were in the range 25-70, with a mean of 40 p.p.m. Sc.

(ii) When only 1-3 mg of sample was available - for example, in the case of some minerals removed from coals - a microspectrographic method was used. The sample was mixed with lithium tetraborate plus graphite powder (usually 2+3+5 mg respectively), and filled into a small graphite electrode. The arcing procedure was the same as before. New standards were prepared, and the detectability was 20 p.p.m. for Sc 2552 and 40 p.p.m. for Sc 3269.

For the determination of scandium in minerals separated from coal (for example, pyrite, siderite and calcite) separate tests were carried out to ascertain the suitability or otherwise of the standards, and corrections were made, if necessary. The standard Sulphide Ore-1 (Canadian Association of Applied Spectroscopy) was found to contain ~20 p.p.m. Sc compared with the recommended value of 25 p.p.m.

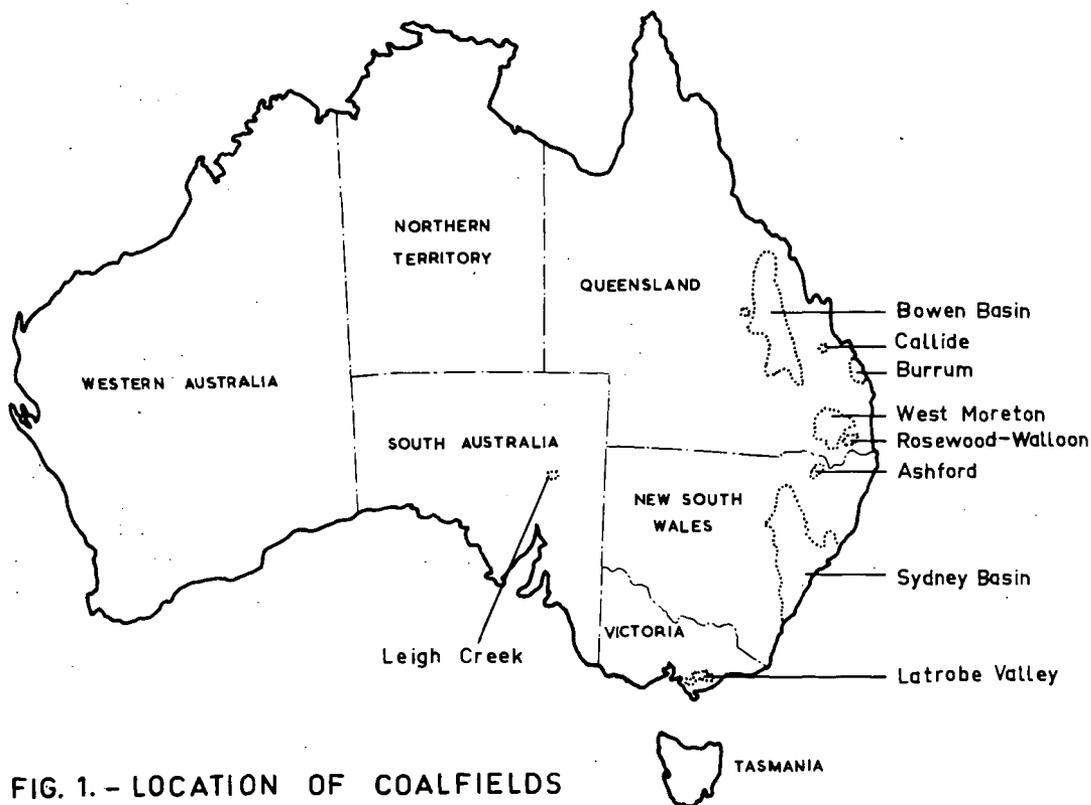


FIG. 1. - LOCATION OF COALFIELDS

TABLE 1. CONTENT OF SCANDIUM IN AUSTRALIAN COALS

Coalfield	Geological Age	No. of Seams Sampled	No. of Samples	p.p.m. Sc			
				On Ash Basis		On Air-dried Basis	
				Range of Values	Mean	Range of Values	Mean
<b>QUEENSLAND (bituminous)</b>							
Callide	Triassic	1	1	-	30	-	4
West Moreton	Triassic	12	24	30-150	60	7-30	15
Rosewood-Walloon	Jurassic	2	7	25-40	35	5-8	7
Burrum	Cretaceous	1	1	-	30	-	3
Bowen Basin	Permian	10	12	10-50	30	1.5-6	3
<b>NEW SOUTH WALES (bituminous)</b>							
Ashford	Permian	1	1	-	20	-	2
Sydney Basin	Permian	20	88	<10-40	20	<0.4-6	2.5
(coal subsection samples)		20	282	<10-100	20	<0.3-10	2.5
(whole-seam composites)		20	26	<10-40	20	<1-6	2.5
<b>VICTORIA (soft brown)</b>							
Latrobe Valley	Tertiary	2	22	-	<10	-	<0.5
(low ash, i.e. < 5%)							
<b>SOUTH AUSTRALIA (hard brown)</b>							
Leigh Creek	Triassic	3	37	*	-	-	-

Note. The above results refer to clean-coal composites, except where otherwise stated.

\* Detected in 36 samples, but standards were not available for semi-quantitative estimation.

TABLE 2. CONTENT OF SCANDIUM IN VITRAINS

Coalfield	No. of Samples	p.p.m. Sc			
		On Ash Basis		On Air-dried Basis	
		Range of Values	Mean	Range of Values	Mean
<b>QUEENSLAND</b>					
Callide	1	-	150	-	2.5
West Moreton	27	100-600	350	4-20	10
Rosewood-Walloon	11	60-300	150	2-10	6
Bowen Basin	6	100-150	120	1.5-3	2
<b>NEW SOUTH WALES</b>					
Sydney Basin	20	30-250	100	0.9-7	2.5
<b>SOUTH AUSTRALIA</b>					
Leigh Creek	1	-	40	-	4

TABLE 3. SCANDIUM IN MINERALS OR MINERAL-RICH SAMPLES SEPARATED FROM COALS

Main Constituent	No. of Samples	Brief Details of Samples	p.p.m. Sc
Pyrite	6	4 from Queensland and N.S.W. coals; 2 from Leigh Creek coal	< 20
Siderite	1	From a Sydney Basin coal - 'nodular'	30
Siderite	1	From a West Moreton coal - 'nodular'	40
Siderite	1	From a West Moreton coal - 'massive'	< 15
Siderite	1	From Leigh Creek coal - 'nodular'	< 15
Calcite	3	From Sydney Basin coals	< 10, 10?, ≤10
Secondary carbonate (high in Ca)	1	Cleat filling from a West Moreton coal	40
Gypsum	1	From Leigh Creek coal	< 10
Mudstone	1	From a dirt band in a Sydney Basin coal	10
Bentonite	1	From the roof measures of a Rosewood-Walloon coal	< 10
Kaolinite	1	From a Rosewood-Walloon coal	15
Kaolinite	1	From a Sydney Basin coal	25

TABLE 4. CONTENT OF SCANDIUM IN COKE, BOILER DEPOSITS AND FLY-ASH  
(Values are in p.p.m. Sc)

Description of Samples	No. of Samples	Range of Values	Mean	Scandium in Ash of Coal Used
Cokes made from N.S.W. coals	14	25-40	30	-
Cokes made from Queensland coals	3	60-100	80	-
Fused material and deposits from walls of carburettor in water-gas plant	8	-	15	20
Deposits from various parts of a spreader-stoker-fired boiler, burning bituminous coal	32	20-30	25	20
Deposits on super heater tubes of chain-grate stoker fired boiler, burning bituminous coal				
Inner deposits	4	10-20	10	30
Outer deposits	1	-	30	-
Deposits from screen tubes and superheaters of boiler, burning Leigh Creek coal under p.f. conditions	10	<10-20	10	-
Fly-ash from a N.S.W. bituminous coal	21	25-30	30	30
Fly-ash from Leigh Creek coal	2	20,30	25	-

## The Effect of Molten Caustic on Pyritic Sulfur in Bituminous Coal

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### Introduction

In a study related to the improvement of basic raw materials in the steel industry, the Applied Research Laboratory of the United States Steel Corporation has been investigating the behavior of chemical reagents on mineral matter in coal. The effect of various chemical reagents on pyrite in coal has been investigated as a part of this study.

It is well known that some mineral matter can be removed from coal by physical separation techniques; however, the effectiveness of such methods is limited by the degree of pulverization that is practical and the quantity of finely dispersed mineral matter that is present. Physical methods do not appear to be capable of removing either organic sulfur from the coal or finely dispersed pyritic sulfur that is embedded in the coal matrix. For example, after removal of pyrite by mechanical means, the sulfur content of Robena coal decreases from 2.5 percent to about 1.7 percent.

Chemical methods for removing mineral matter from coal have been reported to be quite successful. Chemical methods reported<sup>1)\*</sup> include leaching with aqueous solutions of nitric acid, chlorine, hydrofluoric acid, and caustic, as well as extraction with various organic solvents to remove the coal from the residual mineral matter. The effect of microorganisms on pyritic sulfur in coal has been reported by the U. S. Bureau of Mines.<sup>2)</sup> The effect of molten-caustic solutions on the mineral matter in coal has not been reported previously.

Molten-caustic solutions have been used with success previously for heat-transfer media, heat treating, metal-finishing baths, and electrolytic refining processes. The addition of various basic compounds such as sodium carbonate during graphitization or carbonization has also been reported. The investigation reported in this paper describes the effect of molten-caustic solutions on the pyritic sulfur in bituminous coal.

