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INORGANIC CONSTITUENTS IN AMERICAN LIGNITES

Technical Report 21

By  
M. E. Morgan  
R. G. Jenkins  
P. L. Walker, Jr.

April 1980  
Date Published

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The Pennsylvania State University  
Coal Research Section  
University Park, Pennsylvania

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**PREPARED FOR  
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**Under Contract No. EX-76-C-01-2030**

**COAL RESEARCH SECTION  
THE PENNSYLVANIA STATE UNIVERSITY  
UNIVERSITY PARK, PENNSYLVANIA 16802**

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## ABSTRACT

Both the discrete mineral phases and the ion-exchangeable inorganic components of lignites from Texas, North Dakota and Montana have been studied. The ion-exchangeable cations and the carboxyl groups with which they are associated were characterized by ion exchange methods utilizing ammonium acetate and barium acetate, respectively. Na, K, Mg, Ca, Sr, and Ba were found to be present in all three coals. It was found that Ca and Mg were the most abundant cations and that 40-60% of the carboxyl groups in the raw coals were exchanged with cations. Also, significant variations in the relative and absolute concentrations of all the cations were observed. The discrete mineral phases in these lignites were studied by semi-quantitative x-ray diffraction and infrared spectroscopy. The importance of the cations in this analysis was shown when the mineralogical analyses of the low temperature ash of the coals with the cations removed and the raw coals were compared. Results show that up to 50% of the low temperature ash of these raw coals can be attributed to the existence of metal cations and that fixation of sulfur, carbon, and oxygen to form sulfates and carbonates is the major reason for this contribution.

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## 1. INTRODUCTION AND STATEMENT OF PROBLEM

This investigation is concerned with the inorganic constituents of American lignites. The majority of the domestic reserves of these low-rank coals are found in the western United States. Large deposits can be found in thick seams which are relatively close to the surface. The mode of occurrence of these seams makes them relatively cheap and easy to mine by standard strip mining techniques.

In the past lignites have not been used to a great extent for a number of reasons. First, the deposits occur in remote regions with no population centers to provide a market for their use. Second, their high water content (up to 50%) and low calorific value make transportation uneconomical. Finally, America has been utilizing oil and gas for the major energy source. These fuels have been relatively cheap and abundant. However, recent events have shown that our oil and gas reserves are diminishing and foreign supplies are not dependable. Thus coal will become an increasingly more important source of energy in the United States.

Utilization of coal has a number of drawbacks. Combustion of coal leads to large amounts of pollution, especially from sulfur. Also, coal is much more difficult to transport than oil or gas. Coal conversion processes offer a way of ridding coal of some of its sulfur and creating a fuel which is easier to transport. Research on conversion processes has shown that lignites display behavior that is markedly different from that of higher-rank coals. This behavior is believed to be greatly influenced by the inorganic constituents present in lignites.

The inorganic material present in any coal can be broken down into three classes:

- 1) Discrete mineral phases (mineral matter) such as sulfates, carbonates, alumino-silicates, and sulfides.
- 2) Organo-metallic compounds such as chelated elements and exchangeable cations.
- 3) Trace elements associated with the discrete mineral phases.

The most significant feature of the inorganic constituents of lignites is the large amount of exchangeable cations. These cations are mainly alkali and alkaline-earth metals associated with carboxyl groups. They are in high concentration in lignites. By contrast, negligible concentrations of carboxyl groups and, hence, cations associated with these groups are found in coals of rank higher than sub-bituminous B. Hydroxyl groups are also found in low-rank coals. These groups are also capable of undergoing exchange reactions, but require a pH of greater than 8.0 to do so. Since coal is formed in somewhat acidic environments, these groups are not believed to undergo exchange in situ.

The cations associated with these carboxyl groups are felt to be responsible for much of the behavior of lignites in coal conversion and utilization processes. United States Bureau of Mines investigators (50) have found that the slagging behavior of low-rank coals in combustion processes is greatly influenced by the amount of ion-exchangeable cations. They investigated methods of removal of these cations.

Walker et. al. (65) and Hippo (27) have found that exchanged cations can act as very active catalysts when lignites are gasified.

The effectiveness of the cation depends on the element in question and the gasification conditions.

Walker et. al. (63,64) have also investigated the formation of inorganic reactor solids when low-rank coals are liquefied. It appears that cations can produce carbonates under liquefaction conditions and that these reactor solids can produce undesired effects by blocking of the reactor and abrasion of pipes and pumps.

Miller (38,39) noted the effect of exchanged cations on the analysis of mineral matter in lignites. He found that the cations present formed sulfates under the conditions present in the low-temperature asher. This resulted in mineral matter values that were higher than those existing in the coal.

Although these researchers have shown cations to be important in the processes described, satisfactory techniques for the analysis of the cations, the carboxyl groups, or the mineral matter in lignites have not been fully developed. These analyses are the main interest of this investigation. The approach to this problem can be stated as follows:

- 1) A literature survey to synthesize the information gained by past studies into a reasonable experimental approach.
- 2) Choice of a sample base which is comprised of lignites from the major lignite regions in the United States.
- 3) Determination of simple, accurate techniques to analyze:
  - a) Amount of carboxyl groups present,
  - b) Amount and type of exchanged cations present,
  - c) Amount of mineral matter and a semi-quantitative analysis of the phases present.

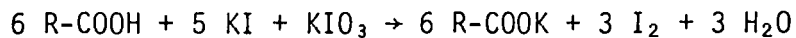
## 2. LITERATURE SURVEY

### 2.1 Carboxyl Group Determination

Carboxyl groups only exist in significant concentrations in coals of low rank. However, these groups have generated considerable interest recently because of the increase in interest in utilization of low-rank coals. There are a number of methods used for the determination of carboxyl groups in organic liquids and mono-acidic systems. Very few of these have been applied to coal successfully. Good reviews of methods to determine carboxyl groups can be found in the literature written by Cronauer and Ruberto (14), Blom et. al. (5), Schafer (57), and van Krevelen (62).

#### 2.1.1 Iodometric Techniques

This method utilizes the irreversible reaction of potassium iodide with carboxyl groups in the following manner:



The iodine produced is taken up by the thiosulfate present in the solution. The excess thiosulfate present is then titrated and the amount of iodine present determined. The method was investigated by Blom et. al. (5) on a suite of coals, including: a brown coal, vitrinites from one American and two European lignites, and vitrinites from six European bituminous coals. He studied both raw and oxidized samples of these coals. Blom et. al. found that the results for the iodometric technique were irreproducible and higher than the values found by other methods.

### 2.1.2 Methylation Techniques

This method utilizes methylation of the acid groups with methanol-HCl, dimethyl sulfate, or diazomethane. Both phenolic and carboxylic acid groups are methylated yielding methoxyls and esters, respectively. The carboxyl contents can be calculated from the difference of the methoxy content, as determined by the Ziesel method (42), before and after saponification of the esters (hydrolysis in a base). The Ziesel method utilizes treatment with boiling hydroiodic acid which causes the release of  $\text{CH}_3\text{I}$  from methylated phenolic and carboxylic acid groups. Blom et. al. (5) studied this method on the same suite of coals that was previously mentioned and found that the reaction time for methylation was too long.

### 2.1.3 Decarboxylation Techniques

Decarboxylation of carboxyl groups by refluxing in quinoline was first proposed by Hubacher (28). He studied the use of several catalysts, and finally chose cupric carbonate. After studies on a large number of organic acids, he concluded that about 80% of the carboxyl groups were decomposed to yield  $\text{CO}_2$ . Blom et. al. (5) also studied this reaction for use in coal analysis. He quantified the amount of undecomposed groups by exchange with calcium acetate. He concluded that about 80% of the carboxyl groups decomposed. Both workers state that the reproducibility is fair.

### 2.1.4 Non-Aqueous Titration Techniques

This method has gained the attention of researchers for use as a standard carboxyl group determination method. It was first developed by Moss et. al. (43) to determine the amount of phenols in pure organic compounds. The material to be analyzed is potentiometrically



titrated in ethylenediamine by sodium aminoethoxide. Ethylenediamine is used as a solvent to enhance the acidic strength of these weak acids. A titration of a multi-acidic complex yields several inflection points. From these points the contribution of each acid can be determined.

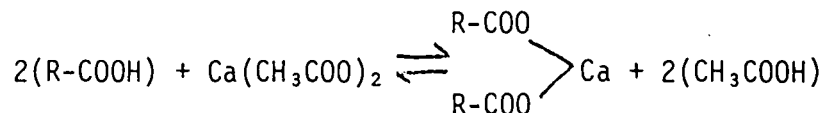
Katz and Glen (32) applied the technique to the titration of phenols in coal hydrogenation oils. Maher et. al. (8,34,35) investigated the use of this method in the determination of carboxyl groups in coal. One of the principle advantages for its use on coal is that ethylenediamine causes swelling. Thus, the carboxyl groups are believed to be more accessible to the titration agent.

When coals are titrated by this technique two or three inflection points are found. Carboxyl groups are thought to be responsible for the first one or two points, while phenols are responsible for the final point. One of the problems with this technique is that the inflection points are not always sharp. Moss et. al. showed an increase in the acidity of phenols when the basic ethylenediamine is used. This results in a much sharper endpoint for phenols. In coal or multi-acidic complexes the phenol endpoint is sharp but the carboxyl endpoint is less distinct. Therefore, total acidities can be measured more accurately than component acidities.

Maher and Schafer (35) found that the carboxyl contents determined with non-aqueous titration were always higher than those found by exchange with barium acetate. They infer from these results that some of the phenols may be titrating with the carboxyl groups due to the effect of the basic solvent ethylenediamine.

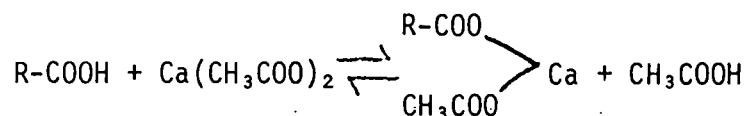
### 2.1.5 Ion Exchange Techniques

This is the most widely used method for carboxyl group determination. The method involves mixing the coal with a weak base such as calcium acetate. The calcium exchanges with the carboxyl groups in the following manner:



The released acetic acid can then be titrated to determine the quantity of carboxyl groups exchanged.

Blom et. al. (5) investigated this technique. They exchanged the coal with calcium acetate by stirring at room temperature for 15 hours. They discuss the point that the reaction mechanism proposed above is valid only if the correct steric conditions prevail. If not the following reaction occurs:



However, titration detects the hydrogen released from the exchange as acetic acid. Therefore, the carboxyl groups exchanged would be determined correctly if either or both of the reactions are correct.

Brooks et. al. (7-10) experimented with Australian brown coals. They exchanged carboxyl groups by shaking the acid treated coals in 3N sodium acetate for 16-20 hours at room temperature. The excess acetic acid was back titrated with barium hydroxide. The acid treatment involved refluxing of the coal under nitrogen in 5N HCl. This step was taken to avoid errors due to ion exchange with the clays present and to maintain all the carboxyl groups in the acid

form, thereby facilitating complete exchange. They also performed the exchange with barium and calcium acetate and found good agreement.

Lynch and Durie (33) modified the procedure by refluxing the coal in sodium acetate for 4 hours. However, use of sodium acetate has drawbacks. Low-rank coals are somewhat soluble in the reagent. This makes titrations with indicators very difficult. Potentiometric titration does not alleviate this problem because of the strong buffering action of sodium acetate.

One serious oversight in the early work was that no attempt was made at achieving precise pH control. Schafer (56-58) investigated the dependence of the amount of acid groups exchanged on pH. He found an inflection point in the curve at a pH of about 8.25-8.30 and attributed this to the point at which all carboxyls but no phenols exchange. A pH of 13 was found to be necessary for complete exchange of phenols. However, he cites work that shows ortho-diphenols may exchange at a pH of about 8.0.

Schafer also investigated the problem of whether a divalent cation exchanges with one or two carboxyl groups. This was accomplished by determination of the amount of barium put on the coal when exchanging with barium acetate. To study the amount of barium exchanged, he back-exchanged the coal by boiling the barium-loaded coal in perchloric acid for 20 minutes. The barium released was determined by atomic adsorption spectrometry. He found that, within the limits of experimental error, two carboxyl groups exchange with one barium ion.

The technique Schafer finally describes involves refluxing the acid treated coal in 1N barium acetate (pH of 8.25-8.30) under

nitrogen for four 4-hour periods. After each period, the solution is titrated back to the original pH of 8.25-8.30 with sodium hydroxide. The exchanged coal is then washed with a sodium acetate solution at a pH of 8.25-8.30 under nitrogen and back-exchanged by boiling in 0.2N perchloric acid for 20 minutes. The use of nitrogen is necessary to prevent oxidation of the coal under the alkaline conditions used.  $\text{CO}_2$  can combine with  $\text{Ba}^{++}$  to form  $\text{BaCO}_3$ . This will lead to a value for the carboxyl group content that is too high when considering the amount of sodium hydroxide used to titrate the acetic acid released.

