CHARACTERIZATION OF MINERAL MATTER AND TRACE ELEMENTS IN COAL

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I. Introduction

There are probably two major reasons why more attention has not been paid in the past to the relation between the character of mineral matter and trace elements in coal and the behavior of coal in conversion processes. First, the major conversion process of commercial importance, until recently, has been combustion. This reaction is rapid, and can be carried out at elevated temperatures (with no equilibrium problems). Thus there has been little interest in whether the mineral matter or trace elements catalyze the combustion reaction and certainly no thought of deliberately adding potential catalysts. It is true that in combustion there have been major problems with boiler tube deposits reducing heat transfer and rated furnace performance. Accordingly, there has been interest shown in possibly relating boiler tube deposition to the nature of the mineral matter in the coal used. However, negligible effort in this direction has been made because of the absence, until recently, of the low-temperature ashing (LTA) approach to separate the mineral matter from the coal essentially unchanged. Gluskoter in the material included in this report discusses LTA briefly and gives appropriate references.

By contrast with the carbon-oxygen reaction, the carbon-steam, the carbon-carbon dioxide, and the carbon-hydrogen reactions are much slower. Walker et al (1) estimate that in the absence of significant mass transport resistance the relative rates of the $C-O_2$, $C-H_2O$, $C-CO_2$, and $C-H_2$ reactions under similar temperature and pressure conditions are 10^5, 3, 1, and 10^{-3}, respectively. That is, there is essentially a 10^8 spread in these reactivities. For the C-H_2O and C-CO_2 reactions, this spread can be alleviated by operating at increasing temperatures to increase rates without encountering equilibrium conversion limitations. Obviously, however, from the standpoint of cost of materials of construction used in gasification reactors there is an incentive to not operate at too high a temperature. When one considers the C-H_2 reaction to produce methane, the situation becomes much more serious. Not only is this the slowest gasification reaction; but since it is exothermic, increases in temperature increasingly restrict the upper limit of conversion to methane. Therefore, there is no doubt that the roll which mineral matter and trace elements might play in catalyzing the gasification reactions will become a subject of major interest -- and rightly so.

If it is further appreciated that since the mineral matter in coals appears to lead to ashes with high catalytic activity and reactivity for removal of H_2S and COS from product streams from gasifiers, interest in mineral matter is further stimulated. That is, the Morgantown Energy Research Center of the U. S. Bureau of Mines has reported results on the removal of H_2S from a simulated producer gas at temperatures between 600-850°C and, pressures between 1-8 atm using a 25% Fe_2O_3-75% sintered fly ash.

In the conversion of coal to a clean liquid fuel, there is again much interest in catalysis. There is much incentive to keep the temperature down to maximize liquid yield and to minimize gas yield. There is also much incentive to eliminate sulfur from the system as H_2S concurrently with liquefaction of the coal. To operate at lower temperatures and to effectively remove sulfur from the product, catalysts are needed. Again there is much interest in the possible catalytic activity of the mineral matter and also much concern that some trace elements may poison a catalyst which is deliberately added to the system.

Therefore, there is no doubt that characterization of the mineral matter and trace elements in American coals is of prime importance if coal gasification and coal liquefaction processes are to be optimized. Indeed, it is now recognized that the same is probably true for the combustion of coal.

II. Status of Characterization of Mineral Matter and Trace Elements

As discussed by Gluskoter in the material included in this report, much progress has been made in characterization in the past decade. The use of LTA has enabled us to separate the mineral matter from the coal. Using X-ray diffraction and infra-red approaches O'Gorman and Walker (2,3), among others, have shown that it is possible to present semi-quantitative or quantitative data (depending upon the precision used) on the amounts of the major minerals existing in a coal sample. In addition to the commonly occurring minerals like kaolinite, illite, montmorillonite, calcite, pyrite, and quartz, they show that some coals have significant amounts of gypsum, rutile, chlorite, siderite, dolomite, and muscovite. The point is that the quantitative determination of any minerals in coals which exists down to about 1% of the total minerals present can now be made.

