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EPA U.S. Environmental Protection Agency
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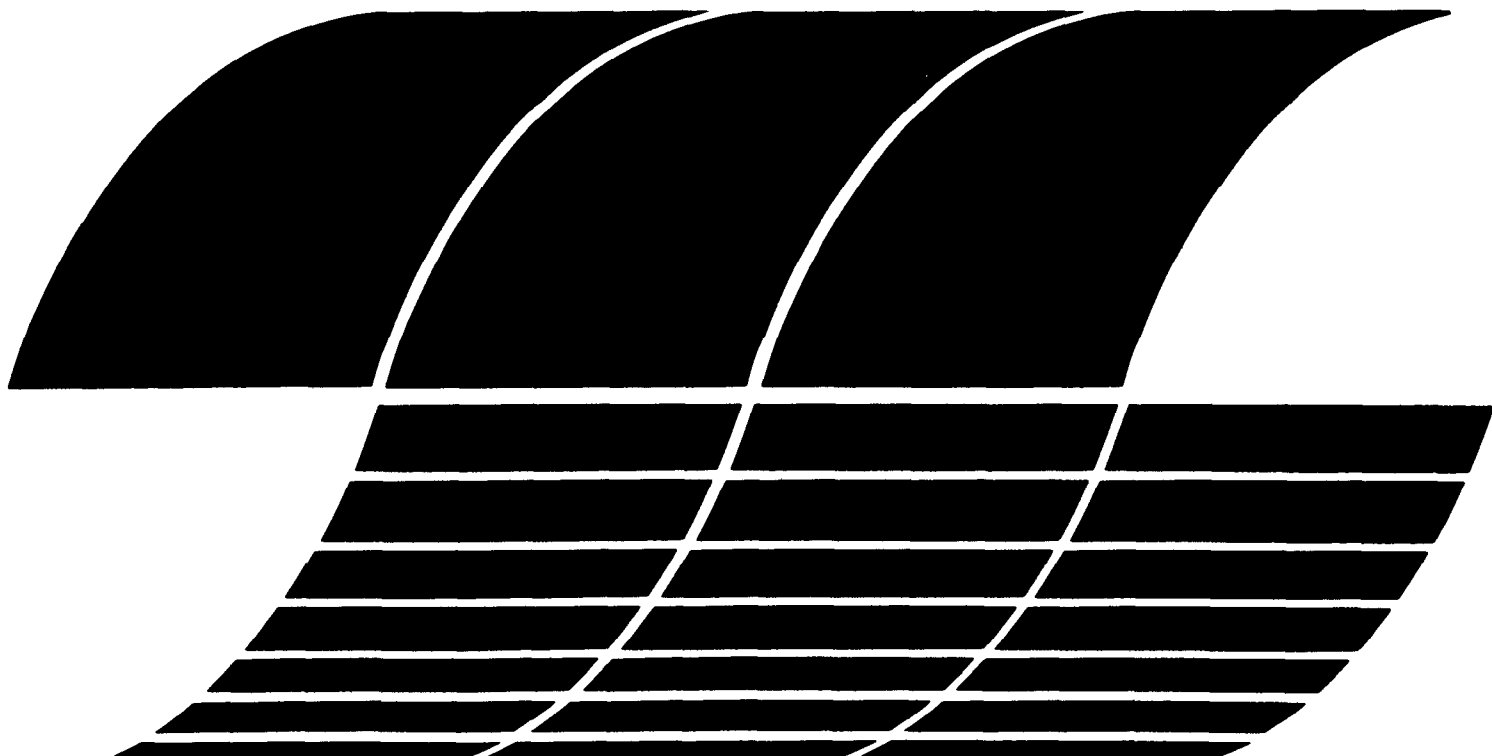# TRACE ELEMENT CHARACTERIZATION OF COAL WASTES-- FIRST ANNUAL REPORT

Interagency
Energy-Environment
Research and Development
Program Report

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EPA REVIEW NOTICE

TRACE ELEMENT

CHARACTERIZATION

OF COAL WASTES--

FIRST ANNUAL REPORT

JULY 1, 1975 TO JUNE 30, 1976

by

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FIRST ANNUAL REPORT

Eugene M. Wewerka and Joel M. Williams

ABSTRACT

The literature search on the chemistry and environmental behavior of trace elements in coal cleaning wastes has been completed, and an interpretive report of the findings from the literature has been written. Techniques and methods for analyzing trace elements and minerals in coals and coal cleaning wastes have been developed and are documented in this report. Standard coal and ash samples were used to establish the precision and accuracy of these methods. High-sulfur coal-waste materials have been collected from three coal cleaning plants in the Illinois Basin, and cleaning wastes from a low-sulfur coal have also been collected. Analytical studies of the trace elements and minerals in these wastes are progressing, and investigations of the effects of weathering and leaching on the trace elements in the refuse have been started.