One of the main criticisms of this technique is the possible lack of accessibility of the carboxyl groups to the exchange medium. Brooks and Sternhell (9) found that in the particle size range of 75 to 20,000 microns the rate of exchange was substantially faster for the small particles; however the carboxyl group content was independent of particle size if they allowed 16-19 hours for exchange to occur. If the groups are inaccessible, one would predict a decrease in the groups exchanged with an increase in the particle size because of the opening of closed pores in the small size ranges. Furthermore, infrared spectroscopy studies by Brooks et. al. (7,9) and Lynch and Durie (33) provided evidence which shows no acidic carboxyl groups present after exchange with various metal acetates. De et. al. (15) investigated the adsorption of HCl by the coal during the demineralization step. They found that a small amount of HCl was tenaciously held by the acid treated coal. They refluxed the acid treated coal in  $\text{CO}_2$ -free distilled water for 1 hour. After this treatment, no effect of adsorbed HCl was seen in the carboxyl group determination.

## 2.2 Ion-Exchangeable Cation Determination

Many of the inorganic elements in coal are believed to be associated with the organic fraction. These elements are divided into two main classes. Some are thought to be exchanged on the carboxyl groups found in low-rank coals. These elements are mainly the alkali and alkaline-earth metals. The other class mainly involves transition elements which are bound more strongly than the previous class in coordination or chelate complexes.

One method of inferring organic association utilizes float-sink separation of coal (25,38,68). In this method the fractions of coal are separated according to specific gravity by use of a series of liquids of known densities. The concept is that mineral matter will accumulate in the heaviest fraction while the organic matter will concentrate in the lighter fractions. If an element is associated with the mineral matter, it will be more concentrated in the fraction with the greatest amount of mineral matter. Alternatively, if an element is associated with the organic fraction, it will concentrate according to the amount of organic matter in the fraction.

There have been a number of studies on the chelate complexes in coal (25,38,68). These elements are extractable with dilute HCl. Miller (38) found that Be, Cr, Ni, Sc, V, Y, Yb, and Zr were associated with coal in this manner.

Ion exchangeable elements are the main subject of this section. In the past, most of the work on ion exchange has been performed on inorganic materials such as clays (1), soils (28), and zeolites (1,6). Although these systems are very different than coal, the studies have revealed much about the ion exchange process.

In general, the ion exchange behavior of any system is a function of the following (6): cation size and charge, anion, temperature, concentration, and solvent. The result of the effect of cation size and charge is an affinity series for any given set of elements. In cations of the same valence, the cation size or cation charge density is the controlling factor (26). The charge density is defined by the charge to volume ratio. In the case of aqueous solutions the volume that is important is the hydrated volume. The hydrated ion radii and charge densities for the cations studied in this work are listed in Table 1. The resultant affinity series are:  $K^+ > Na^+$  for the alkali metals, and  $Ba^{++} > Ca^{++}$ ,  $Sr^{++} > Mg^{++}$  for the alkaline-earth metals. When comparing cations of different valence, the general rule is that the cation of higher valence is preferred. The reasons for this are explained by the Donnan potential (26), which is the term used to describe the effect of the forces imposed on the system by the charges created in the exchange medium and the coal. Briefly, a negative charge builds up in the coal and a positive charge builds up in the solution. This is due to the fact that both cations and anions diffuse into the coal, but only cations diffuse out. Therefore there is an electrostatic force created which tends to repel anions and attract cations to the coal. This force is proportional to the charge of the cation. The concentration of the cation also plays an important role. If the concentration of a weakly held cation, such as  $Na^+$ , is large enough, it can replace a strongly held cation, such as  $Ba^{++}$ . However, the equilibrium nature of ion exchange dictates that a portion of the cations will remain on the solid if there are some cations in solution. Therefore, to achieve complete or almost complete

TABLE 1  
RADII AND CHARGE DENSITIES OF SOME HYDRATED CATIONS (41)

Element	Radius (nm)	Charge Density $\times 10^{24}$ (coulombs/nm <sup>3</sup> )
Na <sup>+</sup>	0.22	3.7
K <sup>+</sup>	0.18	7.1
Mg <sup>++</sup>	0.30	3.0
Ca <sup>++</sup>	0.27	3.8
Sr <sup>++</sup>	0.27	3.8
Ba <sup>++</sup>	0.25	5.0

exchange of, for instance  $Ba^{++}$  by  $Na^+$ , one would have to use a series of exchanges with fresh solution in which no  $Ba^{++}$  is present. The anion is important in the strength with which it holds the cation.

Characterization of the exchangeable cations in peats was attempted by Bel'kevich and Chirtova (3). They studied  $Na^+$ ,  $K^+$ ,  $Ca^{++}$ , and  $Ba^{++}$  by extraction with ammonium chloride. They recognized the importance of pH on exchange in these materials. In a study of the acidic groups on peats, they found an almost linear increase in the amount of exchange with pH. They found an inflection point in the range of pH around 7.5-8.5 and concluded that above this range exchange was mainly due to interaction with carboxyl groups, while at lower pH carboxyl groups were the main participants in ion exchange. This and work on organic acids implies that there is a distribution of acidic strengths in these materials. The strongest acids will exchange at low pHs while the weaker ones will require high pHs to remove the hydrogen. Therefore, since the pH of peat bogs has been found to be acidic, only a portion of the acid groups are capable of exchange. Furthermore, the carboxyl groups in coal are known to exchange at pH values as high as 8.5 so that exchange with the groundwater should be exclusively with these groups.

A number of investigators have been concerned with ion exchange in low-rank coals (17, 18, 36, 38, 51). Paulson and Fowkes (51) studied  $Na^+$ ,  $K^+$ ,  $Mg^{++}$ , and  $Ca^{++}$  by extraction with HCl and  $CaCl_2$ . They found the exchange time to decrease with particle size in the range of 6 to 50 mesh. They also showed that the ability of  $CaCl_2$  to exchange with Na was diminished by the presence of Na in the solution.



Durie (17) studied the same cations as Paulson and Fowkes did in two Australian brown coals. He discussed the need for successive washings with fresh solution to ensure complete exchange. He used  $H_2O$ ,  $NaCl$ ,  $MgCl$ , and  $HCl$  for exchange and found that  $Ca$  and  $Mg$  were the dominant cations in the coals studied, with lesser amounts of  $Na$  and very little  $K$ . Durie (18) also pointed out that extraction with dilute  $HCl$  can cause errors due to the solubilization of mineral fractions such as carbonates, sulfates and clays.

Miller (38) undertook the most recent and comprehensive study of ion exchangeable cations in American lignites. He extracted five American lignites with 1N ammonium acetate ( $pH = 7.0 - 7.2$ ) for two 2-hour periods with fresh solution added for the second extraction. Miller studied a large number of elements and concluded that  $Na$ ,  $K$ ,  $Mg$ ,  $Ca$ ,  $Sr$ , and  $Ba$  were present in ion exchange form. Some, such as  $Na$ ,  $Mg$ , and  $Sr$ , were present almost totally in ion exchange form while others were also found in association with the mineral matter. Examples of mineral matter association are:  $K$  with illite and  $Ca$  with calcite and gypsum. Miller also cites the fact that a  $pH$  of  $7.0 - 7.2$  is sufficient for removal of cations in coal since the  $pH$  of the ground water associated with coals is significantly lower. In the coals studied, he found  $Ca^{++}$  and  $Mg^{++}$  to be the major cations and  $Na^+$ ,  $K^+$ ,  $Sr^{++}$ , and  $Ba^{++}$  to be present to lesser extents.

It should be evident that much work is needed in the characterization of exchangeable cations in coal. Most studies were not concerned with the major factors affecting the exchange. The most neglected factor is the need for successive washings. Also few researchers have addressed the possibility of ion exchange with clays

and other inorganic ion-exchangers or the possibility of solubilizing minerals by treatment with the reagents used for the exchange.

### 2.3 Mineral Matter Determinations

There are two topics discussed in this section; separation of mineral matter and semi-quantitative analysis of the phases present. Since separation of the mineral matter is usually necessary for mineralogical analyses, this is a natural coupling. Good reviews of these subjects can be found in the literature by Jenkins and Walker (30), Walker et. al. (63), Selvig (59), and O'Gorman (45).

#### 2.3.1 Separation of Mineral Matter

For analysis of the mineral matter in coal, it is imperative that a good separation technique is used. Classically, coal minerals have been concentrated by gravity separation. This technique is similar to coal preparation processes and depends on the mineral having a higher specific gravity than the coal organic matter. One drawback is that whereas it produces a mineral enriched portion, total separation is never attained. For many analyses an enriched portion is not good enough. Gravity separation can also result in mineral segregation.

Ashing is another procedure that has been used for mineral separation. A standard ASTM procedure calls for oxidation of the organic matter at 750°C in 1 atmosphere of air. It has been found that under these conditions many of the minerals are altered: pyrite is oxidized, clays lose water, and carbonates and sulfates form oxides. The only major mineral unchanged is quartz.

Brown et. al. (11,12) developed a low-temperature technique which oxidizes coal in air at 370°C. They were somewhat successful in gaining unaltered samples except for decomposition of ferrous carbonate and

dehydration of clays. The main problem is that the technique takes on the order of 200 hours for completion.

A fairly recent technique which has gained widespread use is low temperature ashing in a low pressure oxygen plasma. In this instrument low pressure oxygen (1-2 torr) is passed through a high energy electromagnetic field produced by a radio frequency oscillator. These conditions produce an oxygen plasma which is described by Gleit (23), the principal developer of the instrument, as a mixture of atomic and ionic species, as well as electronically and vibrationally excited states. Under these conditions the organic matter is oxidized at a relatively low temperature of 100-250°C (21,24,46).

Gluskoter (24,54), Miller (38,39) and Frazer and Belcher (21) studied the use of low temperature ashing for mineral separation. They found the tool to be relatively rapid and reproducible for obtaining samples of mineral matter from coal. Miller found that some pyrite samples oxidize, and sulfates can form from the interaction of calcite with oxides of sulfur present in the LTA. However, he concluded that adjustment of the operating conditions can minimize this behavior.

All of the above oxidation techniques share special problems when analyzing low-rank coals. The cations present have been found to fix sulfur and form sulfates. Miller found that the lower the radio frequency power the more sulfur is fixed. Karr et. al. (31) found that alkali nitrates can also be formed in this process when ashing low-rank coals. Miller suggested treatment of the coal with ammonium acetate to remove the cations and prevent the problem.

### 2.3.2 Qualitative and Semi-Quantitative Mineralogical Analyses

The following section investigates the major analytical methods for coal mineralogical analyses. The importance of this analysis has led to numerous techniques, however, only the most viable ones will be discussed in detail. Qualitative analysis entails the identification of the major minerals in the coal or LTA residue. Quantitative analysis entails measurement of the amount of each mineral present. A list of the minerals which are most commonly identified in qualitative analyses of American coals can be seen in Table 2.

#### 2.3.2.1 X-Ray Diffraction

X-ray diffraction can be used as both a qualitative and a quantitative tool for coal mineralogical analyses. The technique identifies the minerals by their characteristic lattice spacings. When dealing with minerals from coal, a number of problems occur. The most prominent is mineral orientation caused by the platy nature of some minerals, especially clays. Since powder diffraction techniques depend on random orientation, the preferred orientation of platy minerals removes quantitative correlations between peak intensity and concentration of particular minerals. Rao and Gluskoter (54) describe a mounting technique which can give reproducible results. This technique is called cavity mount; and although it does not eliminate orientation, it allows for a reproducible amount of orientation. Once mounted the sample is irradiated with x-rays and scanned to find the characteristic peaks. For qualitative analyses, the goniometer can be set for the relatively fast speed of  $2-4^{\circ}$  (20) per minute. The diffraction patterns can then be compared to standard tables for mineral identification.

TABLE 2

## COMMONLY OCCURRING MINERALS IN COALS

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Clays:	Kaolinite, Montmorillonite, Illite, Mixed-Layer Clays (Alumino-Silicates)
Sulfides:	Pyrite or Marcasite ( $\text{FeS}_2$ ), Sphalerite ( $\text{ZnS}$ )
Carbonates:	Calcite ( $\text{CaCO}_3$ ), Siderite ( $\text{FeCO}_3$ ), Ankerite ( $\text{CaFe}(\text{CO}_3)_2$ ), Ankerite ( $\text{CaFe}(\text{CO}_3)_2$ ), Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ )
Oxides:	Quartz ( $\text{SiO}_2$ ), Rutile ( $\text{TiO}_2$ )
Sulfates:	Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )

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The analysis of clays other than kaolinite presents special problems. One reason is that the term "illite" or "montmorillonite" refers to a group of clays. All the clays within a group show gross chemical similarities but have varying composition because they can exchange cations. This exchange (or intercalation between layer planes) causes swelling. Because of the irregular nature of the exchange, these clays exhibit a range of interlayer spacings and, hence, a range of x-ray diffraction peaks, making identification and quantification of amounts present difficult.

