

ANALYSIS OF THE INORGANIC CONSTITUENTS IN AMERICAN LIGNITES

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INTRODUCTION

The relatively untapped reserves of lignite coals in the western United States have generated a large amount of interest in the past few years. In general, lignites exist in relatively thick seams which are close to the surface. Thus they are amenable to extraction at a low cost. These coals tend to react quite differently in coal conversion processes than coals of higher rank. All of the reasons for this behavior are not well understood. One of the characteristics peculiar to low rank coals is the amount of ion-exchangeable inorganics. These inorganics are usually taken to be cations in association with carboxyl groups. These cations are believed to be responsible for catalysis of gasification, formation of calcite during liquefaction, and the behavior of lignite ash during combustion. However, characterization of this organic-inorganic system has not been satisfactorily accomplished for American lignites.

The research described here was concerned with the characterization of the ion-exchangeable cations and the carboxyl groups with which they are associated for three important deposits of American lignites. This has been accomplished by ion-exchange techniques, utilizing ammonium acetate and barium acetate, respectively. The cations analyzed for were Na, K, Mg, Ca, Sr, and Ba. Also the amounts of the major discrete mineral phases present in the lignites have been determined. This was accomplished by the use of semi-quantitative x-ray diffraction and infrared spectroscopy techniques.

EXPERIMENTAL

The carboxyl group analysis was modeled after that of Schaefer (1,2). Briefly, demineralized coal (3) which has been ground in N_2 to pass 200 mesh is mixed with 1N barium acetate solution at a pH equaling 8.25 to 8.30. The slurry is refluxed in a flask through which purified N_2 is passed to prevent oxidation of the coal and subsequent formation of barium carbonate. After 4 hr, the solution is cooled, the pH recorded, and enough 0.05 N barium hydroxide is added to restore the original pH of the solution. After three 4 hr periods, the slurry is filtered under N_2 and washed with 1N sodium acetate at a pH equaling 8.25 to 8.30. The hydrogen ions released from the exchange are quantified by the total amount of barium hydroxide added to the solution. The exchanged barium is then removed by boiling the coal in 0.2 N perchloric acid for 20 min. The barium released is quantified by emission spectrometry.

The cations were analyzed by extraction of the coal with 1N ammonium acetate as suggested by Miller (4). Using this procedure, the coal is stirred at room temperature in the ammonium acetate solution (pH equals 7.0 to 7.2) for 3 hr. The slurry is then filtered and the coal transferred back to the beaker with fresh ammonium acetate for another 3 hr extraction. This is followed by three more 3 hr extractions, followed by extraction overnight and a final 3 hr period in the morning. Each of the extracts is then analyzed for Na, K, Mg, Ca, Sr, and Ba by emission spectrometry. The use of fresh ammonium acetate is essential to achieve complete exchange since the existence of any cations in the slurry will result in an equilibrium value on the coal.

Characterization of discrete mineral phases present in the low temperature ash (LTA) of the lignites was accomplished by x-ray diffraction and infrared spectroscopy. The procedure for LTA follows that described by Miller (4). Calcite, quartz, and pyrite are analyzed by x-ray diffraction, while kaolinite and anhydrite are analyzed by infrared spectroscopy. Techniques for these analyses are described by Jenkins and Walker (5). It has been shown (4,5) that mineral phases can form in the LTA process when lignites are ashed. That is, cations present fix sulfur, carbon, and oxygen to form carbonates and sulfates. In order to study this phenomenon, mineralogical analyses of both the raw lignites and the ammonium acetate treated lignites were performed.

RESULTS AND DISCUSSION

Table 1 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 shown. In order to investigate the accessibility of the carboxyl groups to the reagent, both minus 80 and minus 200 mesh fractions of PSOC 623 were investigated. There was no effect of particle size on the results. Table 1 also shows carboxyl group values calculated using the barium release method for selected runs. Carboxyl group contents are calculated assuming that two carboxyl groups are exchanged with one barium ion. Close agreement of these results supports this assumption and confirms the accuracy of the technique. The choice of three 4 hr refluxes was based on the finding that, in all cases, less than 5% of the carboxyl groups were exchanged in the final 4 hr period. The oxygen contained in the carboxyl groups of these coals accounts for 46% (North Dakota), 37% (Texas), and 42% (Montana) of the oxygen by difference value calculated in the ultimate analysis.

TABLE 1. CARBOXYL CONTENTS OF LIGNITES

PSOC Coal	State	Seam	Carboxyl Content, Mequiv/g DMMF	
			Titration	Ba Released
246	N. Dakota	Hagel	3.13 ± 0.05	3.24
623	Texas	Darco	2.11 ± 0.08	2.22
833	Montana	Fort Union	3.00 ± 0.07	3.07

Table 2 lists concentrations of cations associated with carboxyl groups found on the lignites. The values shown represent the average of four runs and have a precision of ± 3% or better. Calcium and Mg are the predominant cations. However, there are significant variations in concentration of the cations among the coals studied. For these coals, it was estimated that 43% (North Dakota), 44% (Texas), and 60% (Montana) of the total carboxyl groups are associated with the cations listed in Table 2. The basis for the selection of a 27 hr total exchange time is displayed in Figure 1, where the cumulative percentage of the total exchange versus time is plotted for Mg and Ba. Magnesium is essentially totally exchanged in 12-15 hr, while Ba exchange proceeds more slowly to completion. These results confirm the evidence of other investigators (4,6) who show that Ba should be more strongly held than Mg. Among the divalent cations, the ions with smaller hydrated ion radii have been found to be held most strongly.