SUMMARY OF TASK PROGRESS

The major objective of this research program is to assess the potential for environmental pollution from trace or minor elements that are discharged or emitted from coal preparation wastes, and to identify suitable environmental control measures should they be needed. An additional objective is to investigate methods to economically recover useful trace elements or minerals from coal refuse matter. The technical accomplishments in each of the main areas of the program for the period July 1, 1975, to June 30, 1976, are presented in this report.

As outlined in the Work Plan, the technical activities of this program for the current fiscal year are broken into major tasks and subtasks. These are shown in Table I. Generally, we succeeded in accomplishing the project objectives and milestones as outlined.

The activities under Task 1, Literature Search and Program Planning, have been completed. An extensive literature search on the chemistry and environmental behavior of trace elements in coal preparation wastes has been completed, and a report and commentary on the literature as it pertains to the present work has been written (Subtask 1.1). Subtasks 1.2 through 1.5 concern

TABLE I

TASK BREAKDOWN
TRACE ELEMENTS CHARACTERIZATION
AND REMOVAL/RECOVERY

TASK 1	TASK 2	TASK 3
LITERATURE SEARCH AND PROGRAM PLANNING	LABORATORY PROGRAM FOR TRACE ELEMENTS CHARACTERIZATION	LABORATORY PROGRAM FOR TRACE ELEMENTS REMOVAL/RECOVERY
1.1 LITERATURE SEARCH ON TRACE ELEMENT CHEM. AND COAL CLEANING PROCESSES	2.1 STANDARDIZE ANALYTICAL TECHNIQUES AND DEVELOP METHODS	3.1 EVALUATE NEW CHEMICAL OR PHYSICAL REMOVAL PROCESSES
1.2 EVALUATE PREVIOUS WORK ON CLEANING PROCESSES AND WASTES	2.2 COLLECT COAL AND WASTE SAMPLES	3.2 SUGGEST NEW OR MODIFIED STEPS TO EFFECT REMOVAL
1.3 REVIEW TECHNOLOGY OF COAL CLEANING PROCESSES	2.3 DETERMINE TRACE ELEMENT DISPOSITION IN CLEANING PROCESS	
1.4 REVIEW CHEMISTRY OF TRACE ELEMENTS IN RESIDUES	2.4 IDENTIFY TRACE ELEMENTS OF CONCERN	
1.5 IDENTIFY TRACE ELEMENTS OF INTEREST	2.5 CHARACTERIZE CHEMISTRY OF WASTES	
1.6 CHOOSE CLEANING PROCESS AND RESIDUES	2.6 CHARACTERIZE ENVIRONMENTAL BEHAVIOR OF WASTES	
	2.7 DEVELOP PROCEDURES FOR TRACE ELEMENT SEPARATIONS	

topics which were addressed in the literature search, and a commentary about each is given in the following section on task progress and in the literature search report. Subtask 1.6 was completed when the decision was made to initially concentrate our studies on coal preparation wastes from the Illinois Basin.

We have also made considerable progress on Task 2—Laboratory Program for Trace Elements Characterization. Methods for analyzing trace elements in coals and coal refuse have been developed and standardized (Subtask 2.1). Also, representative samples of both fresh and weathered coal preparation wastes have been collected (Subtask 2.2). We did not conduct a complete trace element balance of a coal cleaning plant, as was originally planned in Subtask 2.3; however, a preliminary indication of the fate of trace elements in the cleaning plants studied can be obtained from the analyses of the feed and cleaned coals and reject waste materials from each plant. Work on Subtask 2.4 is progressing. A preliminary identification of the trace elements of environmental concern in coal preparation wastes will be made on the completion of the initial characterization work, it is hoped, early in FY 77. As outlined in Subtask 2.5, analytical studies to determine the chemical forms, mineralogy, and associations of the trace elements in the coal waste samples are being conducted and laboratory investigations of the effects of weathering and leaching on the trace elements in coal refuse (Subtask 2.6) are under way. Regarding Subtask 2.7, we are initially investigating the segregation of trace elements according to particle size in coal refuse, and the possibility that particle size can be used as an effective method for separating certain trace elements from coal wastes.