Quantitative analysis by diffraction is difficult because of overlapping peaks, orientation, and minerals with varying degrees of crystallinity. Also, obtaining a representative sample of the coal mineral matter is very difficult. The concentration of coal minerals can vary greatly in coal seams both vertically and horizontally. Grinding and sieving can result in mineral segregation. Therefore, care must be taken to obtain a representative sample, and the analysis must be performed a number of times to ensure accuracy. However, calcite, quartz and pyrite can be analyzed in a semi-quantitative manner if the above mentioned problems are taken into account. These are the best minerals for semi-quantitative work because problems with overlapping peaks, orientation and degree of crystallinity can be minimized. Rao and Gluskoter (54) and O'Gorman (45) describe a technique to do this, which utilizes calcium fluoride as an internal standard. Therefore, the peak heights or areas of the minerals are compared to those of calcium fluoride, removing the necessity of relating absolute peak intensities to concentration. Utilizing this technique, calibration curves are prepared by comparing the ratios

of x-ray diffraction peaks for minerals in a calibration mix to their known concentrations. The calibration mixes consist of pyrite, calcite, quartz, a clay mixture and calcium fluoride. Calcium fluoride is then mixed with the unknown, and ratios of the same x-ray diffraction peaks can be compared to the ratios in the calibration mixes.

The method is described in more detail elsewhere (45,54); it does give reproducible results. However, in addition to the problems listed earlier, problems exist with the stability of the x-ray equipment, obtaining a good solid-solid mixture, and obtaining a mineral standard which is crystallographically the same (that is, crystalline size and density of defects) as the mineral in coal. Because of these problems, x-ray analyses are only accurate to  $\pm 10\%$  at best.

#### 2.3.2.2 Infrared Spectroscopy

In this section the use of both dispersive infrared spectroscopy and Fourier transform infrared spectroscopy will be discussed. The use of dispersive infrared spectroscopy (IR) for analysis of mineral matter from coal has been shown to be an effective analytical tool. Tuddenham and Lyons (61) and Estep et. al. (19) investigated the use of IR for quantitative analysis of minerals in coal. They both used pressed alkali halide pellets for suspension of the sample in the IR beam. The matrix elements used in their work are: KBr in the range 2000 to 605  $\text{cm}^{-1}$ , and CsI in the range 650 to 200  $\text{cm}^{-1}$ . They are chosen for their transparency to IR radiation in the specific ranges cited. Quantitative analysis is carried out by creating a number of calibration mixtures to be compared to the unknown. O'Gorman (45,46) utilized the baseline method to calculate the absorption of specific bands with good results.

The main drawback to this technique is overlapping peaks. Estep et. al. (19) and Painter et. al. (48) discuss this problem at length. Kaolinite, in particular, absorbs IR radiation strongly, and its bands overlap those of the other clays. As in x-ray diffraction, obtaining a mineral standard that is representative of the minerals in coal is a problem. Also, most workers have found that the absorbance of a mineral is dependent on particle size (19,48,61). Estep et. al. (19) show that the absorbance increases with decreases in particle size until the mean particle diameter falls between 4-13 microns.

Fourier transform infrared spectroscopy (FTIR) has recently emerged as a very powerful tool for qualitative and quantitative analysis of mineral matter in coal. Theoretically the technique offers several advantages over dispersive IR. The technique and its advantages have been discussed in a number of publications (2,48,49).

The main advantage to FTIR is that all of the IR spectrum which is transmitted through the sample is utilized. This is done by creating an interferogram with a set of fixed and moving mirrors. The transmitted interferogram can then be analyzed by using a Fourier transform. This step is easily performed with the aid of a computer. In contrast to this, dispersive IR restricts the amount of radiation that passes to the detector with prisms and slits. Thus, FTIR utilizes 100% of the radiation while dispersive IR normally utilizes less than 0.2%. The use of a computer for data analysis adds other advantages. It can add successive scans and thereby increase the signal-to-noise ratio. Also, information can be stored in digital form for easy reference and manipulation. Probably the greatest improvement lies in the ability to subtract peaks. When the peaks of the minerals in



the sample are subtracted from the spectra, peaks of minerals that were previously obscured are revealed. Painter et. al. (48,49) have investigated this particular point.

The main drawbacks to this technique are obtaining a representative mineral standard, the effect of particle size, and mineral matter sampling problems. FTIR shares these problems with dispersive IR, but it alleviates the problem of overlapping peaks and allows for an increase in signal-to-noise ratio. It appears that once this technique is more fully investigated it will become the preferred method for mineralogical analyses.

#### 2.3.2.3 Elemental Analysis

If the elemental composition of the low temperature ash is known and if the phases present are known, it is possible to estimate the quantity of each mineral phase present. This is done by assigning various amounts of the element detected to minerals on the basis of the elemental composition of the mineral.

Two approaches to this method merit attention. Medlin et. al. (36) reported a method of elemental analysis of the ash which involves fusing the sample in lithium borate and dissolving the solid in nitric acid. The elements are then detected by emission spectrometry.

Pollack (53) utilizes quantitative x-ray fluorescence of the low temperature ash. By this method he can quantify the amount of Si, Al, Ca, Fe, and K.

The main problem with these techniques lies in the quantitative assignment of elements to minerals by a formula which is deduced from the composition of pure mineral standards. It is well known that most minerals have varying amounts of impurities which are dependent on

the origin of the mineral. This problem is particularly common in clays. However, this technique can be used to supplement or check other techniques, or when an estimate is needed. Using this approach, the Mineral Constitution Laboratory at The Pennsylvania State University estimates the amount of clays other than kaolinite in coals (60). As was discussed earlier, quantification of clays other than kaolinite using x-ray diffraction or IR is difficult.

### 3. EXPERIMENTAL

#### 3.1 Lignites Investigated

Three lignites were investigated in this study. The main criterion for their selection was that they comprise a sample base representative of the lignite deposits in the United States. Therefore, lignites were chosen from Montana, North Dakota, and Texas. These are the states with the largest amounts of lignite reserves.

Tables 3-5 display the ultimate analyses, proximate analyses and maceral analyses for the coals studied. Typical of low-rank coals these lignites have low carbon contents, low sulfur contents, and high oxygen contents. The proximate analyses display the high volatile matter contents of these lignites. The maceral analyses illustrate that the coals are typical in that the main component is vitrinite. All three lignites are channel samples.

#### 3.2 Procedures

##### 3.2.1 Carboxyl Group Determination

The determination of carboxyl group content was performed by ion exchange with barium acetate. The procedure is modeled after that of Schafer (56-58). The first step of the determination is demineralization of the coal. This serves two functions. It puts all the carboxyl groups in the acid form which facilitates complete exchange, and it allows for monitoring of the quantity of exchange by observing the change in pH. Secondly, it removes minerals which can undergo ion exchange, such as clays.

The demineralization technique is adapted from that of Bishop and Ward (4), and is as follows:

TABLE 3  
 ULTIMATE ANALYSES OF LIGNITES STUDIED

PSOC Coal #	246	623	833
State	North Dakota	Texas	Montana
Seam	Hagel	Darco	Fort Union
wt % Dry Basis			
Ash	9.7	16.6	13.0
C	64.9	60.9	61.0
H	4.4	4.5	4.5
N	1.4	1.1	0.9
Total S	0.6	1.1	0.5
O (by difference)	19.8	15.8	20.1

TABLE 4  
PROXIMATE ANALYSES OF LIGNITES STUDIED

	wt % Dry Basis		
	PSOC 246	PSOC 623	PSOC 833
Ash	9.7	16.6	13.0
Volatile Matter	44.7	44.6	40.9
Fixed Carbon	45.6	38.8	46.1

TABLE 5  
MACERAL ANALYSES OF LIGNITES STUDIED

Maceral Group	vol % DMMF Basis		
	PSOC 246	PSOC 623	PSOC 833
Vitrinites	78.7	80.9	74.9
Liptinites	4.1	2.3	2.0
Inertinites	17.2	16.4	23.1

- 1) Six grams of coal, ground under nitrogen to pass 200 mesh, are mixed with 40 ml of 5N HCl in a plastic beaker (125 ml.) This solution is then agitated at 55-60°C for 1 hr on a magnetic stirrer, hot plate apparatus.
- 2) The coal is then filtered and mixed with 40 ml of full strength HF. This mixture is also stirred at 55-60°C for 1 hr.
- 3) The coal is filtered and mixed with full strength HCl for a third 1-hr treatment at 55-60°C.
- 4) The coal is filtered and repeatedly washed with distilled water.
- 5) The coal is transferred to a 1000 ml round bottom flask equipped with a refluxing apparatus. 500 ml of distilled, CO<sub>2</sub> free water is added and the mixture is refluxed for 2 hr.
- 6) The coal is filtered and washed until no chlorine can be detected upon the addition of silver nitrate.

Steps 5 and 6 were added in accordance with the findings of De et. al. (15). As discussed in the literature survey, these steps are necessary to remove any HCl remaining following the demineralization step. Adsorption of HF does not appear to be a problem. Bishop and Ward (4) showed that the adsorbed acid on demineralized coals was almost entirely HCl.

The coal is then stored in a vacuum desiccator until the carboxyl content is determined. The use of a vacuum desiccator results in the drying of the coal and prevents oxidation. The carboxyl group determination is conducted as follows:

- 1) One-half gram of demineralized coal is transferred to a 500 ml round bottom flask equipped with a refluxing apparatus. The flask is also equipped with a fritted cylinder to bubble  $N_2$  through the mixture. The  $N_2$  is purified by passing it through a liquid  $N_2$  trap to remove  $CO_2$  and a copper turnings trap to remove  $O_2$ .
- 2) The flask is then flushed with  $N_2$ .
- 3) Using a graduated cylinder, 250 ml of 1N barium acetate is added. The pH of the solution being adjusted to 8.25-8.30 by the addition of barium hydroxide.
- 4) The solution is then refluxed for 4 hr.
- 5) The solution is cooled to room temperature and the pH is determined and recorded.
- 6) Barium hydroxide of a known normality (about 0.05) is added until the pH is the same as the starting pH. (The normality of the barium hydroxide must be checked periodically since it tends to react with  $CO_2$  and precipitate barium carbonate.)
- 7) Refluxing and titration are continued for two additional 4-hr periods.
- 8) The amount of carboxyl groups exchanged is calculated from the total number of moles consumed in restoring the pH.

Carboxyl groups are reported on a dry mineral matter free basis (DMMF). To accomplish this, a moisture and residual mineral matter determination was carried out on another sample of the coal. The moisture was determined by heating to  $110^\circ C$  for 1 hr, and the residual

mineral matter was determined in the low temperature ash, as described later in this section.

A check on the determination of carboxyl group content is performed using the back exchange of barium on the exchanged coal.

The procedure is as follows:

- 1) The exchanged coal is washed into a Buchner filter with a minimal amount of 1N sodium acetate (pH of about 8.25-8.30). The use of this wash solution is important since all the excess reagent must be removed without hydrolysis or exchange of the barium on the coal. The filtered coal is washed twice with 25 ml of the wash solution.
- 2) The exchanged and washed coal is then transferred to a plastic beaker with distilled water to which 50 ml of 0.2N perchloric acid is added.
- 3) The solution is stirred and boiled for 20 min.
- 4) The coal is then filtered and washed with distilled water.
- 5) The extract is then diluted to 100 ml and analyzed via emission spectrometry for the concentration of barium.

### 3.2.2 Exchangeable Cation Determination

The technique for the determination of exchangeable cations employs exchange with 1N ammonium acetate at a pH of about 7.0-7.2.

The technique is as follows:

- 1) One-half gram of as-received coal, ground to pass 200 mesh, is mixed with 50 ml of 1N ammonium acetate in a plastic beaker (125 ml).
- 2) The slurry is stirred at room temperature for a period of 3 hr with a magnetic stirring apparatus.



- 3) The slurry is transferred to a Buchner funnel, filtered, and washed repeatedly with a total of 25 ml of ammonium acetate.
- 4) The filtrate is then transferred to a 100 ml volumetric flask to which 5 ml of glacial acetic acid is added for acidification. The solution is then further diluted with 1N ammonium acetate to 100 ml.
- 5) The flasks are shaken and the solution stored in plastic bottles until analyzed.
- 6) The coal from the filter is transferred back to the plastic beaker with 1N ammonium acetate and diluted to 50 ml.
- 7) The procedure of steps 2 through 6 is repeated for four more 3-hr periods, followed by stirring overnight, and one additional 3-hr period in the morning.

In order to report the analysis on a DMMF basis both the mineral matter and the moisture content are determined. The moisture content is determined as described earlier, and the mineral matter is determined on a sample of the ammonium acetate treated coal.

The extracts are analyzed for  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Sr}^+$ , and  $\text{Ba}^{++}$ . The particular unit used is a SMI Spectrospan III, Plasma Emission Spectrometer. This unit is very convenient since all six elements can be analyzed simultaneously. One thousand ppm standards of each element were prepared as outlined in the literature (52). These standards are then diluted with 1N ammonium acetate and glacial acetic acid (in the proportions used earlier) to make 100 ppm multi-component standards of all six elements. For analysis of the cations, 10, 8, 6, 4, 2 and 1 ppm standards are usually sufficient; but some

samples with lower concentrations of cations require further dilution.

The main problem with emission spectrometry is that the ratio of spectrometer output to element concentration tends to vary with time. The technique employed in this analysis is structured to minimize this problem, and is as follows:

- 1) The multi-component standards are analyzed in the order of lowest to highest concentration.
- 2) The unknowns are then analyzed in the order which they were collected.
- 3) The unknowns are analyzed in reverse order.
- 4) The standards are analyzed in reverse order.
- 5) The duplicate determinations are then averaged.
- 6) Calibration curves are drawn by relating standard concentration to spectrometer output.
- 7) The concentration of the elements in the unknown sample can be determined by relating the spectrometer output of the unknowns to the calibration curves.