Further, the major and trace elements in coals can be measured quantitatively using either the high temperature ash or the LTA material (2). It is, of course, simpler to produce an ash sample by air oxidation at an elevated temperature than it is to produce an LTA sample. In most cases, insignificant vaporization of the elements occurs during this ashing and thus it can be used. However, there are major exceptions, for example mercury which vaporizes significantly under high temperature ashing (4). In this case, analysis of the LTA material is required. Elements present in major amounts are generally determined by atomic adsorption (5). Elements present in trace amounts are determined either by atomic absorption or emission spectroscopy. Neutron activation analysis and x-ray fluorescence analysis can also be used. The point is that the know-how is present to analyze for the major and minor metallic elements in coal.

There is absolutely no excuse for the characterization of mineral matter and trace elements in coals not being made, as described briefly above, if the data appear to be of importance. It is suggested that today a significant segment of the electric power industry utilizing coal is not aware that these characterization procedures exist. A recent letter from Professor Gould is included to support this point. Gluskoter concludes that there are only four laboratories in the United States which, to his knowledge, have demonstrated competence in the chemical, mineralogical, and petrographic analysis of coal: Illinois State Geological Survey, Pennsylvania State University, U. S. Bureau of Mines, and U. S. Geological Survey. In some way effective coupling must be set up between the electric power industry and these laboratories so that the industry can benefit from the laboratories expertise. Some continuing support from EPRI for these laboratories would appear to be in order to assure their continuing capabilities in this characterization area.

III. Additional Information Which We Want on Mineral Matter and Trace Elements

It is clear that if we are truly going to understand the relation between mineral matter and trace elements in coal and their role in catalysis of coal conversion processes (as well as other important processes to EPRI such as filtration of coal solutions and preparation processes) there is much more that we need to know about these materials. At least a partial list of additional characterization parameters we would like to be able to measure is as follows:

a. Distribution in particle size and shape of the major minerals as they occur in coal.

b. Association of minerals with particular macerals.

c. In a particle assemblage of ground coal, a weight or volume percent distribution of particles going from 100% coal to 100% mineral -- and identification of what mineral or minerals are in each particle.

d. Trace elements associated with major minerals and coaly region, their distribution and bonding.

IV. Approaches Being Studies at Penn State to Obtain Additional Data

Whereas some of the approaches described below may also be in the process of being studied in laboratories other than Penn State, this writer will confine his remarks to Penn State studies since he knows them the best. It is certain, in any case, that not much total effort is underway in the United States at this time.

A. CESEMI

Consider, first, item IIIa above. White and co-workers at Penn State have been studying the characterization of coal mine dust for the past four years (6,7). In essence the research tool developed by Dr. White called CESEMI (Computer Evaluation of Scanning Electron Microscope Images) involves computerization of the scan control and data output of a JSM-1 scanning electron microscope (SEM) so that the size and location of any given particle in the field being scanned is coded into the computer. By energy discrimination on the characteristic x-ray emission spectra, it is possible to discriminate among elements from Na up, and estimate the amounts present at the extremely small point at which the instrument is focused. By comparing the ratios of elements present, a mineral identification of each particle can be made together with its size and shape. When a statistically significant number of particles have been analyzed, data are processed by computer to summarize the size and shape distribution characteristics of each particle type. See Tables 1(a) and 1(b) for an example of such an analysis.

In the present apparatus a series of x-ray detectors have been optimized for the simultaneous detection of C, Al, Si, S, Ca, and Fe. As is seen in Table 1(a), this permits the identification of 31 different particle types including carbon (coal), alumina, quartz, kaolinite, calcite, illite, gypsum, and pyrite. Obviously the x-ray detectors can be set to look for other elements if desired, that is, if other elemental compositions giving other minerals are of interest.

Table 1(b) summarizes the form in which the data are supplied. The important information for each particle type includes: percentage of total number of particles, percentage of total area of particles, average surface area, average equivalent circular diameter, and weight % of actual particles. This approach is particularly suitable for the <10μm material and can be used directly on the screened LTA material of less than this size. For sizes >10μm, the particles can be imbedded in an appropriate mounting medium and characterized as polished sections. Studies are now underway to evaluate CESEMI for characterization of mineral matter particles and to compare values obtained for weight distribution with that obtained by chemical characterization of the mineral matter as described in Section II.

The technique also appears to be useful in the characterization of mineral matter particles in the size range 0.5-100μm in polished sections of coal. Studies along this line should also be pursued.