### Experimental Work

Robena coal was the principal coal studied in this investigation. Samples of Illinois coal and Wyoming coal were also examined to extend the scope of the study. Properties of the coals can be seen in Table I. Ordinary reagent-grade pellets of sodium hydroxide and potassium hydroxide were used to prepare the molten-caustic media. The experiments were conducted in a 1500-milliliter stainless steel vessel with an outlet valve at its base for removal of molten materials.

The procedure employed for the treatment consists of preparing a molten-caustic solution by melting together equal parts of sodium hydroxide and potassium hydroxide. The caustic is heated to the desired temperature, stirred vigorously, and the coal is added slowly as a powder to avoid foaming and overheating. About 4 parts of caustic to 1 part of coal are used to obtain a readily handled melt. The treatment is exothermic and some gases are evolved, especially during the coal addition. After the treatment is completed at the desired temperature and for the appropriate length of time, stirring is stopped, and about five minutes are allowed for separation of the coal from the molten caustic. The molten caustic is removed through the bottom outlet valve, and the coal layer is then cooled quickly in a

\* See References.

water bath and subsequently slurried in 40 to 50 percent aqueous caustic to disperse the coal and remove residual inorganic materials. The coal is filtered off and washed with water to remove residual caustic. The samples are then dried under vacuum at 70 to 80 C and stored in sealed containers.

The coals were analyzed for sulfur content, ash, volatile matter, carbon, and hydrogen. Data were also obtained on free-swelling index and Gieseler plasticity.

### Results and Discussion

Laboratory studies demonstrated that the pyritic sulfur in bituminous coal can be completely eliminated by molten-caustic treatment. Although a number of highly alkaline materials such as sodium acetate, sodium hydroxide, potassium hydroxide, and calcium hydroxide were investigated, a 1-to-1 melt of sodium hydroxide and potassium hydroxide appears to be the most suitable medium because of its thermal stability and low melting point.

The effect of temperature on the extent of desulfurization is quite pronounced, Table II and Figure 1. At temperatures between 150 C and 225 C only pyritic sulfur is removed from the coal, and below 150 C no observable pyrite removal occurs. A part of the organic sulfur of coal also appears to be removed as the temperature is increased above 225 C. Pyrite removal by molten caustic is a very fast process at either 250 C or 400 C, Figure 2, and appears to be complete after about five minutes at either temperature. The sulfur content of the coal increases with a long treating time at 400 C because of the formation of stable sulfur compounds by reaction of the coal with sulfides in the molten caustic.

The effect of coal size on the molten-caustic treatment appears to be important only below 300 C. Table III shows that plus 1/4-inch coal can be treated effectively at 400 C and that pyrite removal is poor at temperatures below 300 C unless minus 40-mesh coal is employed. Robena coal appears to become "plastic" at about 325 C and interaction between the caustic and pyritic sulfur is thereby enhanced. A high degree of pulverization is necessary to obtain good results at low temperatures since only sulfur at the surface of solid particles can be contacted by the caustic when the coal is not plastic.

The properties of coals treated with molten caustic appear to be somewhat different from those of the original coal. A comparison of proximate analysis, free-swelling index, Gieseler plasticity, and other properties can be seen in Table IV. Coals treated at 400 C and higher exhibit the most significant change in properties.

Although Robena and Illinois coal can be treated readily by this technique, low-rank coals such as Wyoming coal are seriously decomposed by molten caustic. Data on molten-caustic treatment of Wyoming coal and Illinois coal are shown in Table V.

The molten-caustic treatment may be suitable for preparing carbonaceous materials for special applications where low-sulfur and low-ash contents are of importance. This technique may also be useful as an analytical method for determining pyritic sulfur in coal.

### Summary

An experimental investigation of the effect of molten caustic on pyritic sulfur in coals of various rank has been conducted. Laboratory tests showed that all pyritic sulfur can be removed from Robena coal by treatment with molten caustic. Robena coal and Illinois coal appear to perform similarly in molten caustic; however, Wyoming coal is severely decomposed during treatment.

This technique may be useful in preparing low-sulfur, low-ash carbonaceous materials for special applications. Molten-caustic treatment of coal might also serve as an analytical method for determination of pyritic sulfur.

### Acknowledgements

The assistance of Mrs. Genevieve Dudgeon, Max Katz, and J. D. Clendenin of the Applied Research Laboratory is appreciated. Mrs. Dudgeon and Mr. Katz provided analyses of the various samples of coals and coke, and Mr. Clendenin supplied the coal samples and evaluation of coking properties for this investigation.

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2. M. H. Rogoff, M. P. Silverman, and I. Wender, "The Elimination of Sulfur from Coal by Microbial Action." Presented before the Division of Gas and Fuel Chemistry, American Chemical Society, New York Meeting, September 11 to 16, 1960.

Table I

Coal Samples Used in Molten-Caustic Studies

<u>Coal Sample</u>	<u>Screen Size</u>	<u>Total Sulfur, percent</u>	<u>Pyritic Sulfur, percent</u>	<u>Organic Sulfur,* percent</u>
Robena 354	-40 mesh	1.64	0.58	1.06
Robena R415	1/4 by 0 in.	1.85	--	--
Illinois, Orient	1/4 by 0 in.	3.03	0.80	2.23
Wyoming, Elkol	-40 mesh	0.72	negligible	0.72

\* Calculated difference between total sulfur and pyritic sulfur.

Table II

Molten-Caustic Treatment at Various Temperatures  
(Minus 40-Mesh Robena Coal)

<u>Temperature, C</u>	<u>Time, minutes</u>	<u>Sulfur in Coal, %</u>	<u>Coal Yield, %</u>
150	30	1.56	93
200	30	1.14	92
250	30	1.04	94
300	30	0.99	89
350	30	0.80	92
400	30	0.51	93
450	30	0.56	--

Table III

Comparison of Molten-Caustic Treatment of Various-Sized Robena Coal

<u>Coal Size</u>	<u>Treatment Temperature, C</u>	<u>Treatment Time, minutes</u>	<u>Sulfur in Coal, %</u>
1/4 by 0 in.	250	10	1.40
-40 mesh	300	30	0.99
1/4 by 0 in.	300	30	0.96
1/2 by 1/8 in.	350	10	0.91
-40 mesh	400	5	0.90
1/4 by 0 in.	400	5	0.99
1/4 by 0 in.	400	30	0.36
1/2 by 1/4 in.	400	15	1.13

Table IV

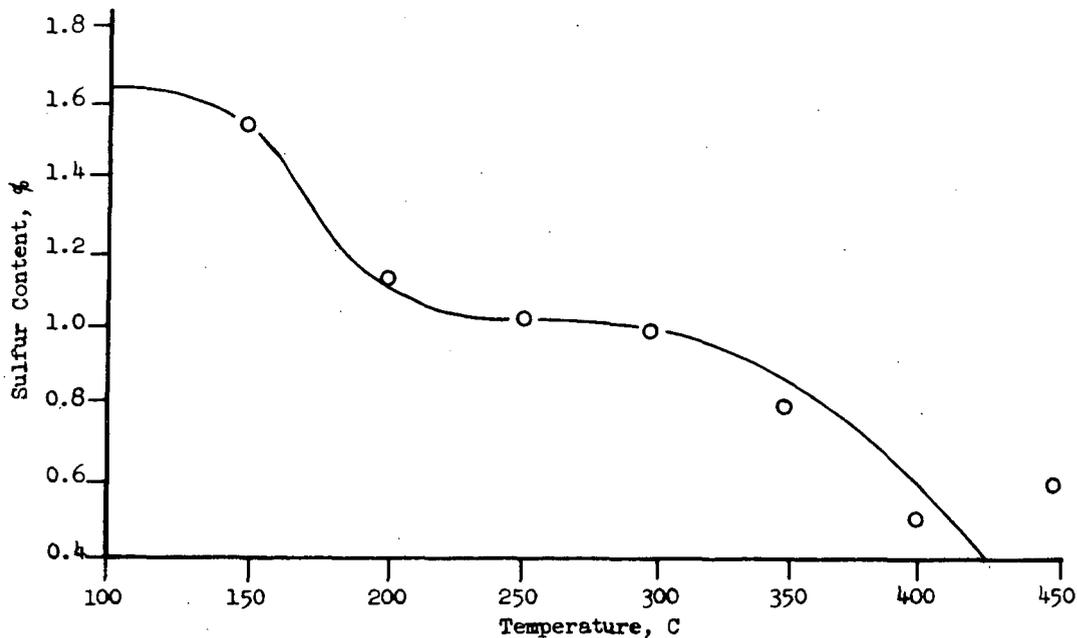
Comparison of Properties of Untreated and Molten-Caustic-Treated Robena Coals

<u>Treatment</u>	<u>Sulfur, %</u>	<u>Ash, %</u>	<u>Volatile Matter, %</u>	<u>Fixed Carbon, %</u>	<u>H<sub>2</sub>O, %</u>	<u>Free-Swelling Index</u>	<u>Gieseler Maximum Fluidity</u>
Robena coal	1.64	7.31	36.1	55.6	1.05	6-1/2	34,000
Robena coal extracted with tap water	1.64	6.93	36.4	56.4	0.25	7-1/2	17,300
Robena coal							
1/2 hr at 150 C	1.56	6.16	35.2	57.9	0.74	5-1/2	--
1/2 hr at 250 C	1.04	5.86	39.3	60.8	0.97	5	4,380
1/2 hr at 300 C	0.99	5.35	33.7	59.9	1.07	3-1/2	--
1/2 hr at 350 C	0.80	6.06	32.2	60.0	1.80	3	1.0
1 hr at 350 C	0.92	5.75	--	--	0.13	2-1/2	0.5
1/4 hr at 350 C	0.91	5.22	33.0	61.1	0.68	3-1/2	7.7
5 min at 400 C	0.90	6.22	32.5	61.2	0.00	3	0.3
1/2 hr at 400 C	0.51	4.9	23.6	63.1	8.1	0	-