### 3.2.3 Mineral Matter Determination

#### 3.2.3.1 Mineral Separation

The first step in the mineral matter analysis is the separation of the organic and inorganic material. This is accomplished in a low temperature asher (LTA). The particular unit used is a double chamber unit manufactured by the International Plasma Corporation (PM-248).

Both the raw and the ammonium acetate treated coals were ashed in the LTA. The procedure is adapted from that of Miller (38,39) and is as follows:

- 1) One to 1.5 g of coal, ground to minus 200 mesh, is dried at 110°C for 1 hr in weighing bottles.
- 2) The bottles are capped, cooled in a desiccator, and weighed to determine the moisture content.
- 3) The dry coal is transferred to a Petri dish for use in the LTA. The sample density should not exceed 30 mg/cm<sup>2</sup>.
- 4) Ashing should take place at 50 watts of power per channel and a pressure of 0.13-0.26 kPa of O<sub>2</sub>.
- 5) Samples are stirred three to four times in the first 16-hr period and then oxidation is allowed to proceed overnight.
- 6) Following the initial 24-hr period, the samples are stirred and weighed every 4 to 6 hr. In order to minimize the weight gain due to moisture adsorption the sample is cooled in the chamber to room temperature under vacuum and quickly weighed.
- 7) The sample weight should be checked three to four times a day during ashing until a constant weight is attained. The total ashing time depends on the coal used. Raw lignites require 4-5 days, while ammonium acetate washed lignites require 1-2 days.

#### 3.2.3.2 Qualitative Mineralogical Analysis

Qualitative analyses were accomplished by three techniques. X-ray diffraction is probably the most useful technique. The cavity

mount method was used. The mount consists of an aluminum holder with a rectangular cavity in it. A glass slide is taped to one side and the LTA residue is put in and leveled. Another glass slide is then taped over the open side of the cavity. The whole mount is then carefully turned over and the first slide removed. The sample can then be put in the diffractometer and scanned at a speed of  $2-4^{\circ}$  ( $2\theta$ )/min. The diffraction peaks can then be compared to standard tables for mineral identification. The particular unit used was a Rigaku Geigerflex x-ray diffractometer (#2173D).

Infrared spectroscopy is also used to identify some of the minerals present. A Perkin-Elmer 283B infrared spectrometer was used for this work. The sample preparation technique utilized a double press method in a vacuum die. One mg of sample is mixed with 200 mg of KBr in an agate mortar and pestle. The mixture is then placed in the die and the system is evacuated for 3 min. Excavation is done to remove most of the water that may be in the sample. The mixture is then compressed at 10 tons/in<sup>2</sup> for 5 min. Evacuation and compression are then repeated. The resultant pellet is then scanned using radiation from 4000 to 200 cm<sup>-1</sup> for mineral identification. For qualitative purposes a total scan time of 6 min is sufficient.

Optical microscopy was also used for mineral identification. This is a particularly useful tool since it provides information on the coal without the difficulties or alterations imposed by the LTA. This work was performed by the Coal Research Section at The Pennsylvania State University.

### 3.2.3.3 Semi-Quantitative Mineralogical Analysis

This analysis was performed on both the raw and ammonium acetate treated coal LTA residues. A combination of techniques was used. Calcite, pyrite and quartz were analyzed by x-ray diffraction. Kaolinite and anhydrite were analyzed by infrared spectroscopy. A rational or normative analysis was used to estimate the amounts of other clays, that is, the total amount of clays other than kaolinite. The remainder of the inorganic constituents were quantified by difference.

For semi-quantitative determination of the mineral composition by x-ray diffraction, the cavity mount was used, as described earlier. The method used for quantification employs an internal standard. In accordance with the technique of Rao and Gluskoter (54), calcium fluoride is added to the sample in the proportion 0.2 g calcium fluoride to 1 g of sample. The mixing took place in a Spex mixer/mill for a total time of 30 min in all cases.

In order to utilize x-ray diffraction it is necessary to first analyze a set of calibration mixes of known composition. Therefore, mixtures of calcite, quartz, pyrite, a clay mixture (1:1 kaolinite: montmorillonite), and calcium fluoride were prepared. The mineral standards were all ground to minus 325 mesh before mixing. These standards were all obtained from Wards Natural Science Establishment, and the origins of the minerals can be seen in Table 6. The composition of the calibration curves are given in Table 7. After the calibration mixtures are prepared, the quantity of the mineral present can be related to the peak area of the mineral in question. This is done on a relative basis. The number compared to the mineral

TABLE 6  
SOURCES OF THE MINERAL STANDARDS

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Calcite:	Chichuhua, Mexico
Kaolinite:	Mesa Alta, New Mexico, U.S.A.
Montmorillonite:	Chambers, Arizona, U.S.A.
Pyrite:	Sonora, Mexico
Quartz:	Minas Gerais, Brazil

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TABLE 7  
COMPOSITION OF X-RAY CALIBRATION MIXTURES

Mixture Number	wt % of Mineral				
	Calcite	Quartz	Pyrite	Clays	Fluorite
1	0.00	0.40	0.40	0.20	0.20
2	0.04	0.36	0.36	0.24	0.20
3	0.08	0.32	0.32	0.28	0.20
4	0.12	0.28	0.28	0.32	0.20
5	0.16	0.24	0.24	0.36	0.20
6	0.20	0.20	0.20	0.40	0.20
7	0.24	0.16	0.16	0.44	0.20
8	0.28	0.12	0.12	0.48	0.20
9	0.32	0.08	0.08	0.52	0.20
10	0.36	0.04	0.04	0.56	0.20
11	0.40	0.00	0.00	0.60	0.20

composition is the ratio of the peak area of the mineral in question to that of the internal standard. The peaks used in this analysis are ( $\text{CuK}\alpha$ ): quartz,  $26.7^\circ$ ; calcium flouride,  $28.3^\circ$ ; calcite,  $29.4^\circ$ ; and pyrite,  $33.0^\circ$  ( $2\theta$ ). The areas of the peaks are analyzed with the aid of a PDP-11 computer in conjunction with the diffractometer. The program used can be summarized as follows:

- 1) A step scan is run over the region  $25-32^\circ$  ( $2\theta$ ). In this scan the goniometer stops and records counts at angles in  $0.1^\circ$  ( $2\theta$ ) intervals. The readings last for 2 sec at each point.
- 2) The step scan is analyzed to find the angles at which only the background counts are being recorded.
- 3) The integrating function is then used. The goniometer scans each peak over an angular range that was determined by the step scan. This is done at  $0.1^\circ$  ( $2\theta$ ) intervals with the readings lasting 6 sec at each angle. The computer then determines the contribution of background at each angle and subtracts it from the total number of counts. This procedure is repeated three times to increase the accuracy. Finally, the total number of counts for the peak is computed by adding the contribution of each angle.

The ratio of the area of the peak in question to that of fluorite is then computed. By using all of the calibration mixes, a calibration curve can be created.

The unknowns are then analyzed by adding fluorite in the same proportion and manner that was used for the known samples and computing the peak area ratios in the same manner as was done for the calibration



mixes. These ratios can then be compared to the calibration curves created by analyzing the mixtures with known composition.

In the case of the raw coal LTA residue, additional treatment is necessary. This stems from the existence of bassinite in the LTA residue. Bassinite is a dehydrated form of gypsum. Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is the sulfate form found in the raw coal, but bassinite ( $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ ) and anhydrite ( $\text{CaSO}_4$ ) are the only form of this mineral found in LTA residues. The  $29.8^\circ$  peak of bassinite overlaps the  $29.4^\circ$  peak of calcite. When the LTA residue is heated to  $500^\circ\text{C}$  in flowing  $\text{N}_2$  for 2 hr, any bassinite present is dehydrated to anhydrite. Anhydrite has no peak around  $29^\circ$ , and thus the percentage calcite can be calculated.

Kaolinite and anhydrite are analyzed by infrared spectroscopy. The pellets are prepared as discussed earlier. Calibration curves are created by preparing a number of pellets with varying amounts of pure kaolinite or anhydrite. Infrared spectroscopy is not prone to the matrix problems of x-ray diffraction which necessitate the preparation of calibration mixtures with a number of minerals in them. All calibration pellets were prepared with one component. The absorbance of the  $670 \text{ cm}^{-1}$  band for anhydrite and the  $910 \text{ cm}^{-1}$  band for kaolinite were measured for known concentrations to create a calibration curve. The absorbance was calculated in the manner described by O'Gorman and Walker (45) and demonstrated in Figure 1. Using this method, absorbance is equated to  $\log(I/I_0)$ , where  $I$  is the transmitted radiation and  $I_0$  is the incident radiation.

The LTA residues contained both bassinite and anhydrite. Both minerals have a peak at  $670 \text{ cm}^{-1}$ , so they had to be converted to one

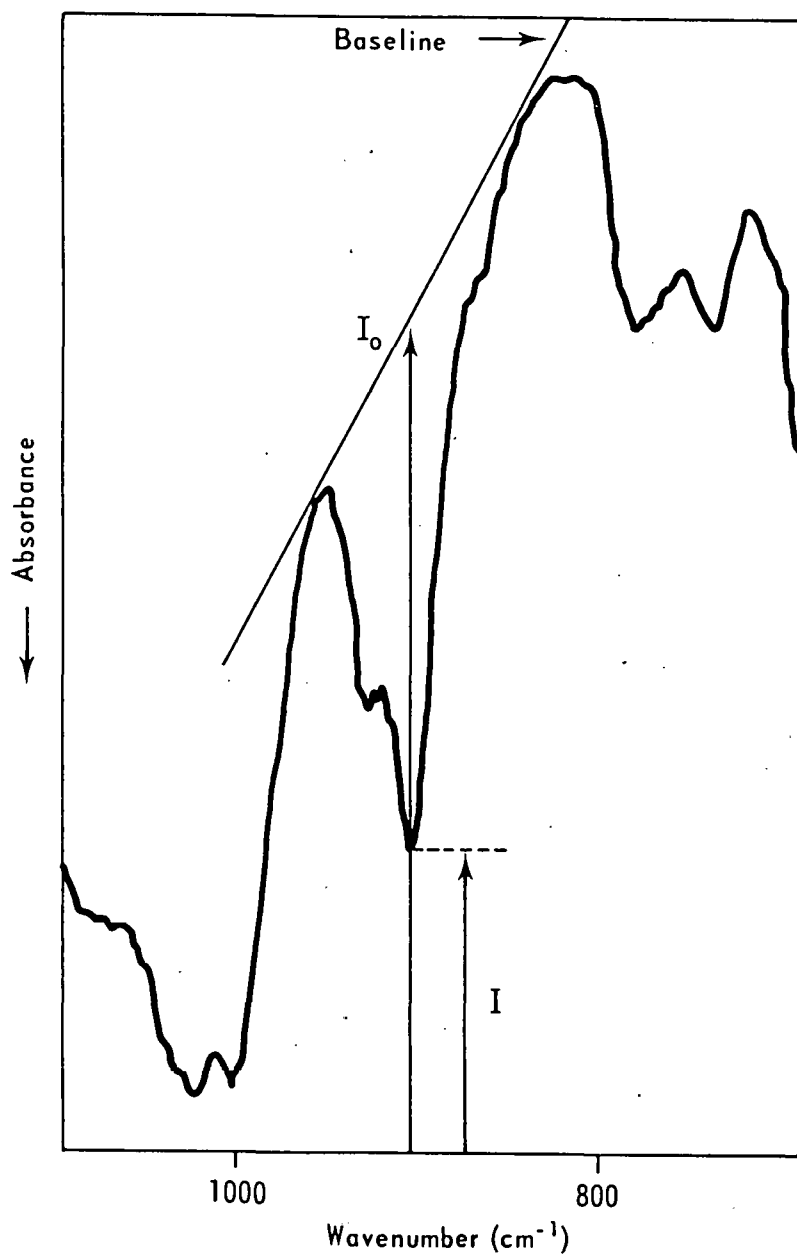


Figure 1. BASELINE METHOD FOR THE DETERMINATION OF ABSORBANCE USING INFRARED SPECTROSCOPY (45)

form of the sulfate mineral. Bassinite was dehydrated to anhydrite as discussed earlier. However heating to 500°C destroys the clay structure and the kaolinite bands disappear. Therefore, infrared scans of the LTA residue are used to quantify the amount of kaolinite; and analysis of the 500°C treated sample was performed to quantify the amount of anhydrite.

As discussed earlier the amount of total clays other than kaolinite was determined by a rational or normative method. To perform this analysis one must have a measure of the concentration of Si and Al and a semi-quantitative analysis of the amounts of kaolinite and quartz in the LTA residue. When this information is gained, the amount of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  involved with the quartz and kaolinite in the LTA residue can first be calculated. This quantity can then be subtracted from the total amount of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the LTA residue. Then a reasonable figure for the percentage of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the other clays can be used to calculate the amount of other clays. The figure used in this study is based on information gained by Deer and Howie (16). Their work shows that clays such as illite, montmorillonite, and mixed layer clays are composed of approximately 25%  $\text{Al}_2\text{O}_3$  and 50%  $\text{SiO}_2$ , by weight.