It is estimated that it would require over $175,000 to duplicate this CESEMI apparatus. A system with improved resolution using an available JSM-50A SEM and a dedicated computer (like the PDP 11/20) could be developed

TABLE 1A

PARTICLE TYPE IDENTIFICATION USED IN CESEMI ANALYSIS OF COAL MINE DUST

	IDENTIFICATION	CHANNEL 1 SEC. ELEC.	CHANNEL 2 ALUMINUM	CHANNEL 3 SILICON	CHANNEL 4 SULFUR	CHANNEL 5 CA	CHANNEL 6 IRON
0	COAL	X					
1	AL2O3	X	X				
2	QUARTZ	X		X			
3	KAOLINITE	X	X	X			
4	ROCK FRAGMENT	X			X		
5	ROCK FRAGMENT	X	X		X		
6	ROCK FRAGMENT	X		X	X		
7	ROCK FRAGMENT	X	X	X	X		
8	CALCITE	X				X	
9	ROCK FRAGMENT	X	X			X	
10	ROCK FRAGMENT	X		X		X	
11	ILLITE/FELDSPAR	X	X	X		X	
12	GYPSUM	X			X	X	
13	ROCK FRAGMENT	X	X		X	X	
14	ROCK FRAGMENT	X		X	X	X	
15	ROCK FRAGMENT	X	X	X	X	X	
16	IRON OXIDE	X					X
17	ROCK FRAGMENT	X	X				X
18	ROCK FRAGMENT	X		X			X
19	ROCK FRAGMENT	X	X	X			X
20	PYRITE	X			X		X
21	ROCK FRAGMENT	X	X		X		X
22	ROCK FRAGMENT	X		X	X		X
23	ROCK FRAGMENT	X	X	X	X		X
24	ROCK FRAGMENT	X				X	X
25	ROCK FRAGMENT	X	X			X	X
26	ROCK FRAGMENT	X		X		X	X
27	MICA	X	X	X		X	X
28	ROCK FRAGMENT	X			X	X	X
29	ROCK FRAGMENT	X	X		X	X	X
30	ROCK FRAGMENT	X		X	X	X	X
31	ROCK FRAGMENT	X	X	X	X	X	X
32	TOTAL OF ALL ROCK FRAGMENTS						

TABLE 1B

SUMMARY TABLE FOR COAL MINE DUST SAMPLE FOR CESEMI ANALYSIS

PARTICLE TYPE	DENSITY GRAMS PER (CM**3)	NUMBER OF PARTICLES	STATISTICAL NUMBER OF PARTICLES	PERCENT OF TOTAL NUMBER OF PARTICLES	AREA OF PARTICLES SQUARE MICRONS	PERCENT OF TOTAL AREA OF PARTICLES	AVERAGE SIZE AREA SQUARE MICRONS	AVERAGE EQUIVALENT CIRCULAR DIAMETER MICRONS	WEIGHT OF AVERAGE PARTICLES 10**-12GM	WEIGHT % OF AVERAGE PARTICLES	WEIGHT OF ACTUAL PARTICLES 10**-12GM	WEIGHT % OF ACTUAL PARTICLES
0	1.30	705	705	81.88	6097.5	82.23	8.65	3.32	17535.4	61.8	40586.2	73.7
1	4.00	7	7	0.81	38.3	0.52	5.48	2.64	269.9	1.0	391.3	0.6
2	2.65	29	29	3.37	431.2	5.82	14.87	4.35	3315.1	11.7	4032.3	7.4
3	2.65	5	5	0.58	96.4	1.30	19.28	4.95	843.8	3.0	1408.4	2.6
4	3.00	17	17	1.97	124.2	1.68	7.31	3.05	759.0	2.7	1442.1	2.6
6	3.00	3	3	0.35	3.6	0.05	1.19	1.23	8.7	0.0	10.0	0.0
8	2.72	66	66	7.67	259.0	3.50	3.94	2.24	1056.6	3.7	1629.0	2.9
12	2.30	1	1	0.12	11.6	0.16	11.56	3.84	68.0	0.2	68.0	0.1
16	5.20	18	18	2.09	247.8	3.34	13.77	4.19	3596.6	12.7	5494.4	9.9
18	3.00	1	1	0.12	19.8	0.27	19.78	5.02	198.9	0.7	198.5	0.4
20	5.00	1	1	0.12	0.8	0.01	0.83	1.02	2.9	0.0	2.9	0.0
24	3.00	7	7	0.81	53.1	0.72	7.59	3.11	330.2	1.2	484.2	0.9
26	3.00	1	1	0.12	31.1	0.42	31.11	6.29	391.6	1.4	391.6	0.7
32	3.00	29	29	3.37	231.6	3.13	7.99	3.19	1478.0	5.2	2469.5	4.5

for another $50,000.