Table V

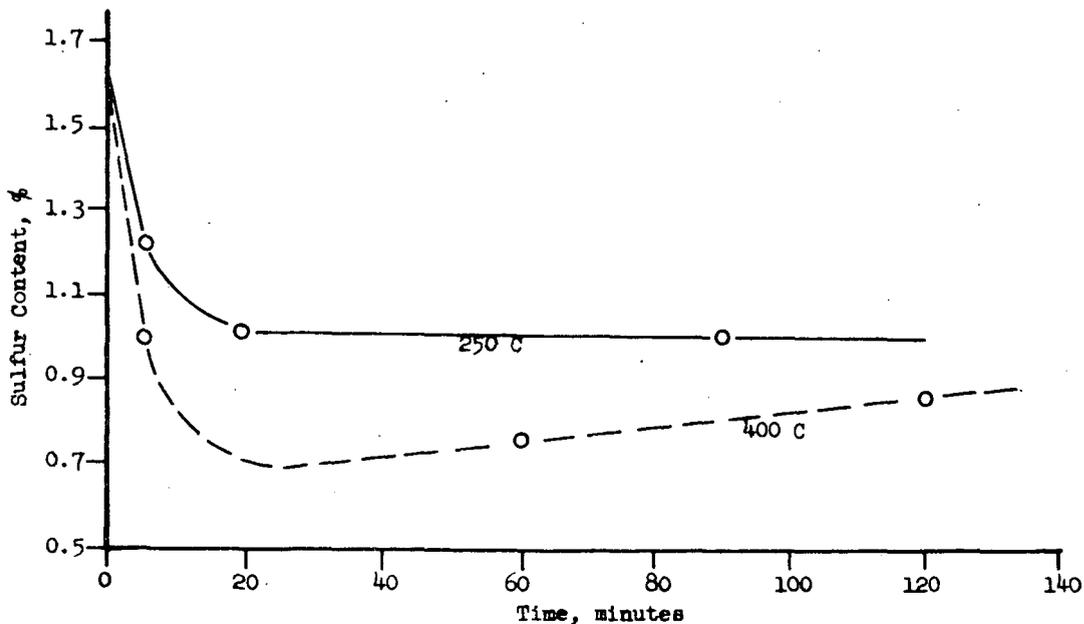
## Data on Molten-Caustic Treatment of Illinois and Wyoming Coal

Coal	Temperature, C	Time, minutes	Sulfur in Treated Coal, %	Yield, %	H <sub>2</sub> O, %	Volatile Matter, %	Fixed Carbon, %	Ash, %	Free-Swelling Index	Carbon, %	Hydrogen, %
Wyoming	(Not treated)		0.72	-	19.8	35.0	42.2	2.96	1-1/2	60.26	5.57
Wyoming	200	30	0.50	52	9.4	41.9	47.7	0.96	1-1/2	68.56	5.78
Illinois	(Not treated)		3.03	-	5.7	34.8	50.0	9.49	2	69.03	5.17
Illinois	300	30	2.19	91	3.9	31.9	54.3	9.13	0	70.30	5.15
Illinois	400	30	0.97	76	2.1	29.5	61.7	6.67	0	76.31	4.14



MOLTEN-CAUSTIC TREATMENT OF -40 MESH ROBENA COAL AT VARIOUS TEMPERATURES

Figure 1



MOLTEN-CAUSTIC TREATMENT OF ROBENA COAL AT 250 C AND 400 C

Figure 2

## Attempted Removal of Sulfur from Coal and Coke

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The purpose of this paper is to report briefly on some experiments designed to remove inorganic sulfur from coal or to prevent its retention in coke, by chemical means. It may be said at once that although some success was achieved, no method with promise of industrial practicability was found.

A substantial proportion of the sulfur in coals occurs as ferrous disulfide,  $\text{Fe}^{+2}\text{S}_2^{2-}$ , usually in the mineral form known as pyrite. It is well known that pyrite dissociates to ferrous sulfide and sulfur, the dissociation pressure becoming appreciable at 450-500°. Ferrous sulfide is stable and undergoes little change before 1300-1400°. Various lines of work show that the sulfur released by the pyrite in coal during carbonization becomes fixed in the carbonaceous matter of the coke. Thus Cernic carbonized a series of coals in the presence of finely dispersed synthetic pyrite labelled with  $\text{S}^{35}$ ; she found that in all cases a more substantial proportion of the radioactivity was retained in the coke than could be accounted for by the ferrous sulfide.

Mazumdar, Lahiri and their co-workers<sup>2</sup> investigated the reaction of sulfur with coal at 250-350°. Much hydrogen sulfide was released, which they attributed to dehydrogenation of hydroaromatic structures in the organic matrix; others have suggested that in addition dehydrogenation and cross-linking of aromatic nuclei takes place<sup>3</sup>. If the coal is heated with sulfur at 300-350° and then carbonized, the yield of volatile matter is drastically reduced and the coke has an increased sulfur content<sup>2</sup>. Some known sulfur compounds decompose at 500-600° with formation of hydrogen sulfide or mercaptans<sup>4</sup>; the latter substances, released during coal carbonization, could react elsewhere on the coal surface to give some firmly bound type of sulfur-carbon complex, their sulfur thus remaining in the coke.

It is evident therefore that a number of reactions involving sulfur can take place during coal carbonization, in which both inorganic and organic components play a part. Some of these reactions result in the formation of very stable organically bound sulfur complexes. Hence one possible way to reduce the sulfur content of coke would be to interfere with these reactions at temperatures below 600°, preferably in such a way that relatively stable volatile sulfur compounds are formed. The above ideas guided one of the series of experiments described in this paper: a coal was carbonized at 600° in the presence of various additives, and the sulfur content of the char compared with that of a standard char prepared in the absence of additive.

The other series of experiments was based on the reported solution chemistry of pyrite<sup>5,6</sup>. Various reagent mixtures are stated to dissolve

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pyrite at temperatures of 20-100°, and it was hoped that one could be found that would remove the disulfide from coal without serious oxidation or other change of the organic substance. It is not clear from the literature what reactions occur in bringing the pyrite into solution. The presumed interpretations of the reactions tested with pyrite in coal are:

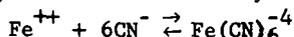
1. Boiling potassium nitrate or chlorate with oxalic acid<sup>7</sup>; the ferrous iron in the presence of the mild oxidizing agent probably gives the very stable ferric oxalate complex, while the sulfur forms potassium sulfite or sulfate.

2. Stannous chloride and hydrochloric acid<sup>8</sup>: the pyrite may be reduced so that ferrous chloride and hydrogen sulfide result.

3. Calcium hypochlorite<sup>9</sup>: the pyrite must be oxidized to ferric sulfate. This reagent has also been used for "sweetening" gasoline, since it removes sulfur from many organic sulfur compounds, including thiophene if the pH is adjusted to weakly alkaline.

4. Aqueous potassium cyanide<sup>10</sup>: it is stated<sup>10</sup> that pyrite does not dissolve on treatment with boiling saturated potassium cyanide for 6 hours. However, the following argument<sup>4</sup> suggests that under the conditions dissolution might take place.

The solubility of pyrite in water is said<sup>9</sup> to be  $4 \times 10^{-5}$  gm mol./l., so that the solubility product would be  $1.6 \times 10^{-9}$  and the concentration of  $\text{Fe}^{++}$  in equilibrium with the solid  $4 \times 10^{-5}$  gm. ion/l. However, recent unpublished work<sup>12</sup> suggests that the figures are considerably too high, but that in view of the instability of the  $\text{S}_2^{-2}$  ion its concentration could be suppressed and that of  $\text{Fe}^{++}$  materially increased by removing oxygen from the system. Now if a suitable ligand were added to the suspension, such that  $\text{Fe}^{++}$  is strongly complexed and its concentration in equilibrium with the complex reduced below that calculated from the solubility product of pyrite, the pyrite should in principle go into solution. One of the most stable complexes formed by  $\text{Fe}^{++}$  is the ferrocyanide:



for which the stability constant at 25° is  $10^{24}$ . Simple calculation shows that if pyrite dissolved in 5N cyanide solution until the ferrocyanide concentration became 0.1 N, the equilibrium concentration of  $\text{Fe}^{++}$  would be  $6 \times 10^{-30}$  gm. ion/l. Even if the solubility product of pyrite is considerably less than  $1.6 \times 10^{-9}$ , it should still dissolve in cyanide solution. Equilibria should be more favorable at room temperature than 100°. Some experiments on the treatment of coal with cyanide solution have been made:

### Results

The coal used in this study was a high-volatile A bituminous coal from Champion Mine of the Pittsburgh seam. Relevant analytical data are given below:

<u>Proximate Analysis</u> :	Volatile matter	35.85%	Ash	11.35%
	Fixed carbon	52.8%	Moisture	1.19%
<u>Ultimate Analysis</u>	(d.m.m.f., Parr's basis) 83.4%C, 5.7%H, 1.6%N, 0.6%S, 8.6% O (by diff.)			