## 4. RESULTS AND DISCUSSION

### 4.1 Carboxyl Group Determination

As stated in the experimental section, carboxyl contents were determined by ion exchange. The exchange procedure is adapted from that of Schafer (56-58). He utilizes barium acetate as the exchange medium. As can be seen in Table 1, barium is a good choice because it is divalent, has a large charge density and a small hydrated radius. The large charge density combined with it being a divalent cation results in the high affinity of barium. The small hydrated radius assures greater access to the micropore system of coal. The use of barium is also important in the back exchange, since a weak ion such as sodium can be used in the wash solution with a minimal amount of exchange. The small degree of exchange is a function of the affinity difference of the two cations, and the fact that the wash time was always less than 1 min.

Another important factor in the technique utilized for exchange is the use of a nitrogen atmosphere at all possible times. Grinding, refluxing, and washing are performed under nitrogen to prevent oxidation of the coal. Coal is particularly susceptible to oxidation during these times. Schafer has shown that oxidation of the coal in boiling barium acetate is significant. This will result in the release of carbon dioxide and the formation of barium carbonate which will cause errors in the results. Also during grinding, sufficiently high temperatures can be attained concurrent with the production of nascent carbon sites, to result in the formation of carboxyl groups on the coal if oxygen is present.

Demineralization of the coal prior to exchange is a third important facet of the technique. First, demineralization opens up the pore structure of the coal, thereby enhancing the rate of ion exchange. Second, acid treatment is necessary in order to attain the correct carboxyl group values by titration since hydrogen ions are necessary to create acetic acid and thereby a characterizable change in pH. Finally, demineralization removes minerals such as clays, which could undergo ion exchange reactions.

Table 8 shows the results of the carboxyl group analysis. Each value, calculated from the titration results, represents the average of six to eight runs, with the value of one standard deviation also given. Also shown are the results of the carboxyl group determination via the amount of barium released in the back exchange. The values shown are for selected runs and are calculated using the assumption that two carboxyl groups are exchanged with each divalent barium ion. All determinations were performed on the minus 200 mesh fraction of the lignites. The amounts of oxygen and carbon in the carboxyl groups are significant when compared to the total carbon and oxygen (by difference) values. The carboxyl groups account for 47% (North Dakota), 35% (Texas), and 42% (Montana) of the total oxygen present; while the carbon in the carboxyl groups ranges from 7.6% (North Dakota), 3.4% (Texas), and 5.2% (Montana).

The standard deviation values shown are within the range which suggests that the technique is quite precise. Furthermore, the close agreement of the values by titration and barium released displays the accuracy of the method. The assumption that two carboxyl groups are exchanged with each barium ion is shown to be a valid concept.

TABLE 8  
CARBOXYL CONTENTS OF LIGNITES

PSOC Coal #	Carboxyl Contents mequiv/g dmmf	
	Titration	Ba <sup>++</sup> Released
246	3.13 ± 0.05	3.24
623	2.11 ± 0.08	2.22
833	3.00 ± 0.07	3.07

Amounts of carboxyl groups reported here are in good agreement with values found in the literature. Schafer (57) studied a suite of low-rank coals from the United States, Australia, Thailand and Hungary. He found a range of 1.0 to 3.4 mequiv/g of carboxyl groups on his samples. Of the samples he studied, he found a Texas lignite to contain 2.3 mequiv/g and a North Dakota lignite to contain 2.2 mequiv/g. Cronauer and Ruberto (14) found an American lignite (origin not reported) to contain 1.1 mequiv/g of carboxyl groups.

Schafer suggests that there is an optimum number of 4-hour refluxes (56-58). That is, one reflux is not sufficient for complete exchange, but excessive refluxes will lead to physical adsorption of barium acetate and barium hydroxide. The reason for the use of three 4-hour refluxes in this study is displayed in Table 9 where the cumulative amount of carboxyl groups exchanged versus time is shown. Each value is the average of six to eight runs. In each case 5% or less of the total exchange occurred in the final 4-hour period. The choice of three 4-hour runs has a few advantages. First, the determination can be completed in one day. This is preferable, since allowing the solution to stand overnight will lead to greater adsorption of barium acetate and barium hydroxide. Second, the choice of three 4-hour refluxes instead of two or four seems justified from the release versus time behavior. Finally, the amount of adsorption seems to be minimal for this technique, since the titration and barium released values agree well. If there were a large amount of adsorption, there would be a greater difference in the results. The disagreement would be predicted to be in the direction of higher carboxyl contents by the titration method. One would predict that the adsorbed barium

TABLE 9  
AMOUNT OF CARBOXYL GROUPS EXCHANGED VERSUS TIME

Cumulative Time (hr)	Carboxyl Group Content mequiv/g dmmf			
	PSOC 246 < 200 mesh	PSOC 623 < 200 mesh	PSOC 623 < 80 mesh	PSOC 833 < 200 mesh
4	2.51	1.75	1.76	2.52
8	2.95	2.02	2.04	2.91
12	3.13	2.11	2.11	3.00



acetate and barium hydroxide would be removed in the wash, so the barium released values would not be sensitive to adsorption. However, adsorption does affect the titration values, since the adsorption of the basic barium acetate and barium hydroxide onto the coal would result in a lowering of the pH of the exchange medium that was not due to ion exchange with carboxyl groups.

Another factor investigated was the effect of particle size. The carboxyl content of PSOC 623 was determined for both the minus 80 and minus 200 mesh samples. As seen in Table 9, there was no significant difference in the results. Because of this it can be concluded that essentially all of the pore surface area containing carboxyl groups is available to hydrated barium ions for exchange. If a significant portion were not available, due to closed porosity, a reduction in particle size would be expected to lead to an increase in the number of carboxyl groups detected. The lack of particle size dependence is in agreement with previous work as described in the literature section.

#### 4.2 Exchangeable Cation Determination

As described earlier, the exchangeable cation determination was carried out by exchange with 1N ammonium acetate, followed by detection with emission spectrometry. To determine the concentration of a particular ion, it is necessary to produce calibration curves by running a number of solutions of known concentration. A typical calibration curve is given in Figure 2, where spectrometer output versus concentration is plotted. A least squares analysis was used to plot the data and determine the concentration of the unknown. In each case a correlation coefficient of 0.99 or greater was found.

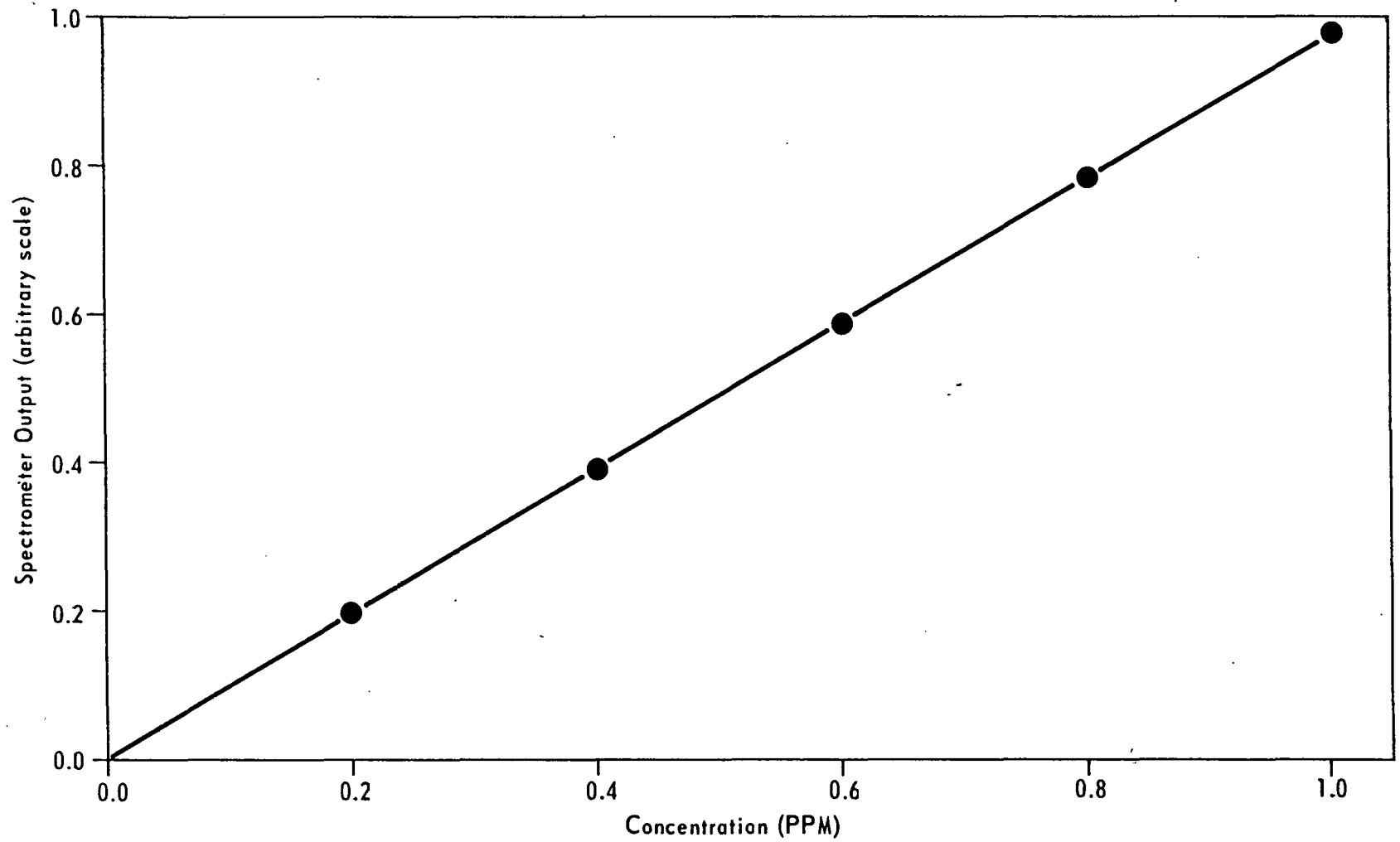


Figure 2. CALIBRATION CURVE FOR Ca BY EMISSION SPECTROMETRY

Ammonium acetate was chosen as the exchange medium for several reasons. First, it was necessary to find a cation for exchange that was not present in the raw coal. Second, 1N ammonium acetate has a pH of about 7.0-7.2, and this is an appropriate range of exchange of the cations present in coal. That is, it is difficult to find a chemical which will only exchange the cations. Hydroxides, for example, tend to solubilize humic acids, especially in lignites. This behavior is usually associated with high pH. Acids with a low pH will solubilize many of the minerals in coal.

In order to investigate the amount of minerals solubilized by 1N ammonium acetate, an experiment was performed in which 1 g of various mineral standards (ground to minus 325 mesh) were stirred overnight at room temperature in 100 ml of 1N ammonium acetate. The minerals were then filtered and the weight of the residue determined. There was some problem in recovering all of the mineral because of loss on filtration. This filtration loss is believed to be of the order of 5%. The results of this study can be seen in Table 10. The only minerals which show significant weight loss are montmorillonite and gypsum. The apparent weight loss of montmorillonite is not due to its solubility, but to the fact that this clay became highly dispersed in 1N ammonium acetate and therefore there was a high loss on filtration. Gypsum appears to be totally soluble in 1N ammonium acetate. This was a persistent problem since 50% of the gypsum was soluble under the same conditions in 0.5N ammonium hydroxide at a high pH. Lower pH exchange mediums will, of course, solubilize carbonates and clays. Therefore 1N ammonium acetate was selected as the exchange medium.

TABLE 10  
WEIGHT LOSS OF MINERALS TREATED IN 1N AMMONIUM ACETATE

Mineral	Weight Loss, %
Calcite	9
Dolomite	10
Gypsum	100
Illite	4
Kaolinite	6
Montmorillonite	18
Pyrite	1
Quartz	0

This selection is not based solely on these results but in combination with factors discussed earlier.

Another source of error is the exchange capacity of clays. Clays are usually found to be present in significant quantities in coals and have been shown to contain exchangeable cations. An estimation of the amount of cations which can be removed from the clays by exchange is given in Table 11. Average values for the exchange capacities of the clays were gained from the literature (1). The second column lists the quantity of cations that could originate from a particular clay, if the lignite contained 10% mineral matter and 25% of the mineral matter was the particular clay in question. The significance of these results will be discussed later.

Tables 12 and 13 summarize results for the cation contents of the lignites. As can be seen,  $\text{Ca}^{++}$  is the predominant cation and  $\text{Mg}^{++}$  is the second most predominant in each case. The other four cations tend to vary in both relative and absolute amounts. Sodium tends to be the most significant of the other cations, especially on a molar basis.

In Table 12 the average value for one standard deviation of each of the elements is also shown. Deviation is acceptable, with the exception of  $\text{K}^+$ . This element tended to be difficult to analyze by emission spectrometry. The main problem was that a drift in the spectrometer output versus concentration behavior was observed. This instrumental difficulty appears to be the main cause of the high percentage of error. However, the absolute values of  $\text{K}^+$  tend to be small, thus the imprecision will not affect the total cation content significantly.