B. Direct Linear Analysis of Mineral Grains in Polished Coal Sections

In the SEM, a backscattered electron signal (the elastically scattered primary electrons and not the low energy electron used for the usual SEM images) yields an image of a polished section of coal in which the brightness is greater for the densest material. All coal macerals are relatively dark in these EBS images because the H,C,N,O, of the organic matter forms a matrix of low atomic number. Silicate and carbonate mineral grains yield a signal of intermediate brightness while pyrite is the brightest of the commonly occurring minerals in coal. Dr. White has shown how EBS can be used to characterize the mineral matter in coal.

This is illustrated in the accompanying micrographs taken from a polished grain mount of coal. Figure 1(a) is the unaltered EBS image taken at 100X magnification. Here the darkest parts of the image are coal and/or mounting epoxy, the gray is from silicate mineral grains and the brightest areas are pyrite. Figure 1(b) is a processed signal image in which all mineral areas are bright and the non-mineral regions are black. Figure 1(c) is a processed signal image showing all pyrite fields as bright while all non-pyrite minerals and carbonaceous material is black. Figure 1 is from a sample concentrated in "heavies". Figure 2 is a SEM micrograph for a more typical polished section of coal grains (-14 mesh). This image, recorded at 300X, is for the NBS standard coal 1631A. Although not resolved in the image, the beam was actually generated by a dense matrix of discrete picture points as picture elements. In this case the beam was advanced by a digital sweep generator scanning at 1024 picture points per line and scanning a total of 512 lines.