Sulfur Distribution:

total	2.46%,	pyritic 1.95%,	organic 0.49%,	sulfatic 0.02%
% of total sulfur:	79%	20%	1%	

A. Change in Sulfur Distribution on Carbonization

A 30 gm. sample of coal (65 x 150 mesh) was placed in a sample holder and lowered into a furnace already preheated to the desired temperature; a flow of nitrogen (1 litre/min.) passed upwards through the furnace. The sample was left in the furnace for one hour after it reached temperature equilibrium, and then cooled in nitrogen. The char was then analysed for the total sulfur and the various inorganic forms of sulfur by standard A.S.T.M. procedures;<sup>13</sup> the organic sulfur is determined by difference. Data were obtained for a series of temperatures from 200-700°. The results are plotted in Figs. 1 and 2, where the sulfur distribution is shown as percentages of the total sulfur in the char and as percentages of the total sulfur in the raw coal respectively; the latter curve includes the proportion of sulfur lost in volatile products (obtained by difference).

It should be noticed that even by 200-300° there appears to be some gain of organic sulfur and loss of pyrite even though no ferrous sulfide could be detected. Possibly the organic material reduces pyrite, forming unstable sulfur-containing groups which subsequently are lost as volatile matter. The points for organic sulfur could be made to lie on a curve having a maximum at 200-250° and a minimum at about 400°, which would support the above suggestion, but the number of points available hardly justifies the drawing of more complex curves than those shown in the figures.

It is clear that by 600-700° most of the pyrite has decomposed, that the sulfur lost by the pyrite is much more than equivalent to the amount of sulfide formed, and that the proportion of organic sulfur in the char has considerably increased.

B. Carbonization in the Presence of Additives

For these experiments, the same apparatus and methods were used as above. For each experiment, 27 gms. of coal and 3 gms. additive were mixed by hand for 30-60 minutes; the mix was apparently dry even when the additive was liquid, owing to adsorption. Two rates of heating were used, 5.5-5.8°/min., and 80-90°/min.; conditions during carbonization were static, that is, no nitrogen flow was used. In the first case the sample was held at the maximum temperature (600°) for 15 minutes, and in the second for 60 minutes. The product, after cooling in nitrogen, was finely ground and analysed for total sulfur by the Eschka method.

Twenty seven substances were tested as additives, of which all but three were organic. They included various alcohols and sugars, which would give water and possibly olefins on pyrolysis; several high polymers, which should give on pyrolysis monomers capable of picking up sulfur; and some aromatic and aliphatic oxygen compounds that might take up sulfur to give a stable but volatile heterocyclic compound. Carbonization in the presence of most of these substances gave a char containing less sulfur than if no additive had been used, but the effect was small. It was appreciable for the four substances listed in Table I. It has been reported<sup>14</sup> that powdered pyrite is slowly decomposed by ammonium chloride, a sublimate of ammonium sulfide being formed; at 335°, 7% sulfur is lost in 25 minutes.

TABLE I

Carbonization of Pittsburgh Seam Coal at 600° in the Presence  
of Additives (10% concentration)

<u>Additive</u>	<u>Heating rate</u> °/min.	<u>% loss in</u> <u>wt. at 600°</u>	<u>% S in</u> <u>Char</u>	<u>S in coke</u> <u>S in coal</u> <sup>x</sup> 100
None	92.2	28.5	2.11	61.3
	5.6	23.8	2.22	68.8
Benzene-1,2,4,5-tetra- carboxylic dianhydride	80.0	21.5	1.60	51.0
	5.6	16.2	1.42	48.4
p. diphenyl-benzene (Santowax P)	77.5	29.7	2.03	58.0
	5.4	23.6	1.57	48.8
Sodium borohydride, NaBH <sub>4</sub>	72.5	10.0	1.64	60.0
	5.63	6.72	1.47	55.7
Ammonium chloride	72.5	23.0	1.68	52.3
	5.6	21.4	1.32	42.2

It will be noticed that sulfur removal was more effective at the lower rate of heating. With the diphenylbenzene and the borohydride, hard cokes were obtained. Ammonium chloride yielded a very soft coke. The dianhydride gave a soft granular product, and the plastic zone appeared to have been destroyed or greatly reduced. At 5% concentration of additive the use of ammonium chloride showed some reduction of sulfur (1.87 and 1.93% S in the char at 70.5 and 65.6°/min. heating rate respectively); the other substances had little effect.

C. Treatment with Aqueous Solutions

1. Potassium Cyanide. 200 ML of 10% cyanide solution (approx. 1.5N) were allowed to percolate through 30 gm. coal in a column. The coal was (a) 65 x 150 mesh, and (b) -200 mesh, and percolation took 105 minutes and 36 hours respectively. No attempt was made to remove oxygen from the system. The product was washed with 200 ml. water, dried at 110° and carbonized as before. The total sulfur contents of the char were (a) 2.44, (b) 2.00%.
2. Potassium Cyanide and Potassium Nitrate. 15 Gm. coal (65 x 150 mesh) was refluxed gently for 6 hours in a solution of 0.15 mole each of cyanide and nitrate in 250 ml. water. The filtered, washed and dried coal contained 1.90% S (compared with 2.46% in the untreated coal).
3. Potassium Nitrate and Oxalic Acid. A suspension of 15 gm. coal in 250 ml. of a solution of 0.01 mole oxalic acid and 0.02 mole nitrate was left at room temperature for 24 hours, and then refluxed for 8 hours. The sulfur content of the product was 1.94%.
4. Stannous Chloride and Hydrochloric Acid. The treatment was as in #3 (0.01 mole each SnCl<sub>2</sub> and HCl). The sulfur content of the product was 2.35%.
5. Calcium Hypochlorite. A solution of 10 gm. hypochlorite in 190 ml. of water, adjusted to pH8 by addition of acetic acid, was allowed to percolate through 30 gm. 65 x 150 mesh coal (this took 3 hours). The ash content of the product was 13.3% (untreated coal, 11.35%) and the sulfur content 2.13%

D. Discussion and Conclusions

The preliminary experiments on sulfur distribution confirmed that

sulfur from pyrite becomes fixed in the organic matter of the char on carbonization, and that any interference with this process must take place at 350-500° if it is to reduce the sulfur content of the char. Carbonization in the presence of certain additives did cause a marked removal of sulfur, though probably not as much as would be desirable in industrial practice. Under the conditions used, the amount of additive needed was relatively large and would be costly in practice; in two cases weak cokes were obtained. In addition, the use of ammonium chloride would give rise to serious corrosion problems. However, the principle that sulfur fixation can be interfered with and reduced in extent is confirmed. For effective action it is no doubt necessary that the additive should volatilize and penetrate the coal particles (if the latter are as big as 65 x 150 mesh) or diffuse readily through the fused mass. If very finely divided coal could be charred in a fluidized bed up to 500-600° as a pretreatment in a fluidizing gas containing a fair partial pressure of ammonia, hydrogen, or possibly moist carbon dioxide, it is likely that the sulfur content of the char could be greatly reduced.

None of the treatment with aqueous solutions was particularly effective. However, it is striking that the cyanide treatment had no effect on 65 x 150 mesh coal with a contact time of 1 3/4 hours, but an appreciable one on -200 mesh coal in 36 hours. Of the other treatments, potassium nitrate/cyanide and potassium nitrate/oxalic acid had an appreciable effect even on the coarser coal size.

There seems little doubt that the primary difficulty in all the sulfur removal processes tested is in getting adequate contact between the reagent and the finely dispersed pyrite grains. It seems probable that with a more sophisticated appreciation of pyrite chemistry much of the pyrite could be removed from a coal with an aqueous solution of a suitable complexing agent, provided finely pulverized coal can be used.

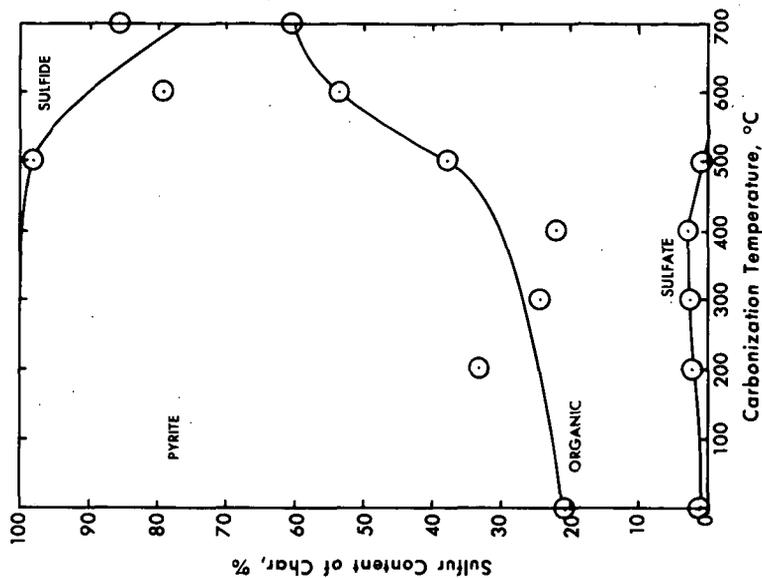
#### Acknowledgement

This work was supported by a contract from the Coal Research Board of the Commonwealth of Pennsylvania.