TABLE 11  
EXCHANGEABLE CATIONS IN CLAYS

Clays	Exchange Capacity (1)	Contribution to Exchangeable Cation Content
	$10^{-3}$ moles/g clay	$10^{-6}$ moles/g dmmf coal
Kaolinite	0.02 - 0.10	0.50 - 2.50
Illite	0.13 - 0.42	3.25 - 10.5
Montmorillonite	0.80 - 1.50	20.0 - 37.5

TABLE 12  
 CATION CONTENTS OF LIGNITES ASSOCIATED WITH CARBOXYL GROUPS

PSOC Coal	Cation Concentrations, $10^{-4}$ g/g dmmf						Total
	Mg <sup>++</sup>	Ca <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ba <sup>++</sup>	Sr <sup>++</sup>	
246	34.4	171	27.8	1.89	6.51	3.30	244.9
623	22.6	129	8.69	3.42	3.36	2.38	169.5
833	59.8	212	10.0	5.30	10.9	3.34	301.3
1 S.D.	2.4%	3.3%	8.5%	44%	5.0%	3.3%	

TABLE 13  
 CATION CONTENTS OF LIGNITES ASSOCIATED WITH CARBOXYL GROUPS

PSOC Coal	Cation Concentrations, $10^{-6}$ moles/g dmmf						Total
	Mg <sup>++</sup>	Ca <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ba <sup>++</sup>	Sr <sup>++</sup>	
246	141.7	426.2	121.2	4.85	4.73	3.77	702.5
623	93.0	320.0	37.8	8.74	2.44	2.72	464.7
833	245.9	529.1	43.6	13.58	7.96	3.81	844.0



The contribution of cations coming from the clays to the total cation concentration can now be judged. In every case, the contribution due to the clays is less than 1% of the total amount of cations released (using the assumptions made). Kaolinite is usually found to be the most abundant clay, and it exhibits the least amount of exchange.

The possible effect of the contribution of  $\text{Ca}^{++}$  from solubilized gypsum may be significant. Optical microscopy studies have concluded that the amount of gypsum in these raw coals is relatively small. These studies are qualitative in nature, but from the mineralogical analysis it seems reasonable to assume that the quantities in these lignites do not exceed 5-10% of the mineral matter. If this is the case and assuming the coal to contain 10% mineral matter and 1.5% exchangeable  $\text{Ca}^{++}$  (by weight), one can calculate that about 10% of the exchangeable  $\text{Ca}^{++}$  is from the solubilization of gypsum. The point should be made that gypsum is commonly believed to be a product of weathering and that the gypsum formed this way might well be from the presence of exchangeable  $\text{Ca}^{++}$ . If this is so, the contribution of  $\text{Ca}^{++}$  from solubilized gypsum will depend on the extent to which the lignite was weathered.

The concentrations of exchangeable  $\text{Ca}^{++}$  are in good agreement with the limited results given in the literature. Walker et. al. (64) studied exchangeable  $\text{Ca}^{++}$  in a North Dakota lignite and a Wyoming subbituminous coal by extraction with barium acetate. They found 1.84% wt%/g dry coal for the North Dakota lignite and 1.03 wt%/g dry coal for the Wyoming coal. Murray (44) studied a Victorian brown

coal from Australia and estimated the quantity of exchangeable cations to be 0.39%  $\text{Ca}^{++}$ , 0.55%  $\text{Mg}^{++}$ , and 0.48%  $\text{Na}^+$  on a dry basis. Similar results were found by Durie (17) on a Morwell brown coal from Australia.

The amount of cations present are exchanged on a significant quantity of the carboxyl groups. Assuming two carboxyl groups to be exchanged with divalent cations and one with monovalent cations, the percentage of carboxyl groups associated with cations is estimated to be 43% (North Dakota lignite), 44% (Texas lignite), and 54% (Montana lignite).

One must be careful in putting too much emphasis on these results on an absolute basis. The sample base used was broad but small, and the nature of the cations exchanged on these lignites is a function of the immediate conditions of the groundwater near the point of sampling. The reversibility of these reactions leads one to conclude that the concentration of any element is a function of the groundwater associated with the coal in relatively recent times. Whether the cation concentration and distribution is a function of the make-up of the groundwater at the time of mining or of the last 100 years is not known. This would depend upon the permeability of the deposit to the groundwater and the kinetics of exchange of particular cations. But it can be said, with a good degree of certainty, that these properties are not as strongly associated with geological time frames as are the other coal properties. Therefore one would predict that relatively large variations in the cation concentrations associated with coal should exist within coal regions as well as seams. Taking into account the above arguments, it is striking that

the cation concentrations in the three lignites are so similar. Furthermore, it can be concluded that the use of whole channel coal samples is preferred for this analysis. Core samples might give misleading results since the sample is taken on a smaller portion of the seam.

In general, one can predict that the total concentration and distribution of cations are dependent on the cation affinity, temperature, cation concentration, and pH. As discussed earlier, there is a distribution of acid strength among the carboxyl groups on coal. Thus the pH of the groundwater is the determining factor in the amount of carboxyl groups available for exchange. The higher the pH the more carboxyl groups expected to be exchanged. The amount of cations exchanged is also dependent on the temperature of the groundwater. This is because diffusion into the pores of coal is activated, but the long periods of time for equilibrium to be reached should minimize this effect.

The main factors affecting the distribution of cations are the cation affinity and the concentration of cations in the groundwater. The principles behind this statement have been discussed earlier. The principles lead to the fact that for a cation to have a high concentration on the coal it must be in high concentration in the groundwater and/or have a high affinity.

Figure 3 shows the release versus time behavior for  $Mg^{++}$  and  $Ba^{++}$  in PSOC 246. This figure is used to illustrate the choice of and the need for a 26-hour exchange period. As was discussed earlier,  $Ba^{++}$  and  $Mg^{++}$  are the cations with the greatest and least degree of thermodynamic affinity of the divalent cations studied (Table 1).

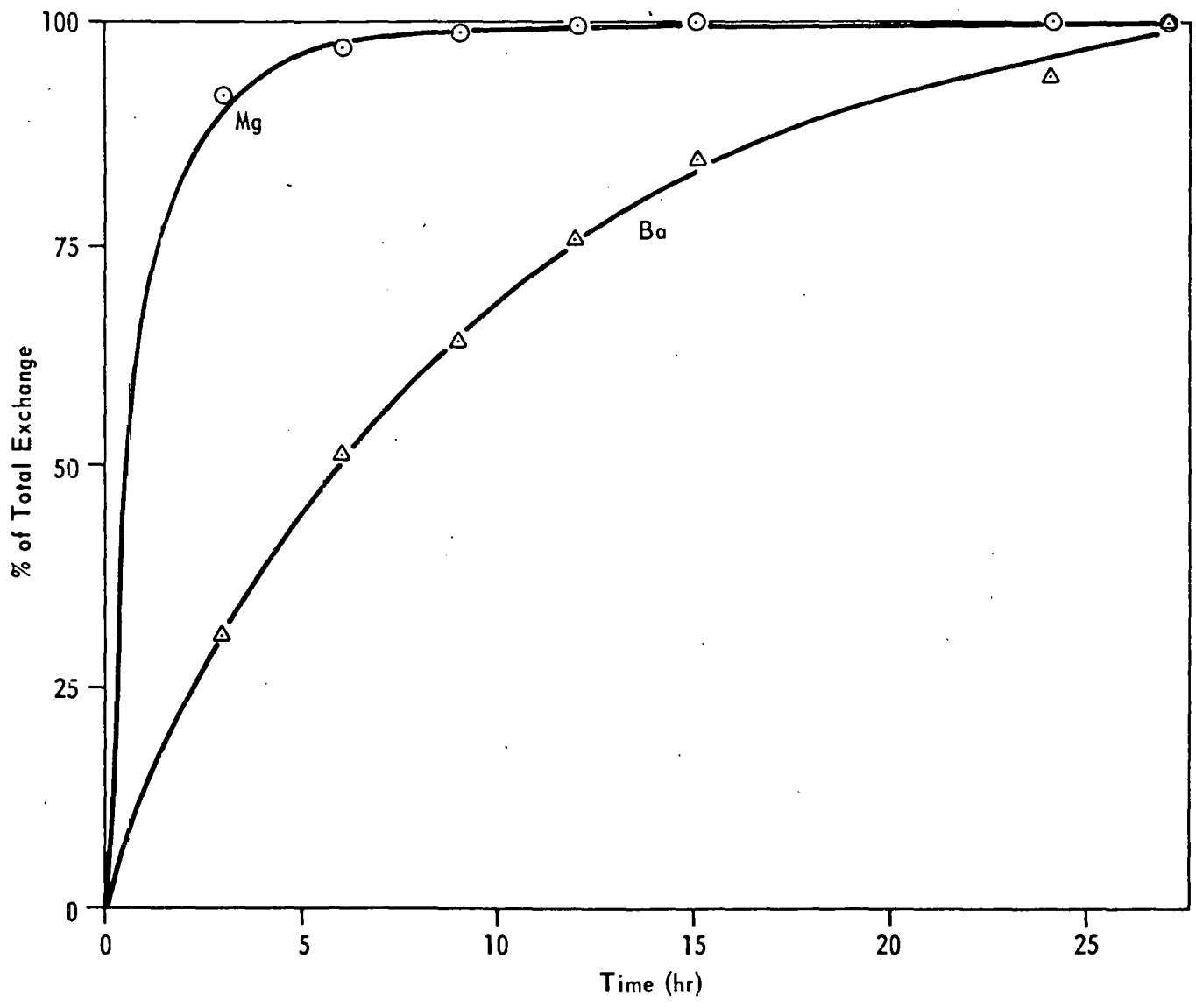


Figure.3. RELEASE OF CATIONS FROM PSOC-246 DURING AMMONIUM ACETATE TREATMENT

Figure 3 appears to bear this point out. As can be seen, virtually all of the  $Mg^{++}$  was released in 15 hours while significant amounts of  $Ba^{++}$  were still being released after this time. In all three lignites studied,  $Ba^{++}$  was always the most tenaciously held cation.

The release versus time behavior is not solely a function of the affinity series. The rate of diffusion out of the coal will also affect this. The rate of diffusion will mainly depend on the diffusivity, concentration gradient and diffusion length for each cation. The variation of the first two factors is obvious, but the difference in path length might also be a factor. This is due to molecular sieving in coal which would limit the pores available to various cations dependent on their radii.

Therefore, Figure 3 cannot be used to confirm the thermodynamic affinity series without further studies. The points on the figure may be at differing stages of approach to equilibrium, depending on the effect of mass transfer. Further studies are warranted on the kinetics of these exchange reactions before further conclusions can be made.

As stated earlier, it was felt necessary to extend the exchange time to 26 hours. An attempt to show that 26 hours is sufficient can be seen in Table 14. Here is shown the percentage of the total amount of a particular cation that was extracted in the final 3-hour period. As can be seen, a relatively small amount of the total extraction occurred in the final period. The most notable exception to this is  $K^+$ , but the difficulties in analyzing this element were discussed earlier.

TABLE 14  
 PERCENTAGE OF CATIONS EXTRACTED IN FINAL EXTRACTION

PSOC Coal	Wt % Extracted in Final Extraction					
	Mg <sup>++</sup>	Ca <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ba <sup>++</sup>	Sr <sup>++</sup>
246	0.2	1.2	0.8	3.8	6.0	0.6
623	0.1	0.4	3.5	7.7	2.9	0.0
833	0.2	0.6	7.2	6.2	4.8	0.7
Average	0.2	0.7	3.8	5.9	4.6	0.4

#### 4.3 Mineral Matter Determination

The mineral matter analysis was performed as discussed in the experimental section. The analysis of calcite, quartz, and pyrite using x-ray diffraction was described and the calibration mixes listed. The calibration curve obtained in this manner can be seen in Figure 4 for quartz. All calibration curves were analyzed by a least squares analysis. In all cases the correlation coefficient was greater than 0.98.