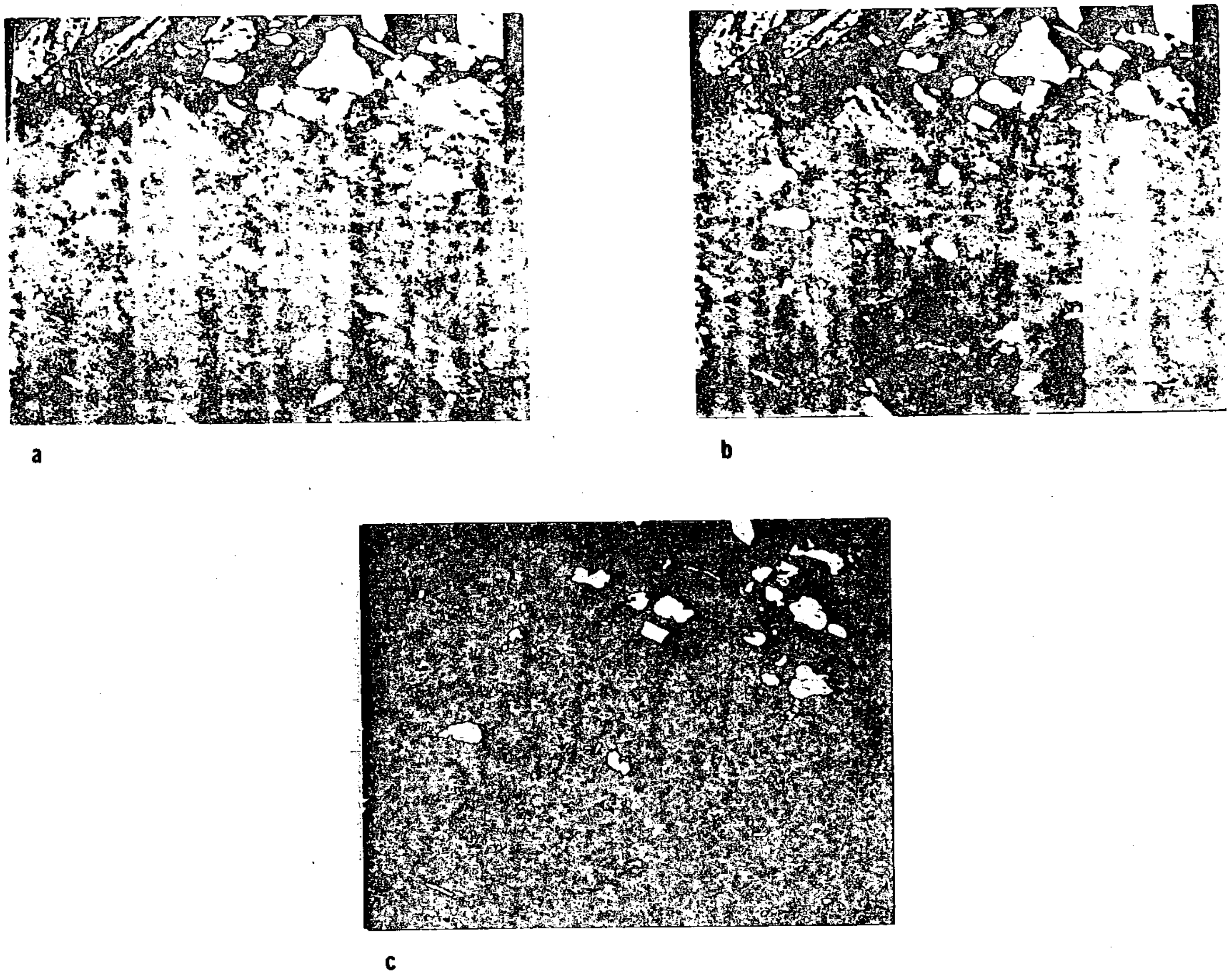

FIGURE 1. Electron Backscattering Images: (a) unaltered EBS image, (b) total mineral is bright, (c) only pyrite is bright. Magnification 100X.

FIGURE 2. SEM Micrograph For a More Typical Polished Section of Coal Grains.

The electronics used to make the black/white images seen in Figures 1(b) and 1(c) also are used to determine the lengths of intercepts for each "on" segment (bright areas) of the scan lines. These "cord lengths" are stored in a multichannel analyses (MCA) in such a way as to build up a spectrum of chord lengths. In the example given here a total of seven frames (images) like the one in Figure 2 were accumulated to form a composite spectrum, with the data being displayed by direct teletype printout. These data in turn are fed into a PDP 11/20 computer programmed to generate grain size distributions using the basic Kahn and Fullman Formula. Information generated includes the number and percentage of particles in particular size ranges, the area and volume percentage occupied by mineral grains, and the average distance travelled between mineral grains. As is suggested by Figure 1(c), if the information is desired only on the pyrite this can be supplied.

C. Mineral Characterization by Reflectance Measurements

Without doubt the mineral in coal which is of most importance is pyrite, not only because it is the precursor of metallic iron which can have high catalytic activity but also because of its importance from the standpoint of pollution considerations. Of all the major minerals in coal, pyrite has by far the highest reflectance to normal light. Its reflectance is also much higher than the coaly material. Reflectances of the major macerals in coal are vitrinite (0.8-1.0%), exinite (<0.4%), and fusinite-micrinite (2.0-7.0%); by contrast, pyrite has a reflectance of about 50%. Thus one approach which has been used to characterize pyrite in polished sections of coal has been based on these major differences in reflectivity. Indeed, commercial Ameda units have been used to some extent for this purpose in the United States.

Drs. Spackman and Vastola, in the Coal Laboratories at Penn State, have begun to automate this approach with considerable success. They have worked with either polished sections of coal or crushed coal samples which are cast in a resin matrix followed by surface polishing. To expedite the characterization of pyrite particle size, an automated system based on a photometric reflectance measuring system, an automatic microscope stage drive and a computerized data acquisition system has been developed. The resolution of the present system is 2μm, using a conventional Lietz microscope. Data obtained by the automated system can be processed by the computer (a PDP-9) to produce an output in the form shown in Table 2 for a particular sample. At the present maximum rate of traverse across the polished section (about 400 optical fields per second), it is possible to characterize about 10,000 particles in 6 min. Not only is it possible in a number of size fractions to give the percentage of coal and percentage of pyrite but also to break down the number of particles going from 0 to 100% pyrite.

Another real possibility will be to study the association of the pyrite particles with particular macerals, since the macerals differ in reflectance. However, since their differences in reflectance are not large (as previously pointed out) it will be necessary to improve the system somewhat to make this discrimination. For example, the incandescent light source presently being used would be replaced by higher intensity illumination from a CW gas laser source. It is estimated that this improved system can be obtained for an additional $20,000. Part of this expense would be involved in obtaining a minimum configuration microcomputer to be used for data acquisition. By interfacing the mini computer with the existing computer facility (PDP-9) it will use the main computer input/output and bulk storage facilities that are already available.