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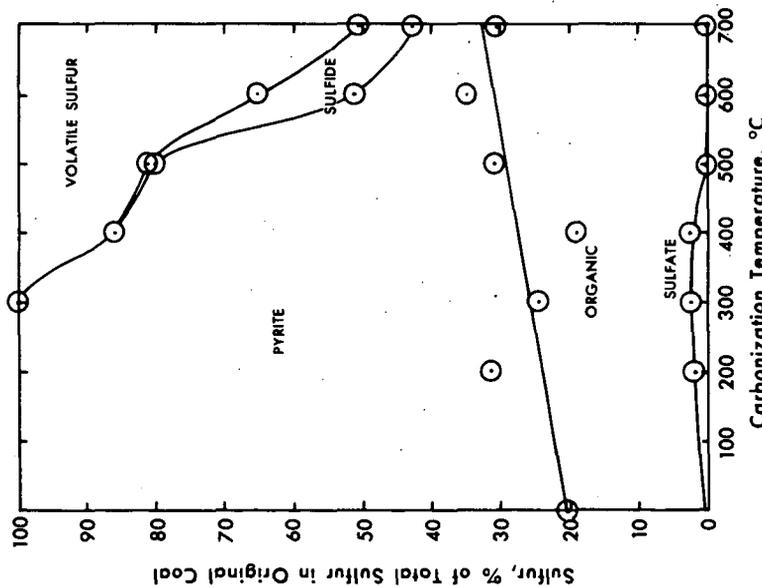
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DISTRIBUTION OF FORMS OF SULFUR IN PITTSBURGH SEAM COAL AND CHARs, EXPRESSED AS FRACTIONS OF TOTAL SULFUR IN SAMPLE ANALYSED

Figure 2



DISTRIBUTION OF FORMS OF SULFUR IN PITTSBURGH SEAM COAL AND CHARs, BASED ON TOTAL SULFUR IN UNHEATED COAL

Figure 1

## FEASIBILITY OF CONTINUOUS ASH MEASUREMENT OF COAL

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An automatic and continuous method of measuring the ash content of coal is needed by the coal industry. Automatic control of coal quality would reduce preparation costs, improve the product, and thus indirectly increase markets for coal. Existing methods of ash analysis involve a laborious process of sampling, sample preparation and chemical analysis, and the results may not be available for several hours--perhaps long after the coal has been shipped. For bulk products like coal, sampling costs can easily become a significant proportion of production costs. The industry needs a continuous method of analysis that will permit immediate control of quality.

One possible method involves a process in which some type of nuclear radiation penetrates a considerable depth into the coal, undergoes a nuclear reaction with the chemical elements, and produces characteristic radiation that emerges from the coal and is measured. For this method, only neutrons and gamma rays will provide the required depth of penetration. When large samples of coal are bombarded by energetic neutrons, three nuclear processes can occur: (1) elastic scattering; (2) inelastic scattering; and (3) capture and subsequent decay. If the energetic neutrons are in the Mev-energy range, the usual sequence of events is for each neutron to make a number of elastic and inelastic collisions, losing energy with each collision, every inelastic collision leaving the bombarded nucleus in an excited state. When the excited nucleus returns to ground state, prompt gamma rays of characteristic energy, called inelastic gammas, are emitted. Eventually, after a large number of elastic and inelastic collisions, the neutron reaches thermal energies (about 0.025 ev) and neutron capture takes place. If the capture process excites the nuclide, prompt gammas are emitted by mechanisms similar to that of the inelastic scattering. These characteristic gamma rays are known as radiative capture gammas. Later, usually after relatively long periods depending on the half-lives of the radioisotopes, the nuclide may decay and emit a beta particle, a gamma ray, or both. These latter gamma rays are known as activation gammas. Both types of gamma rays have energies characteristic of the nucleus of the element from which they were produced, hence the number of such gamma rays can be counted and related to the concentration of elements in the coal.

Measurement and evaluation of gamma rays of different energies involves measurement by a scintillation detector and analysis by a pulse-height analyzer that produces an energy spectrum. Gamma ray spectra from coal show broad base-lines due to various interference effects and peaks that are characteristic and proportional to the individual elements in the material. This method offers the possibility of analyzing large volumes of material--say hundreds of pounds of coal--and since these processes are relatively instantaneous they would be applicable to continuous analysis of tonnage quantities of moving coal.

The mineral matter content of coal, commonly referred to as ash, includes many compounds. Alumina, silica, iron oxide, lime and magnesia generally comprise over 95 percent of coal ash.<sup>1/</sup> If each of the elements in these compounds, Si, Al, Fe, Ca, and Mg, could be measured by the nuclear method described above, a summation of these measurements should give the ash content. To explore this possibility, basic measurements were made in a physical arrangement that could be adapted to tonnage flow of coal.

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Experimental Equipment and Procedure. Apparatus used in this work is shown in figure 1. It consisted of a neutron source, a heavy metal attenuator, and a scintillation crystal detector surrounded by a cylinder of coal. The neutron sources were mixtures of plutonium and beryllium or of americium and beryllium which produce a broad spectrum of neutron energies ranging from 1 to 10 Mev by the reaction of alpha particles with the beryllium target. Radioisotope sources were chosen as neutron sources because they are relatively inexpensive and because they provide long-term unattended operation at constant flux. Commonly, 50-million neutrons per second are produced by a few curies of americium in a 1-inch-diameter steel capsule. The neutron source may be shielded by an inch of lead to reduce the gamma flux without adversely affecting the neutron output. The scintillation crystal detector is shielded from the beam of neutrons by placing it in the shadow of a cone-shaped tungsten attenuator, 8 to 12 inches in length. The detector, consisting of a 3- by 3-inch sodium iodide crystal and photomultiplier tube, is shielded from thermal neutrons by a boron shield surrounding the crystal.

About 50 pounds of coal is placed around the detector in the direct path of the neutrons. Fast neutrons from the source penetrate the coal producing inelastic and capture gamma rays, some of which interact with the detector crystal. Electrical pulses produced by the detector are proportional to the energy of the incident gamma photon. The latter are then measured by the multichannel analyzer and sorted by amplitude to represent the gamma ray spectrum.

Results. Gamma ray spectra were obtained that showed small peaks from the elements in the coal, plus a large amount of interference from unwanted radiation measured by the detector. Figure 2 shows the various interference components together with an unresolved spectrum from high-ash coal. The unresolved spectrum, or upper curve, includes background interference and is that part of the total spectrum between 0.6 and 2.5 Mev. It was obtained after coal, neutron source, and detector were kept in place for 90 minutes to approach equilibrium with respect to neutron activation. Curve A shows several small peaks and two prominent peaks corresponding to the silicon, aluminum, and hydrogen in the coal. Most of the spectrum is due to three major interference components which were estimated by several procedures and are indicated by curves A, B, and C. Curve A shows interference from neutrons transmitted through the attenuator directly into the crystal, curve B represents activation of the crystal detector by transmitted and scattered neutrons, while curve C is only the crystal activation from transmitted neutrons.

Although several improvements were made subsequently, including alteration of the composition and shape of the attenuator, better detector shielding, and different configuration of the coal samples--interrelated interference effects--it was found difficult to remove all of the interference and still retain a physical configuration adaptable to tonnage flows of coal. Improvements in one part of the spectrum often decreased the sensitivity of measurement in another part. Ultimately, however, interference effects were identified and reduced until a spectra was obtained having characteristic peaks that were reasonably sharp and consistent.

Typical results are shown in figure 3, a 50-minute measurement of 40 pounds of bituminous coal containing 9.4 percent combined silicon, aluminum, and iron. Prominent gamma peaks in the spectrum are from carbon, hydrogen, and the major ash constituents--silicon, aluminum, and iron. The 4.43 Mev carbon peak and its two pair peaks being at relatively high energy required special instrument adjustment to obtain good resolution, as shown by the insert to figure 3. The 2.22 Mev hydrogen peak contains some contribution from sulfur at 2.24 Mev, which is difficult to separate; the 1.78 Mev peak of silicon contains some contribution of the 1.77 Mev aluminum peak; and the 1.01 Mev peak of aluminum includes a few counts of the 1.04 Mev silicon peak. Iron appears prominently at 0.84 Mev and adds a small peak at 1.24 Mev, where aluminum

and silicon also contribute small peaks. A small and inconsistent peak appears at about 0.77 Mev, probably from calcium. There should be a fairly sharp peak from magnesium at 1.37 Mev but this particular coal sample did not contain enough magnesium to show it. This spectrum actually is only a part of the total spectrum which extends to 10 Mev. Some indication of an oxygen triple peak was found at 5.12, 5.63, and 6.14 Mev, and amplification gave several other peaks representing unidentified elements.

Sensitivity of Measurement. To estimate the sensitivity of measurement, tests were made on 15-pound samples of Pittsburgh-seam coal containing 3.3-percent and 21-percent ash. The 21-percent ash sample contained 5.8-percent Si, 2.3-percent Al, and 1.3-percent Fe--oxides of these elements comprising 90.4 percent of the ash in this sample. The 3.3-percent-ash sample contained 0.6-percent silica, 0.5-percent Al, and 0.39-percent Fe--oxides of these elements accounting for 90.2 percent of the ash.

Spectra of these two coals are shown in figure 4 at two amplifications. The difference between the 1.78 Mev silicon-aluminum peaks in the two spectra is readily apparent. There are 160,800 total counts under this peak for the low-ash coal and 177,300 total corresponding counts for the 21-percent ash coal, a difference of 16,500 counts. Coals containing 8.1- and 1.19-percent silicon plus aluminum respectively, gave a difference of  $16,500 \pm 581$  counts, a sensitivity of 0.02 percent. Thus a change of 0.02 percent in silicon and aluminum theoretically was detected, although this was not entirely true because silicon and aluminum were assumed to contribute equally on a weight basis to the 1.78-Mev peak. With normal coal samples this estimate probably would not be off by more than a factor of two, so it is reasonable to expect that a change of 0.1 percent in silicon or aluminum content of the coal could be detected.