A correlation coefficient of greater than 0.98 indicates a high degree of precision using this method. High precision can be attributed to triplicate determinations, thorough mixing of solids, and the use of area ratios. However, the level of accuracy is questionable. In any analysis of mineral matter in coal, one is plagued with the problem of the similarity or lack of similarity of the pure mineral standards to those found in coal. That is, differences in crystallite size and the nature and concentration of defects in the minerals can affect intensities of x-ray diffraction peaks. The use of peak areas in this study is an attempt to minimize this problem. Because of these problems, an accuracy of 10-20% is usually taken as the typical range for studies on coal mineral matter. As will be seen shortly, experience gained in experiments in this investigation shows this to be a fair estimate for minerals existing in quantities greater than 10% of the mineral matter. However, smaller quantities of specific minerals are very difficult to determine accurately. The extent of the difficulty depends upon the sharpness of the x-ray diffraction peaks which again depends on the crystallinity of particular minerals. This can lead to problems in defining the baseline; and for quantities of

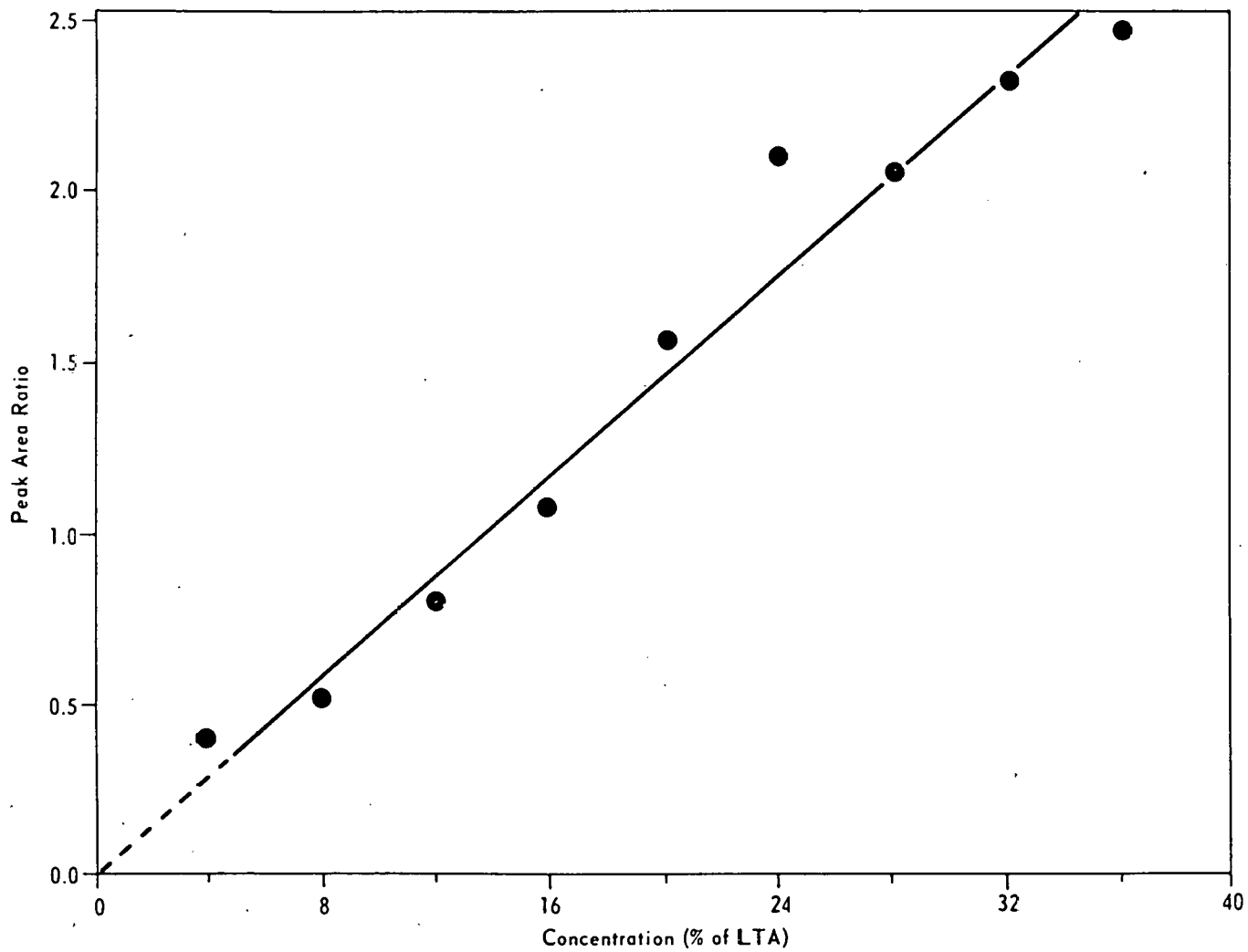


Figure 4. X-RAY CALIBRATION CURVE FOR QUARTZ; USING CaF AS A STANDARD



the mineral matter that are less than 5%, values that are in error by as much as 100%. This logic leads to an accuracy assessment based on an absolute rather than a relative basis. For x-ray diffraction determinations this value appears to be about 2-4%. This means that a value of 40% quartz could vary from 36-44%.

Infrared spectrometry was utilized to quantify the amount of kaolinite and anhydrite in the manner described in the experimental section. An infrared calibration curve for kaolinite is given in Figure 5. The raw data were analyzed in the same manner as the x-ray diffraction data, and all correlation coefficients were greater than 0.99.

As with the x-ray measurements, the high degree of precision is the result of careful sample preparation and analysis. In general, better precision was found in the infrared work. This appears to be a function of the fact that it is fairly easy to achieve a homogeneous mixture using the KBr pressed pellet sample preparation technique. Again the question is to what extent the accuracy of the concentrations reported for kaolinite and anhydrite are affected by the standards not being representative of the minerals in the lignites. As was found in x-ray diffraction, quantification of the minerals existing in small quantities was found to be less precise than analysis of minerals existing in large quantities. Therefore, an accuracy of 1-2% absolute appears to be appropriate.

Although analysis by x-ray diffraction and infrared spectroscopy yields a semi-quantitative understanding of the amounts of calcite, quartz, pyrite, kaolinite, and anhydrite in the lignite LTA residue, a significant portion of the mineral matter remains unaccounted

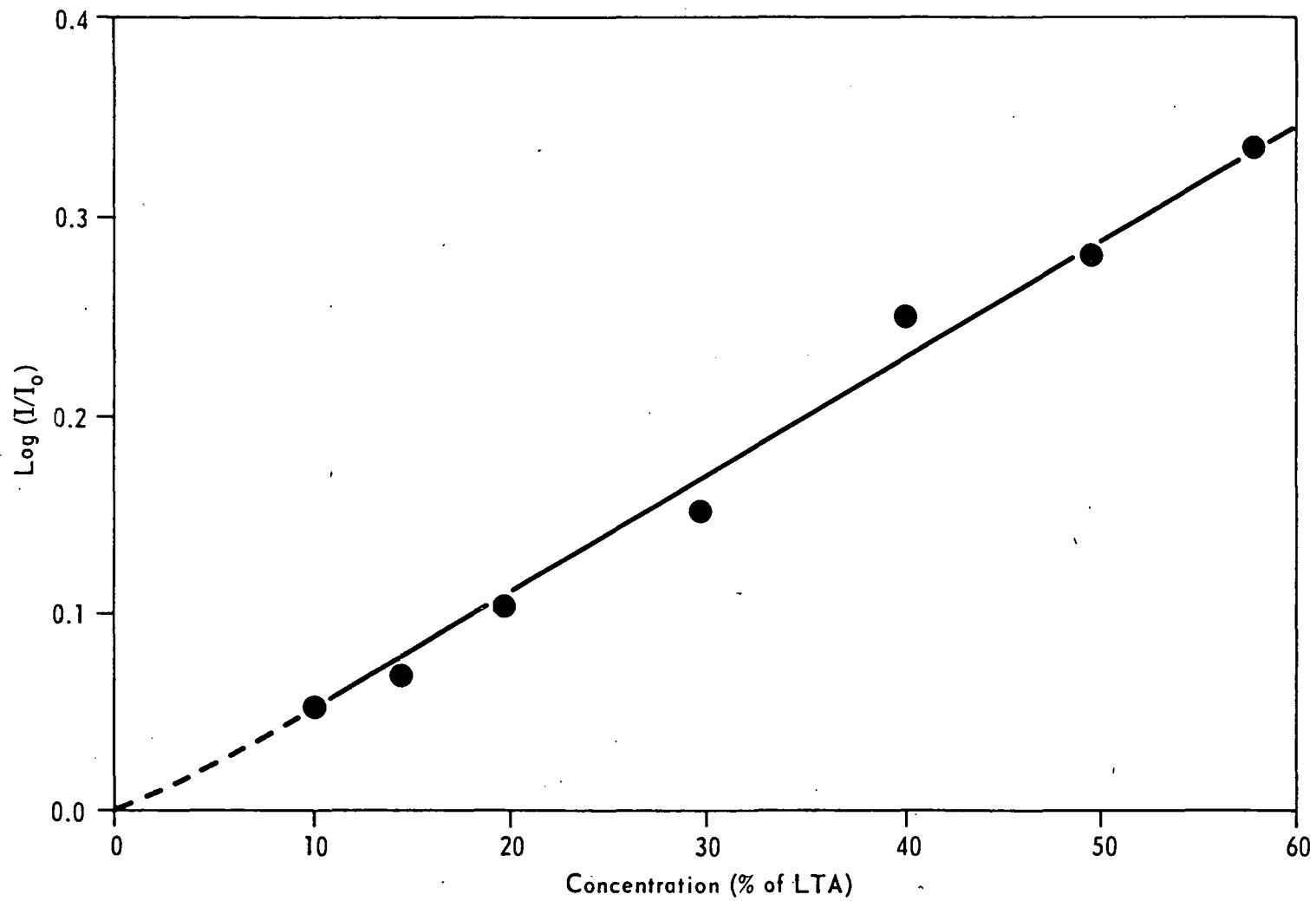


Figure 5. INFRARED SPECTROSCOPY CALIBRATION CURVE FOR 910  $\text{cm}^{-1}$  BAND OF KAOLINITE

for, as will be seen. An attempt was made to estimate what fraction of the unaccounted for mineral matter was "other clays". To do this, an analysis of the total silicon and aluminum content in the ash was needed. This information was supplied by the Coal Research Section, at The Pennsylvania State University. The values, reported in Table 15, are for the high temperature ash of the lignites produced at 750°C in 1 atm of air.

After ash and mineralogical analyses have been obtained, the percentage "total other clays" (that is, illite plus montmorillonite plus mixed layer clays) can be estimated by calculating the amount of  $Al_2O_3$  and  $SiO_2$  remaining in the LTA after the quantities associated with quartz and kaolinite have been accounted for (60).

Mineralogical analyses were performed on the LTA and analyses for total  $Al_2O_3$  and  $SiO_2$  were performed on the HTA. To calculate the amount of  $Al_2O_3$  and  $SiO_2$  remaining in the LTA after the amounts in quartz and kaolinite have been accounted for, the following equation was used:

$$Al_2O_3 = \frac{\%HTA}{\%LTA} \cdot \frac{\%Al_2O_3}{HTA} - \frac{\%Kaolinite}{LTA} \cdot (0.395)$$

$$SiO_2 = \frac{\%HTA}{\%LTA} \cdot \frac{\%SiO_2}{HTA} - \frac{\%Kaolinite}{LTA} \cdot (0.465) + \frac{\%Quartz}{LTA}$$

The derivation of these equations and a sample calculation is given in the appendix. After these quantities are determined, the amount of "other clays" can be calculated using a reasonable figure for the amount of  $Al_2O_3$  and  $SiO_2$  in "other clays". The values chosen for "other clays" consist of 25%  $Al_2O_3$  and 50%  $SiO_2$  (16).

Clearly the calculated quantities of "other clays" have a number of sources of error. First, there is a compounding of errors from

TABLE 15  
INFORMATION ON HIGH TEMPERATURE ASHES FROM LIGNITES

PSOC Coal	% HTA/g Dry Coal	% SiO <sub>2</sub> /g Ash	% Al <sub>2</sub> O <sub>3</sub> /g Ash
246	9.7	21.0	8.5
623	16.6	43.5	21.8
833	13.0	36.1	13.4

all the analyses used: HTA, LTA, analysis for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the HTA and mineralogical analysis. Second, the figures of 25%  $\text{Al}_2\text{O}_3$  and 50%  $\text{SiO}_2$  may not correctly estimate the amounts of these materials in the clays in the coals. Finally other  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  bearing minerals may be present. However, this determination is useful as a rough estimate of the quantity of "other clays".

The results of the mineralogical analyses are given in Table 16. Total LTA contents in the lignites, along with the values for one standard deviation for each determination are given. The LTA wt % values are based on the average of 4-6 runs. Also listed are concentrations of the minerals studied, "other clays", and others by difference value in the LTA. The quantitative analyses of the specific minerals are the average of 3 runs with a value for the spread in the data. Both the value for one standard deviation, for the LTA wt %, and the spread in the data values, for the quantitative analysis of the minerals are on an absolute basis. That is, a value of  $5 \pm 0.8$  means the values varied from 4.2% to 5.8%.

One significant feature of these results is the comparison of the total LTA obtained from the raw and ammonium acetate treated coals. In every case ammonium acetate treatment of the raw coals sharply reduced the LTA subsequently obtained, with reduction of over 50% seen for PSOC 246 and 833. This decrease is more than can be accounted for by removal of all the cations. Referring back to Table 12, one can see that the cation concentrations are 2.4% (PSOC 246), 1.7% (PSOC 623), and 3.0% (PSOC 833). Since the loss of LTA weight is greater than these amounts for each lignite, it can be inferred that the cations play a role in increasing the yield of LTA which is greater

TABLE 16  
MINERAL MATTER IN LTA RESIDUES OF LIGNITES

	LTA Wt %/g coal Dry	Wt %/g LTA						
		Kaolinite	Quartz	Pyrite	Calcite	Anhydrite	Other Clays	Others
<u>PSOC 246</u>								
Raw	11.5 ± 1.3	5 ± 0.8	9 ± 3.3	NIL*	11 ± 0.5	21 ± 0.7	17	37
NH <sub>4</sub> AC	4.6 ± 1.0	8 ± 0.7	15 ± 0.8	NIL	NIL	1 ± 0.0	57	19
<u>PSOC 623</u>								
Raw	20.5 ± 0.3	41 ± 1.1	12 ± 0.9	NIL	2 ± 0.9	14 ± 1.4	7	14
NH <sub>4</sub> AC	16.9 ± 0.4	41 ± 1.6	12 ± 3.1	NIL	NIL	1 ± 0.0	24	32
<u>PSOC 833</u>								
Raw	17.4 ± 0.4	20 ± 0.0	19 ± 1.4	NIL	16 ± 4.0	10 ± 1.3	8	27
NH <sub>4</sub> AC	8.2 ± 0.8	41 ± 1.5	26 ± 1.6	NIL	NIL	4 ± 0.0	24	5

\*NOTE -- NIL refers to minerals detected but in quantities too small to quantify.

than just their weight. This phenomenon will be more fully viewed when the mineralogical analyses are inspected.