Since the cations are thought to be active catalytically in gasification and liquefaction processes, it is of interest to estimate the fraction of total surface area covered by the total cations present. Table 3 shows the CO₂ (total) surface

areas calculated from adsorption at 25°C, the surface areas occupied by the carboxyl groups calculated by assuming 7.7 Å² per site or carboxyl group, and the percentages of the CO₂ surface area occupied by the total carboxyl groups and cations associated with carboxyl groups. A significant portion of the CO₂ surface area is covered by the carboxyl groups and by those associated with cations.

TABLE 2. CATION CONTENTS OF LIGNITES ASSOCIATED WITH CARBOXYL GROUPS

PSOC Coal	Cation Concentrations, 10 ⁻⁴ g/g DMMF						
	Mg	Ca	Na	K	Ba	Sr	Total
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

TABLE 3. SURFACE AREAS OF AND GROUP COVERAGES ON LIGNITES

PSOC Coal	Surface Areas, m ² /g DMMF		Coverage of CO ₂ Surface Area, %	
	CO ₂	Carboxyl	Carboxyl	By Cations
246	200	130	65	28
623	180	78	43	19
833	210	128	61	37

Results of the mineral matter analysis are summarized in Table 4. Each value corresponds to triplicate determinations. In general, a reproducibility of ± 2-4% (absolute) is found. Infrared spectroscopy showed a greater degree of precision than x-ray diffraction, and the larger values are more relatively precise than the smaller ones. The effect of the presence of cations in the raw lignites on the mineral matter analysis is seen. The amount of LTA decreased by up to 50%, when the cations were removed from the lignites prior to ashing. The disappearance of calcite and anhydrite can also be seen. These results show clearly that the yield of LTA produced from raw lignites is enhanced by the formation of sulfates and carbonates. One would predict the existence of other carbonates and sulfates, but their concentrations would be too low to observe by the techniques used.

CONCLUSIONS

- 1) The ion exchange techniques described in this paper to define the carboxyl groups and exchanged cations are relatively precise, simple, and suitable for characterization of American lignites.
- 2) Calcium and Mg are the major cations in the coals studied, but considerable variations in absolute and relative concentrations exist among the cations analyzed.
- 3) The cations and carboxyl groups cover a significant fraction of the CO₂ surface areas of the lignites.
- 4) Up to 50% of the LTA of the raw lignites studied is an artifact of the ashing procedure, which is mainly due to cation fixation of CO₂ and SO₂ to form carbonates

and sulfates.

5) The real significance of this work lies in the ability to correctly characterize the inorganics in lignites. With the information gained by such analyses, effects of inorganics on coal conversion processes and combustion can be more fully understood.

TABLE 4. MINERAL MATTER IN LTA RESIDUES OF LIGNITES

LTA, wt %/g <u>Coal Dry</u>		<u>wt %/g LTA</u>					
		<u>Kaolinite</u>	<u>Quartz</u>	<u>Pyrite</u>	<u>Calcite</u>	<u>Anhydrite</u>	<u>Others</u>
PSOC 246							
Raw	11.5	5	9	nil*	11	21	54
NH ₄ Ac	5.9	8	15	nil	nil	1	76
PSOC 623							
Raw	20.5	41	12	nil	2	14	21
NH ₄ Ac	16.9	41	12	nil	nil	1	46
PSOC 833							
Raw	17.4	20	19	nil	16	10	35
NH ₄ Ac	8.7	41	26	nil	nil	4	29

*minerals detected but in quantities too small to quantify.

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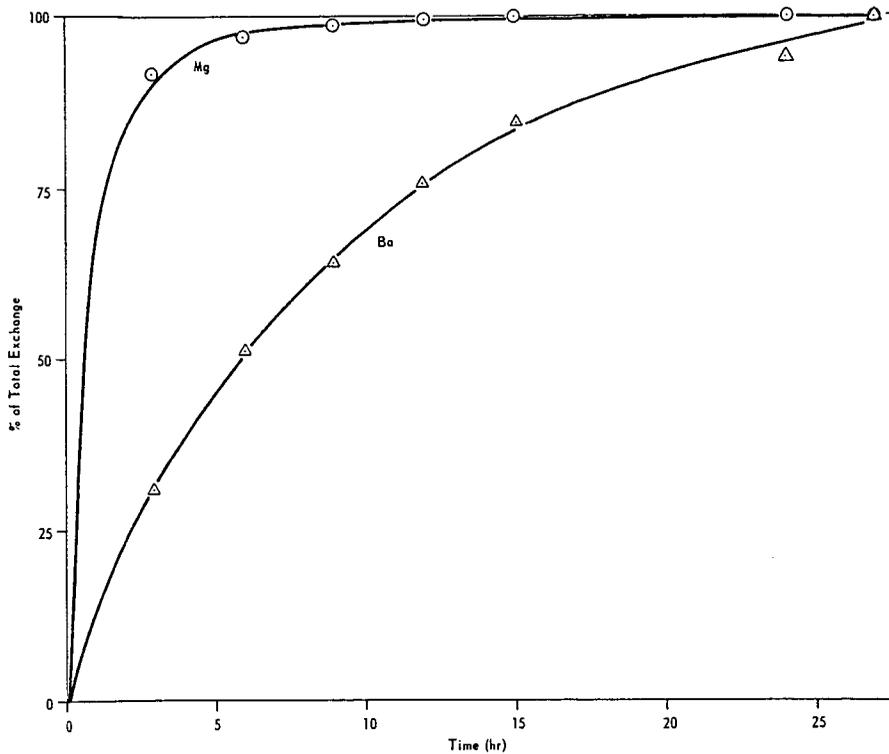


Figure 1. REMOVAL OF CATIONS FROM CARBOXYL GROUPS ON LIGNITE PSOC-246 IN AMMONIUM ACETATE SOLUTION