Subsequently, the actual sensitivity of this method was determined in static tests with coal. Samples of anthracite containing 6.2-, 7.0-, and 7.3-percent ash, respectively, were used in these tests. The small differences in the percentage of ash in these samples approximate the combined errors of sampling and analysis. Spectra obtained from the three samples, using 50-minute counting periods for each, are shown in figure 5. The shift in the 2.22-Mev hydrogen peak indicates a channel drift from instrument instability, so the peaks are blunter than under ideal conditions. A small but definite difference is apparent between the 7.3- and 7.0-percent-ash samples. Iron, aluminum, and silica peaks for the 6.2-percent-ash coal, however, are virtually identical to the coal containing 7-percent ash. (The slight differences are indicated by the dotted line.) The reason for this was shown subsequently to be due to a slight difference in degree of activation of the crystal detector and thus the amount of interference. Although the results cannot yet be considered as completely reliable, they indicate that differences can be obtained between coals differing less than 1 percent in ash content. Minor inconsistencies in the data are just as likely to have been caused by errors in sampling and chemical analysis as by errors in the nuclear method.

Conclusion. In static measurements, the concentration of several of the elements in coal was determined with varying degrees of accuracy by means of gamma rays produced by neutrons from radioisotope sources. Spectra peaks were readily identifiable for carbon, hydrogen, silicon, aluminum, iron; smaller peaks were found for other elements in coal.

The results were promising enough to warrant extension of the work to a pilot-scale system for measurement of the ash content of coal flowing at rates of 1 to 20 tons per hour. Indications are that the concentrations of ash in moving coal can be measured continuously within 1 percent, and perhaps within 1/2 percent.

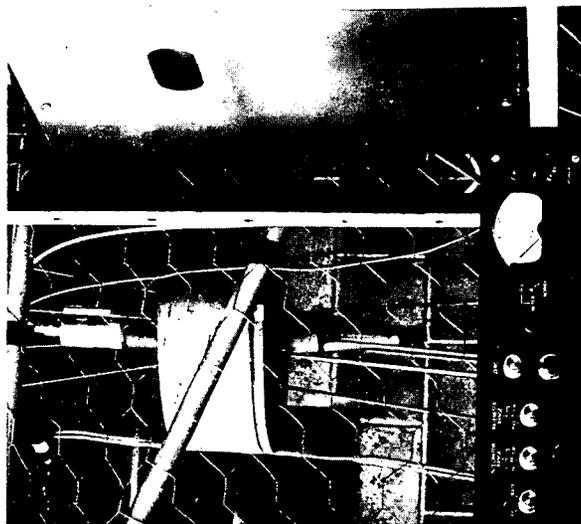
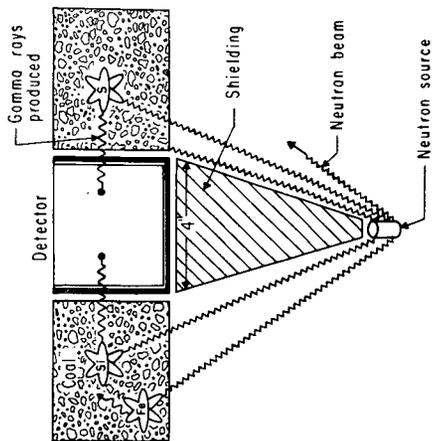
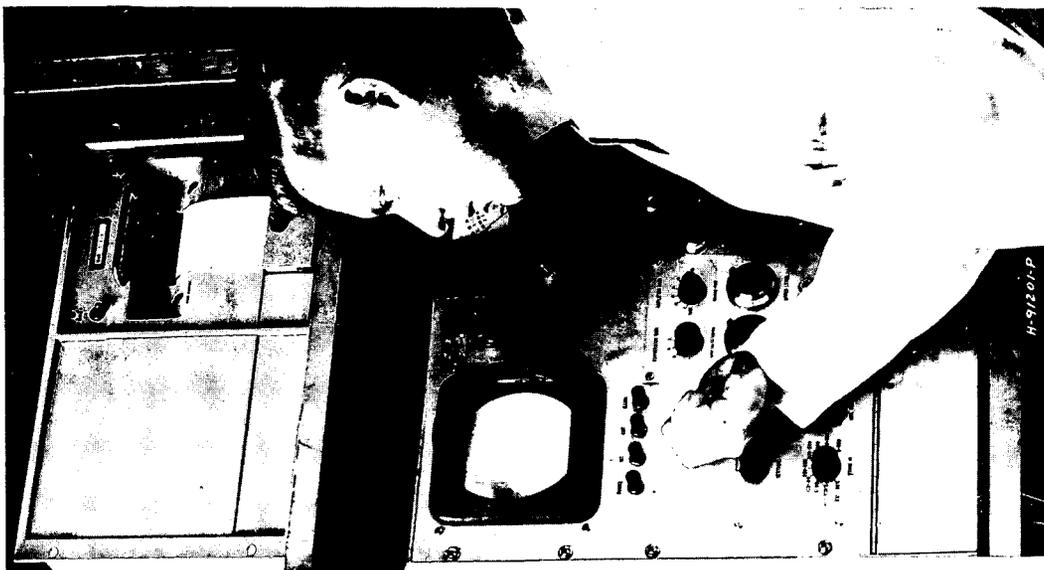


FIGURE 1—Apparatus for Measuring the Gamma Rays Produced by Neutrons Reacting With Ash Elements in Coal