TABLE 2

COMPUTER OUTPUT FROM REFLECTANCE MEASUREMENTS

Total Pyrite %

Total Free Pyrite %

Total Edge Pyrite %

Size Microns	% Distribution		Percent Particles with Pyrite Compositions of					
	Coal	Pyrite	0	20	40	60	80	100%
< 5								
5- 10								
10- 20								
20- 30								
30- 40								
40- 50								
50- 75								
75-100								
100-150								
> 150								

D. Electron Microprobe

There should be interest in the distribution of trace and minor elements in both major mineral regions and organic regions found in coal. Limited efforts to obtain results of this type on coal have been made using an electron microprobe (8). Microprobes have been improved considerably recently in sensitivity and automation. For example, an Applied Research Laboratory instrument, with three spectrometers, with a computer costs about $175,000. However, it is felt that before spending this kind of money studies should be made using older and cheaper models, such as the ARL-AMX unit, to determine how much valuable data can be generated. For example, titanium is of particular interest since it appears to poison the cobalt molybdenum sulfide catalyst used in coal liquefaction. It is felt that the titanium in the rutile (TiO_2) mineral is not causing the problem, but rather the titanium which is thought to be organically bonded in the coal structure. Could the electron microprobe measure the extent of uniformity of distribution of the organically bonded titanium?

Further, we would like to know more about the particular macerals with which the trace elements might be primarily associated. In principal, this type of information can be obtained using the microprobe.

E. Summary

It is certain that the more information of the type discussed above is is possible to obtain the better chance we have of understanding the role of trace elements and mineral matter in catalyzing or inhibiting gasification and liquefaction reactions. Some of these analyses discussed require expensive equipment and are non-routine. They would only be used on particular samples on which meaningful process results have been obtained.

In the meantime, however, the characterization procedures must be thoroughly studied so that confidence is gained in their capabilities and their limitations are fully understood.

REFERENCES

1. P. L. Walker, Jr., Frank Rusinko, Jr., and L. G. Austin, Advances in Catalysis, Vol. XI, pp. 133-221 (1959).

2. J. V. O'Gorman and P. L. Walker, Jr., "Mineral Matter and Trace Elements in U. S. Coals", Office of Coal Research, U. S. Department of the Interior, Research & Development Report No. 61, Interim Report No. 2, 184 pp (1972).

3. J. V. O'Gorman and P. L. Walker, Jr., Fuel, 50, 135 (1971).

4. J. V. O'Gorman, N. H. Suhr, and P. L. Walker, Jr., Appl. Spectroscopy, 26, 44 (1972).

5. J. H. Medlin, N. H. Suhr, and J. B. Bodkin, Atomic Absorption Newsletter, 8, (2), 25 (1969).

6. E. W. White, Annals N.Y. Acad. Sc., 200, 666 (1972).

7. E. W. White, K. Mayberry, and G. G. Johnson, Jr., Pattern Recognition, 4, 173 (1972).

8. R. R. Dutcher, E. W. White, and W. Spackman, "Elemental Ash Distribution in Coal Components - Use of the Electron Probe", Proceedings 22nd Ironmaking Conference, Iron Steel Division, Metallurgical Society, Amer. Inst. Mining Engr., pp. 463-483 (1964).

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16. Abstracts

The use of catalysts in coal conversion processes is reviewed, and a research and development program is recommended for catalysis in future conversion technology. Emphasis is on those processes leading to clean fuels for electric power generation. The argument of the text consists of a series of articles on the subject of catalysis, including catalysts for hydrosulfurization and liquifaction of coal, and catalysts for low-sulfur producer gas for power stations, commense the treatment and the catalytic properties of coals--specifically the beneficial modifications by additives. Also reviewed are Fischer-Tropsch catalysts to produce jet fuel and methanol for peaking power. An article on Lewis acid ($ZnCl_2$) catalytic liquifaction is analyzed, followed by a consideration of supporting research including the mechanism of bond breaking in coal catalysis, and center ring cracking of polynuclear aromatic structures, and lastly a review of new catalyst materials. A literature survey containing abstracts of more than 400 relevant publications is included, many of which are summarized.

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