Concentrations of major minerals in the LTA are typical of those found for lignites in the United States (30,46,47,54). Clays and quartz are the most significant fractions of the mineral matter while pyrite contents are low. In general, an increase in the concentrations of clays and quartz is seen when comparing the LTA of the ammonium acetate treated versus the raw lignite samples. This is due to a concentrating effect; that is, the amounts of clays and quartz are the same, but the total LTA is less. Calcite and anhydrite show the opposite behavior. Significant quantities of these minerals are found in the LTA of the raw coal, but little exists in the LTA of the ammonium acetate treated samples. This behavior and the fact that  $\text{Ca}^{++}$  was the cation in highest concentration in the raw lignites lead to the conclusion that calcite and anhydrite are formed in the LTA process as a result of the interaction of the cations with oxides of sulfur and carbon. Fixation of sulfur as sulfate has been reported in the literature (38,39,48,49), but carbonate formation has not been reported previously.

There is a problem in measuring the amount of anhydrite formation during low temperature ashing of the raw lignite. That is, ammonium acetate was earlier found to solubilize anhydrite. However, anhydrite is not usually found in large quantities in the raw coal. This was confirmed for the samples used in this study by the results of the optical microscopic analysis, which are summarized in Table 17. In no case was gypsum found in significant amounts in the mineral matter; that is, existing in concentrations greater than about 2%.

TABLE 17  
 QUALITATIVE ANALYSIS OF MINERALS IN LIGNITES

<u>OPTICAL MICROSCOPY</u>		
<u>PSOC 246</u>	<u>PSOC 623</u>	<u>PSOC 833</u>
Clays	Clays	Clays
Quartz	Quartz	Quartz
Calcite*	Calcite*	Calcite
Pyrite*	Pyrite*	Pyrite*
Gypsum*	Gypsum*	Gypsum*
<u>INFRARED SPECTROSCOPY AND X-RAY DIFFRACTION: MINERALS OBSERVED BUT NOT QUANTIFIED</u>		
Clays**	Clays**	Clays**
	Illite	Illite
Carbonates***		Carbonates***
Nitrates	Nitrates	Nitrates

- \* - Reported as a minor phase.
- \*\* - Characteristic clay peak found (19.9°, 2θ), but not enough information to show which variety.
- \*\*\* - Characteristic peak of dolomite and ankerite found (30.8-30.9°, 2θ), but not enough evidence to distinguish between the two.



Table 17 also lists other minerals that were identified but not quantified by x-ray diffraction and infrared spectroscopy. As can be seen, only a few additional minerals were identified. Nitrates were identified by a sharp peak around  $1380\text{ cm}^{-1}$  by infrared spectroscopy, in agreement with studies by Karr (31) and O'Gorman (45).

In view of the preceding evidence it appears that both calcite and anhydrite are formed in the LTA. It seems logical, however, that carbonates and sulfates other than these two should have been formed. However, with the amounts of the other cations in the lignites being in much lower concentrations, it is not surprising that their carbonates and sulfates have not been observed.

The preceding discussion displays the difficulties in ash and mineralogical analyses of lignites. This problem is related to the presence of exchanged cations in the lignites. It is very difficult, if not impossible, to remove the cations without affecting other parameters. In this study, the gypsum was removed by ammonium acetate. It is believed that the amount removed is significantly less than the amount reported in the mineralogical analysis of the raw coal LTA. Therefore, this investigation has furthered the ability to analyze the mineral matter in lignites, but a totally comprehensive procedure without interferences has not been gained. Rather, we have gained a greater understanding of the problems and created a method which solves most of them. It is certain that any comprehensive technique to analyze the mineral matter present in lignites will entail a significant amount of work which is not necessary in coal systems of rank where exchangeable cations are not present.

#### 4.4 Significance of Results for Lignite Utilization

The major goal of this study was to investigate and refine methods for the determination of the carboxyl group content, exchanged cations, and the mineral matter in American lignites. However, this research has not been taken solely out of scientific interest. The value in using these techniques lies in the ability to apply the results found in such investigations to problems in coal conversion and utilization processes.

One of the ways this information can be used is in the problems associated with ash slagging in combustors. Some lignites have been found to present greater problems with ash slagging than coals of higher rank (51). The main problem is the sticking behavior of the ash. It is believed to be a function of the alkali metals in the ash, in particular sodium. As seen in the results section, sodium is present in the lignites as an exchanged cation. Miller (38) found that almost all of the sodium present in low-rank coals is present in ion exchangeable form. It is likely that sodium plays a different role when it is ion exchangeable than when it is present in mineral phases. Therefore, one concludes that studying the amount of ion exchangeable cations could lead to the ability to predict the slagging behavior of a coal and subsequently to methods of reducing it.

Another area where exchanged cations are thought to play an important role is coal gasification. Hippo (27) found that the addition of cations to coal by ion exchange greatly increased the subsequent reactivity of the char to steam. Walker et. al. (65) also studied this effect and found that the catalytic activity of a cation is dependent on the reactive atmosphere. That is, cations can exhibit a catalytic

or an inhibitory effect on coal gasification depending on the atmosphere. One of the reasons cations associated with carboxyl groups are thought to be good catalysts is their high degree of dispersion. Once the catalytic effect of these inorganics is better understood, predictions of the reactivity of lignites during their gasification could be made by utilizing analyses such as those discussed in this investigation.

Since any gas-solid reaction is dependent on the surface area of the solid, it is of interest to estimate the fraction of the total surface area covered by the cations present. Table 18 presents surface area results as determined from adsorption of  $\text{CO}_2$  onto the deionized coals at  $25^\circ\text{C}$ . The surface area occupied by the carboxyl groups is calculated by assuming  $0.077 \text{ nm}^2$  per site or carboxyl group. This value can be calculated by considering the area occupied by an edge atom on a carbonate lattice ( $\beta$  graphite) which has an interlayer spacing of  $0.355 \text{ nm}$  and a carbon-carbon bond length of  $0.142 \text{ nm}$  (66). The value of  $0.077 \text{ nm}^2$  is the average of the areas occupied by a carbon atom in the 100 (zig-zag) and the 110 (arm-chair) crystallographic planes. The percentage of the  $\text{CO}_2$  surface area occupied by the total carboxyl groups and carboxyl groups associated with cations are also given. These later values are only estimates, but they show that a significant portion of the  $\text{CO}_2$  surface area is covered by carboxyl groups and by carboxyl groups associated with cations.

The third area of interest is the behavior of lignites under liquefaction conditions. Walker et. al. (64) report that large amounts of inorganic material build-up inside of pilot plane liquefaction reactors. The amount of these inorganic deposits can be ten

TABLE 18  
SURFACE AREAS AND GROUP COVERAGES IN DEMINERALIZED LIGNITES

PSOC Coal	Surface Areas m <sup>2</sup> /g dmmf		Coverage of CO <sub>2</sub> Surface Area (%)	
	<u>CO<sub>2</sub></u>	<u>COOH</u>	<u>BY COOH</u>	<u>BY CATIONS</u>
246	285	145	51	22
623	240	98	41	18
833	250	139	56	30

to twenty times greater when low-rank coals are liquefied as compared to bituminous coals. The main constituent in the inorganic material formed was calcite. This has been shown to originate from the presence of exchangeable calcium and these low-rank coals. The particular coal studied was a Wyoming subbituminous. It can be predicted that the problem would be worse for coals of still lower rank since the  $\text{Ca}^{++}$  content of the Wyoming coal was 1.0 to 1.2 wt % whereas the  $\text{Ca}^{++}$  content of the coals in this study ranged from 1.7 to 2.1 wt %.

## 5. SUMMARY AND CONCLUSIONS

As stated in the introduction, the main emphasis of this investigation was to explore methods for the determination of: the carboxyl group content, the exchangeable cation content, and major minerals present for a set of American lignites. The literature survey led to the approach used experimentally. The experimental techniques were: ion exchange with barium acetate for carboxyl group determination, ion exchange with ammonium acetate for exchangeable cation determination, and low temperature ashing for mineral separation followed by analysis with x-ray diffraction, infrared spectroscopy, and chemical techniques for the mineralogical analysis. The step-by-step processes are outlined in the experimental section, and the reasons for the choice of these procedures are discussed throughout the thesis.

The concentration of carboxyl groups ranged from 2.1 to 3.1 mequiv/g dmmf coal for the three lignites studied. These results were shown to be both accurate and precise and were in general agreement with results given by previous authors for Texas, Montana, and North Dakota lignites.

For the determination of the amount of cations associated with carboxyl groups, it was shown that 26 hours was required for essentially complete exchange. Exchange of cations on clays was shown to have only a small effect on this measurement. The effect of calcium addition to the solution from the dissolution of gypsum in ammonium acetate may contribute a few percent of the total calcium exchanged. The total amount of cations present in the lignites ranged from 1.7 to 3.0 wt %/g dmmf coal, with  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  being the predominant elements. These

results agree with other published data. The technique was shown to yield reproducible and accurate results.

The effect of the presence of cations on the determination of mineral matter in lignites was clearly seen. That is, up to 50% of the low temperature ash from the raw lignites was shown to be derived from the exchangeable cations present. These cations combine with oxides of sulfur and carbon in the low temperature asher to form carbonates and sulfates. The mineralogical determination, in general, showed the least degree of accuracy due to problems with the analytical methods used for this determination. The problems have been discussed.

It was shown that a significant fraction of the surface area in the lignites is covered by carboxyl groups and cations. They will play important roles in coal conversion processes. Thus both the desirable and undesirable roles which cations play in combustion, gasification, and liquefaction processes have been discussed, and an attempt was made to assess the significance of the results gained in relation to these processes.

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## APPENDIX

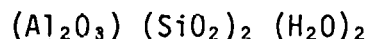
The equations used for calculating the amount of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the mineral matter after the amounts of these quantities in quartz and kaolinite have been accounted for are given below.

$$\text{Al}_2\text{O}_3 = \frac{\% \text{HTA}}{\% \text{LTA}} \cdot \frac{\% \text{Al}_2\text{O}_3}{\text{HTA}} - \frac{\% \text{Kaolinite}}{\text{LTA}} \cdot (0.395)$$

$$\text{SiO}_2 = \frac{\% \text{HTA}}{\% \text{LTA}} \cdot \frac{\% \text{SiO}_2}{\text{HTA}} - \frac{\% \text{Kaolinite}}{\text{LTA}} \cdot (0.465) - \frac{\% \text{Quartz}}{\text{LTA}}$$

The first term in both of the equations is an expression of the total quantity of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the LTA with a correction for the fact that the analysis of these quantities was performed on the HTA and the mineralogical analysis was performed on the LTA.

The second term estimates the amounts of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  accounted for by the quartz and kaolinite in the LTA. The formula for pure kaolinite is usually taken as (1):



Thus kaolinite contains about 39.5%  $\text{Al}_2\text{O}_3$  and 46.5%  $\text{SiO}_2$  by weight. A sample calculation for the amount of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  other than that in kaolinite and quartz for PSOC 246 (raw coal LTA) can be seen below. The data used in these calculations were taken from Tables 15 and 16.

$$\% \text{Al}_2\text{O}_3 = \frac{9.7}{11.5} \cdot 8.5 - 5 \cdot (0.395) = 5.19$$

$$\% \text{SiO}_2 = \frac{9.7}{11.5} \cdot 21.0 - 5 \cdot (0.465) - 9 = 6.38$$

If the values of 25%  $\text{Al}_2\text{O}_3$  and 50%  $\text{SiO}_2$  (16) are taken to represent the amounts of these oxides in the "other clays", a value for "other clays" can be calculated from the average of the values

obtained with the use of the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  balances. This calculation is shown below.

$$\% \text{ "other clays" (from } \text{Al}_2\text{O}_3 \text{ balance)} = 4 \cdot 5.19 = 20.8$$

$$\% \text{ "other clays" (from } \text{SiO}_2 \text{ balance)} = 2 \cdot 6.38 = 12.8$$

$$\% \text{ "other clays" (average)} = 17$$

The data in Tables 15 and 16 can also be used to calculate an "other clays" value for the ammonium acetate treated coals. The HTA data can be used since it yields the amount of  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2/\text{g Dry Coal (raw)}$ . However, this amount must be corrected because the % LTA is in units of g/g Dry Coal (ammonium acetate washed). Therefore, the first term of each equation is multiplied by the value for g Dry Coal (raw)/g Dry Coal (ammonium acetate treated) where g Dry Coal (ammonium acetate treated) equals g Dry Coal (raw) minus g cations extracted. Therefore, the calculation for "other clays" in PSOC 246 (ammonium acetate treated) is as follows:

$$\% \text{Al}_2\text{O}_3 = \frac{9.7}{4.6} \cdot (8.5) \cdot (1.025) - 8 \cdot (0.395) = 15.2$$

$$\% \text{SiO}_2 = \frac{9.7}{4.6} \cdot (21) \cdot (1.025) - 8 \cdot (0.465) - 15 = 26.6$$

The value for "other clays" can now be calculated in the manner described above, and it is 57%.