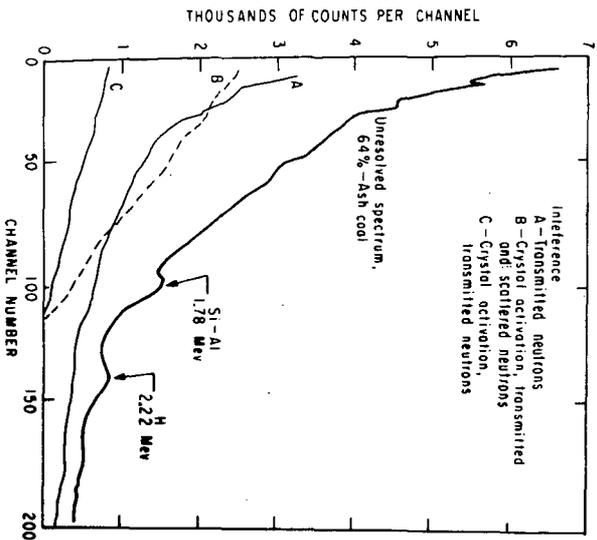


FIGURE 2—Gamma Ray Spectra and Interference Components of High—Ash Coal

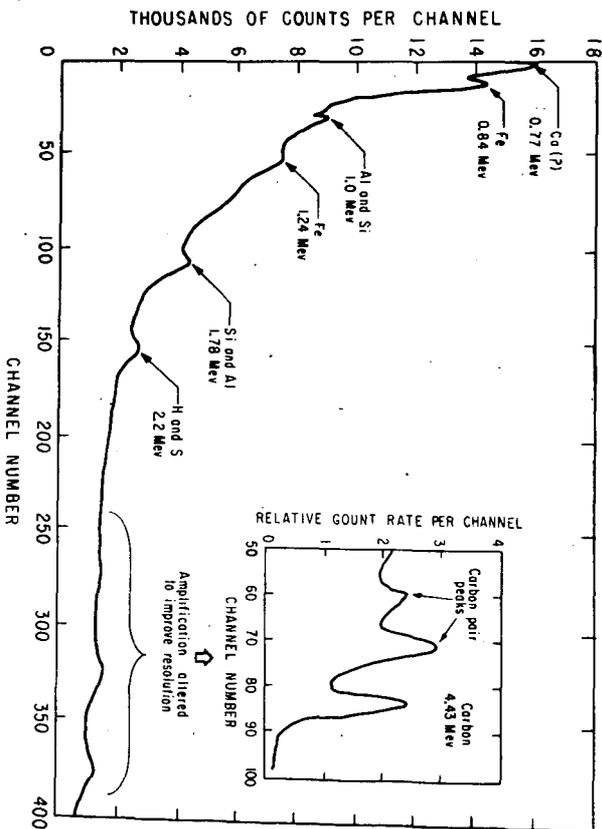


FIGURE 3—Gamma Ray Spectra from Coal Containing 23% Ash

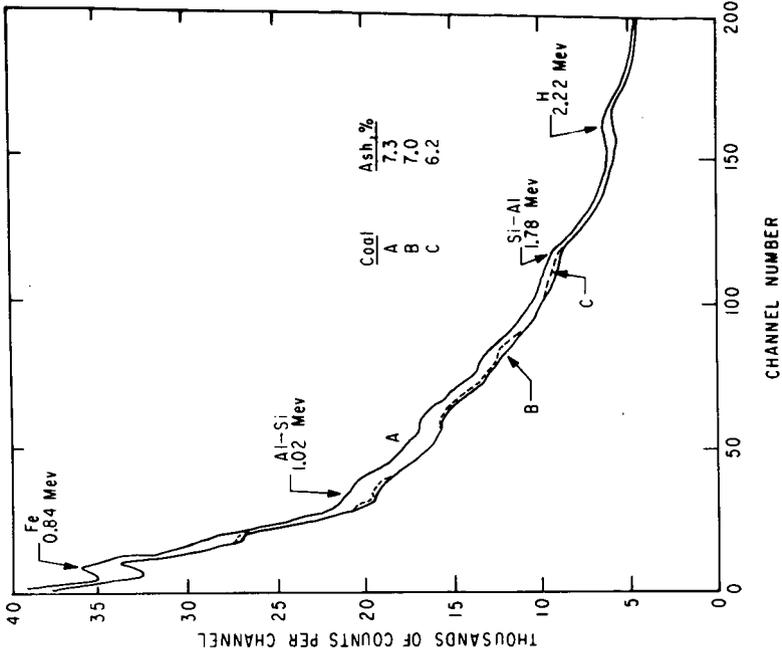


FIGURE 5 — Gamma Ray Spectro from Three Anthracite Samples

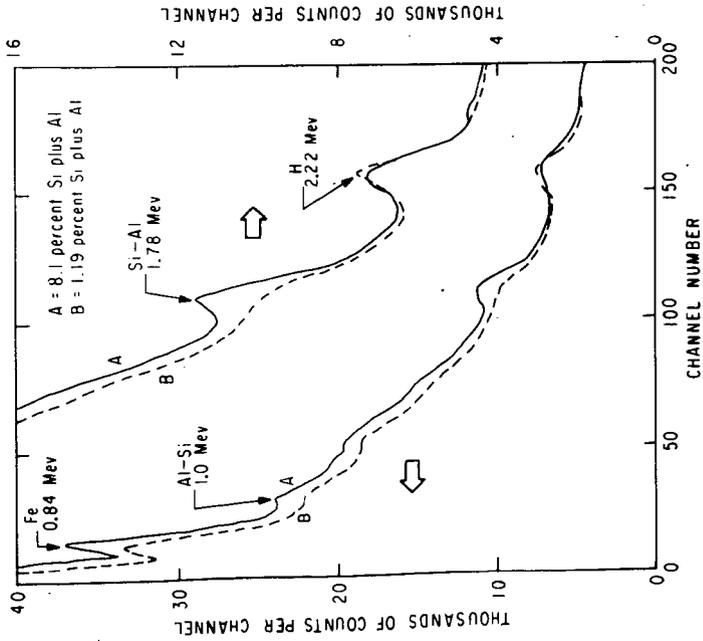


FIGURE 4 — Gamma Ray Spectro of High- and Low-Ash Coals

## A NEW APPROACH TO THE PRODUCTION OF FLY ASH BASED STRUCTURAL MATERIALS

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Fly ash, a major by-product from the combustion of pulverized coal, has become a problem of substantial proportion at coal burning power plants. The distribution and magnitude of fly ash production in 1962 is illustrated in Figure 1. During that year fly ash production exceeded 12 million tons. It is estimated that by 1980 approximately 28 million tons of fly ash will be produced annually.<sup>1</sup> At present, the major portion of fly ash is dumped in a slurry in rapidly dwindling storage areas while in other locations fly ash may be sold for as much as \$4.00 per ton or carried away at a cost to the power plant of as much as \$2.00 per ton. Major commercial uses for fly ash today are soil stabilization in which the fly ash is utilized as a grout; asphalt paving mixes in which the fly ash acts as a filler; and light-weight aggregate in which the fly ash is pelletized and then sintered.<sup>2</sup>

As one facet of many involved in a United States Department of Interior, Office of Coal Research contract for the investigation of coal-associated minerals, work was initiated by West Virginia University's Coal Research Bureau with the objective of utilizing fly ash to reduce the disposal problem at power plants attributable to the lack of adequate markets. The use of a mixture of fly ash and sodium silicate as a means to make structures is documented in previous literature.<sup>3</sup> Early attempts to process a fly ash-sodium silicate mix experienced difficulty because the material set too rapidly for handling, produced blocks with cracks, and gave low compressive strengths. Because of these difficulties a new approach to the production of fly ash-based structural materials was sought which involves in part the use of sand in the fly ash-sodium silicate mix as an agent to increase workability and to decrease fissuring by providing a path for moisture release. Therefore, the objective of this paper is to introduce a method for using a combination of low cost materials in conjunction with modest forming pressures to produce a superior structural product which may be technically feasible. The initial phases of this work have given encouraging results and the United States Department of Interior has recently filed a patent application covering this disclosure.

MATERIALS AND EXPERIMENTAL WORK

The origin and screen analysis of fly ash used in these experiments are given in Table 1. Chemical composition of fly ash is provided in Table 2. Admixed Ohio River sand used to reduce fissuring was screened to pass 28 mesh size. Sodium silicate solution was obtained from the Philadelphia Quartz Company, the composition and properties of which are given in Table 3.

All specimens were formed by use of a floating die into the shape of a brick as a means to facilitate testing. Forming as well as breaking pressures were measured with a Baldwin Model Universal Testing Machine. For firing at high temperatures, a Hoskins electric muffle furnace was used.

In the preparation of test specimens, sand and fly ash in proper proportions were dry mixed for five minutes to insure homogeneity. This mixture was then transferred to vessels where sodium silicate was added in small increments and mixed to form pellets. A quantity of pellets was chosen which would yield a desired brick thickness when formed in the die at a specified pressure.

Generally 400 gram pellet charges were used in order to produce a 2 X 4 X 1-5/8 inch brick test specimen formed at 1000 pounds per square inch pressure (p.s.i.). Cored test specimens were two and later three 1/2 inch diameter holes were adopted as a means to increase surface area, drying, and structural strength.

The newly formed test specimens were subsequently air-dried. Next, compressive breaking strength tests were run on the air-dried bricks or on bricks which were air-dried and then fired at 1100°C.

The final firing temperature of 1100°C was reached through programmed temperature increases over a period of 8 to 10 hours, maintained for four to six hours, and then gradually cooled to room temperature.

Specimens were tested in accordance with the American Society of Testing and Materials (ASTM) method C67-60 entitled "Standard Methods of Sampling and Testing Brick".

### RESULTS AND DISCUSSION

Five basic batch test compositions designated A,B,C,D and E and their proportions are given in Table 4. Fly ash weight percentage ranges from 64.7 to 84.5; sand from 0.0 to 22.7 and sodium silicate solution from 9.1 to 15.5.

The foregoing ranges of composition were chosen as a result of exploratory tests, some of which are not listed, which demonstrated that coarser batch compositions with less than approximately 60 percent fly ash resulted in a marked decrease in specimen strength. This observation is indicated in Table 5 with composition E (tests 16 to 24) where breaking strengths were all 4150 p.s.i. or less. On the other hand, finer batch compositions with greater than approximately 72 percent fly ash showed evidence of good breaking strength, 5060 p.s.i. or more, when air-dried for ten days (See tests 13 and 15, Table 5). However, when these batches were fired, uniform moisture release was obstructed because of their fine consistency which caused fissures and decrepitation. Also, fine compositions tended to be initially unworkable and rapidly hardened in thin superficial layers.

It is apparent from these tests that increased compressive breaking strengths resulted for specimens that could be fired. It would appear that the stronger bricks obtained by firing resulted from a solution reaction whereby the specimen underwent partial vitrification.

Results also indicate that for superior breaking strengths above 5100 p.s.i., less binder is required when using the concentrated RU (See tests 1 to 4) in place of the dilute N-type sodium silicate (See tests 5 to 24) solution. Specimens where the RU-type binder was used with modest pressure (1080 p.s.i.) gave peak breaking strengths when fired (See test 1) and superior breaking strengths when unfired (See test 4). Low (790 p.s.i.) forming pressures also yielded superior breaking strengths when fired (See tests 2 and 3).

Within the limited scope of data, variations in breaking strengths due to different fly ash composition did not appear to be significant. Thus, tests 2 and 3 which were prepared under the same conditions using high silica, high alumina Appalachian and lower silica, lower alumina Willow Island Power Plant fly ash yielded essentially the same breaking strengths (5225 versus 5150 p.s.i.).

Because of the exploratory nature of this initial test work, the effect of the number of cores, forming pressure, water addition and bulk density on breaking strengths is not indicated. The correlation of these factors is currently being investigated over more confined ranges of variation than those presented in Table V.

Additional observations indicate that the bulk density of raw fly ash in compositions A, B, and C for varying test conditions were not significantly different, ranging from 104 to 107 pounds per cubic foot. However, when portions of iron were removed from raw fly ash by magnetic separation, the bulk density of composition B decreased to 96 to 98 pounds per cubic foot. This desirable reduction in bulk density is more than likely accompanied by a decrease in breaking strengths. There is also some reason to believe, based on observations made during testing, that the reduction of iron content in fly ash is accompanied by a favorable increase in workability and a decrease in binder consumption.

In order to examine individual requirements other than physical strength, ASTM tests were undertaken on several typical specimens produced from composition B.<sup>4</sup> Five hour boiling tests were conducted and in no instance did the water absorbed exceed 12 percent of the original weight as compared to a permissible 17 percent for optimum grade SW brick and 22 percent for high grade MW brick. The saturation coefficient was found to be 0.79. This compares favorably with an allowable 0.78 and 0.88 in grades SW and MW bricks respectively. Additional firing shrinkage tests were also conducted and in no case did the shrinkage exceed 1/64-inch for a 4-inch test specimen (0.39% shrinkage). This is well within the allowance of standard ASTM specifications. A severe test to determine the durability of the specimens was designed and undertaken. For a period of 24 hours specimens were alternated between a steam chamber (98°C) and a freezer (-25°C) at hourly intervals in order to test their resistance to thermal and moisture decomposition under extreme temperature change. The specimens were tested while still cold and the compressive breaking strengths were found to be comparable to other test specimens of the same compositions which did not undergo the repeated freezing and heating. No such thermal gradient (123°C) exists in nature over a short period of time, the purpose of this test being only to demonstrate the durability of the specimens.

Since fly ash-based structures may, among other applications, find use as a building material some comparisons are in order. The breaking strengths of the fly ash-based test specimens compare favorably with those of common face, clay based, brick. The measured breaking strengths of six specially prepared common face bricks of dimensions similar to those of the fly ash-based test specimens exceeded approximately 2600 p.s.i. Thus, seventy-five percent of the fired and 58 percent of the unfired fly ash-based test specimens exceeded the minimum breaking strength (2600 p.s.i.) of the common faced brick. The favorable similarities in strength are further enhanced when comparing the relative bulk densities. Bulk density of the best grade pressed brick is approximately 150 pounds per cubic foot while common brick has a bulk density of 125 pounds per cubic foot.<sup>5,6</sup> The highest bulk density obtained from the fly ash-based test specimens did not exceed 107 pounds per cubic foot and indications are that by the removal of magnetic material the bulk density can be further reduced to less than one hundred pounds per cubic foot.

In the absence of scale-up information, a complete cost estimate for the production of fly ash-based structural products is not possible at this time. However, on the basis of information obtained from both inquiries and published sources it is possible to estimate the cost of material.<sup>7,8,9,10,11,12,13,14</sup> At typical prices of \$1.00 per ton of fly ash, \$2.29 per ton of screened sand, and \$2.30 per CWT of RU-type sodium silicate, the cost of materials per thousand fly ash-based bricks amounts to \$11.30. This estimate is based on brick bulk densities of 105 pounds per cubic foot for the fired test specimen of composition A. Thus, \$43.70 per thousand bricks is available for costs of amortization, depreciation, labor, plant operating cost and profit from the \$55.00 per thousand realization value obtainable from the sale of bricks. Work is currently directed at obtaining more detailed information on the factors which affect breaking

strength and bulk density of the bricks. Such factors as materials handling, involving the effect of water additions and mixing time; forming pressure; drying time; firing rates; and firing temperature are critical and a series of factorial design experiments are currently underway.

### CONCLUSIONS

Study of test results shows that the fired test specimens of composition A compare well with ASTM specifications on specimens tested. The acquisition cost of fly ash-based structural material is attractive in that cost is low for the material and long distance transportation is not involved (See Figure 1).

No definite conclusions can be drawn concerning the relationship existing between the effect of water addition, forming pressure, drying rate, and bulk density on breaking strength. The relationship between the number of coring holes and drying rate has not been determined.

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Table 1  
Fly Ash and Screen Analysis

Percentage Retained of Given Mesh Size

Source	Designation	80	100	150	200	270	325	-325
Monongahela Power Company Willow Island Station	Willow Island	0.45	0.40	2.11	3.90	7.70	5.00	80.14
Appalachian Power Company Kanawha River Plant Glasgow, West Virginia	Appalachian (Electric)	0.12	0.01	0.07	0.12	0.24	3.02	95.42

Table 2  
Spectrochemical Analysis of Fly Ash (%)

Designation	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O	Carbon
Willow Island	50.1	22.4	18.5	1.3	1.9	1.0	1.0	1.0
Appalachian (Electric)	58.1	27.5	6.0	1.7	1.6	1.0	1.0	2.5

Table 3  
Composition and Properties of Sodium Silicate Solution

Type	Na <sub>2</sub> O:SiO <sub>2</sub>	%Na <sub>2</sub> O	%SiO <sub>2</sub>	%H <sub>2</sub> O	Specific Gravity	°Baume 68°F	Viscosity (Poises-20°C)	lbs/Gal.
N	1:3.22	8.9	28.7	62.4	1.394	41.0	1.8	11.6
RU	1:2.40	13.85	33.2	53.0	1.559	52.0	21.0	13.0

Table 4  
Percentage Composition of Fly Ash-Sand-Sodium Silicate  
Mixtures

<u>Composition</u>	<u>Fly Ash (% Weight)</u>	<u>Sand (% Weight)</u>	<u>Sodium Silicate Solution (% Weight)</u>	<u>Sodium Silicate (Type)</u>
A	68.2	22.7	9.1	RU
B	65.8	21.9	12.3	N
C	84.5	0.0	15.5	N
D	74.0	13.0	13.0	N
E	64.7	21.6	13.7	N

Table 5  
Compilation of Test Results in Order of Decreasing  
Breaking Strengths According to Composition

<u>Test Number</u>	<u>Composition</u>	<u>1 Breaking<sup>2</sup> Strength</u>	<u>Bulk<sup>3</sup> Density</u>	<u>Method of<sup>4</sup> Hardening</u>	<u>Number<sup>5</sup> Cores</u>	<u>Forming<sup>6</sup> Pressures</u>	<u>Water<sup>7</sup> Addition</u>
1.	A-WI	9190	105-107	F	3	1080	60
2.	A-WI	5225		F	3	790	60
3.	A-AP	5150		F	3	790	60
4.	A-WI	5100	105-107	10 AD	3	1080	60
5.	B-WI	6780	104-106	F	2	1080	0
6.	B-WI-IR	5400	96-98	F	3	1080	0
7.	B-WI	5260		F	2	790	0
8.	B-WI-IR	4500		F	3	1080	0
9.	B-WI-IR	3590	96-98	7 AD	3	1080	0
10.	B-WI	3560	104-106	7 AD	2	1080	0
11.	B-AP	3520		7 AD	2	790	0
12.	B-WI-IR	2800		7 AD	3	790	0
13.	C-WI	5570	104-106	10 AD	3	1080	0
14.	C-AP	1500		7 AD	2	790	0
15.	D-AP	5060		10 AD	3	790	0
16.	E-AP	4150		F	3	790	0
17.	E-AP	3200		F	2	790	0
18.	E-WI	2460		F	2	1370	100
19.	E-WI	2440		F	2	1900	100

Table 5 (Continued)

Test Number	Composition <sup>1</sup>	Breaking <sup>2</sup> Strength	Bulk <sup>3</sup> Density	Method of <sup>4</sup> Hardening	Number <sup>5</sup> Cores	Forming <sup>6</sup> Pressures	Water <sup>7</sup> Addition
20.	E-WI	1900		F	2	960	100
21.	E-AP	1525		10 AD	2	530	0
22.	E-AP	1400		21 AD	2	790	0
23.	E-AP	1220		7 AD	2	790	0
24.	E-AP	1260		7 AD	2	530	0

1. WI = Willow Island Power Plant Fly Ash  
AP = Appalachian Power Plant Fly Ash  
IR = Iron reduced by magnetic separation to approximately 5.6 percent.
2. Breaking strength in pounds per square inch (p.s.i.).
3. Bulk density in pounds per cubic foot.
4. F = Fired at 1100°C  
10 AD = Air-dried for ten days  
7 AD = Air dried for seven days
5. Number of evenly spaced holes of 1/2-inch diameter in test specimen.
6. Forming pressure in pounds per square inch (p.s.i.).
7. Water addition in milliliters.

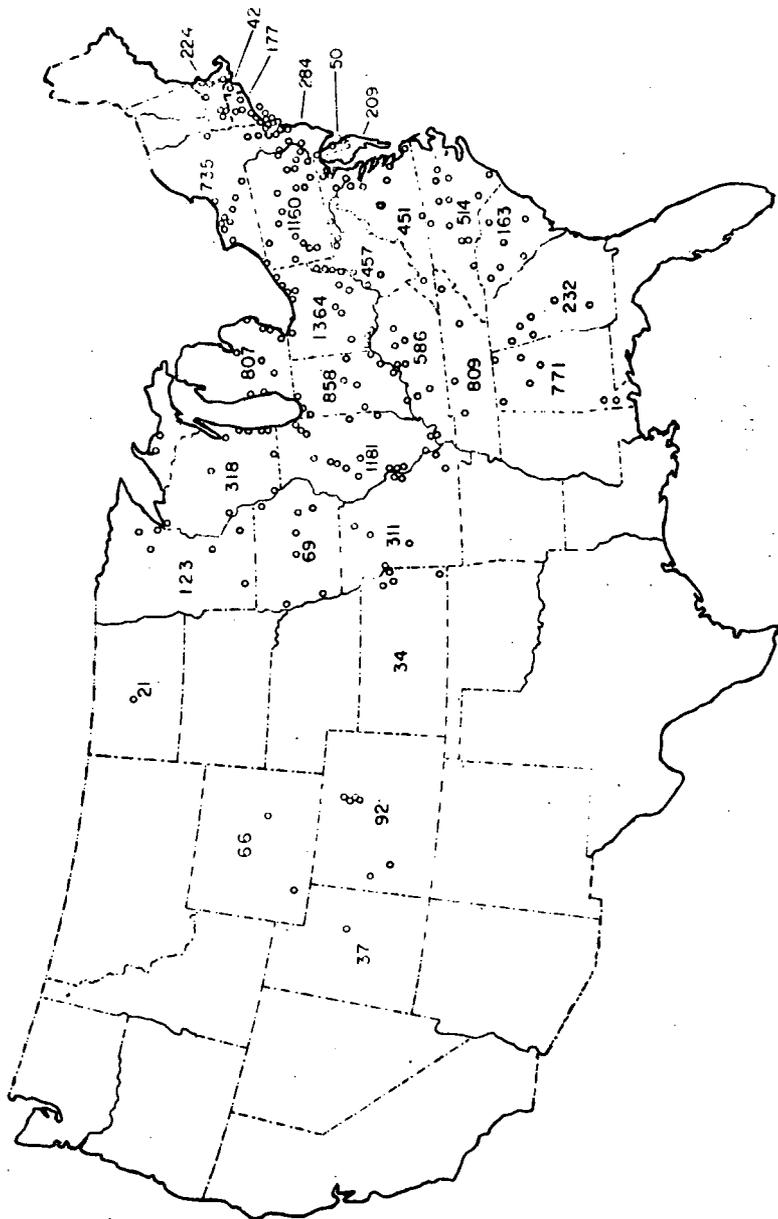


FIGURE 1  
Location of Pulverized Coal Units  
and Fly Ash Production of Individual  
States (in thousands of tons)  
1962