Although we have begun exploring methods to remove or recover specific trace elements from coal preparation wastes as outlined in Task 3—Laboratory Program for Trace Elements Removal/Recovery—it is not likely that we can make a great deal of progress in this area until specific environmental problems are defined by our initial studies. However, some of our work (for example, the separation of trace elements by waste particle size, and the removal or recovery of specific trace elements by aqueous leaching techniques) directly applies to this phase of the program.

TASK PROGRESS DESCRIPTION

TASK 1—LITERATURE SEARCH AND PROGRAM PLANNING

Subtask 1.1—Literature Search

A literature search on the chemistry and environmental behavior of trace elements in coal preparation wastes has been completed. A comprehensive report and commentary on the literature, as it pertains to the present program, has been written. The general content of the literature search report is too broad to be adequately discussed here; however, a summary of the main conclusions which were drawn from our studies of the available literature appear in Appendix A. The literature report is now being reviewed by ERDA and EPA, and preprints should be available during the next quarter.

In addition, a computer interactive storage system, which includes all pertinent references obtained from the literature search has been established. At present, there are about 450 references in the data base, and the list will be updated periodically. A computer search and retrieval system, based on key-word identification can be used to comb the file. Use of this data base by interested individuals or organizations can be arranged upon request.

Subtasks 1.2 and 1.3—Review Previous Work and Technology of Trace Elements in Coal Cleaning Processes

These subtasks, as well as Subtasks 1.4 and 1.5, were addressed as subjects in the literature search. As detailed in the literature report, we found little to guide us concerning either the effects of the various types of coal cleaning methods on the trace elements in raw coals, or the fate of trace elements in general during coal cleaning. Only a few studies in this area have been reported, and most of these are based on laboratory float-sink work.

Subtask 1.4—Review Chemistry of Trace Elements in Coal Preparation Wastes

Only preliminary work on the chemistry of trace elements in coal preparation wastes has been reported. Available information is mainly devoted to the identification of the major minerals in the wastes. Some insight into the chemistry and behavior of trace elements in coal mineral wastes was obtained from studies of raw coals. But here again, little actual chemistry has been investigated; the bulk of the attention has focused on identifying the minerals and trace elements present in coals.

Subtask 1.5—Identify Trace Elements of Interest

Based on available information, an adequate assessment of the extent or seriousness of environmental contamination from coal preparation wastes cannot be made. Certain ions, such as iron, aluminum, and manganese, leach out of coal refuse dumps in toxic amounts; however, there is little information available about the leachability or environmental behavior of most trace elements present in coal refuse. A preliminary identification of the trace elements of environmental concern in coal wastes will be made when our initial characterization work is completed early in the next fiscal year. A more complete assessment of the total potential for environmental pollution from trace elements in coal wastes will be made near the end of the next fiscal year.

Subtask 1.6—Choice of Cleaning Processes and Wastes

Based on the literature search and discussions with authorities in the field of coal chemistry and mineralogy, we have decided to concentrate our initial laboratory work on coal waste materials from the Illinois Basin (U.S. Eastern Interior Region). This area was chosen for several reasons:
  • The coals from the Illinois Basin are widely used; they represent about 25% of the total US production.
  • Illinois Basin coals are highly mineralized—ROM coals typically contain 10-40 wt% mineral matter—and they contain a broad array of trace elements.
  • The coals from this basin contain relatively high amounts (3-5 wt%) of pyritic sulfur.
In addition, there is ample rainfall and surface-water drainage in the region so that extensive waste pile weathering and leaching can be expected. All things considered, we believe that the waste materials from the Illinois Basin present nearly maximum possibilities for environmental contamination, as well as great potential for mineral or trace element recovery, and that they come as close as possible to what could be called "typical" or "representative" coal cleaning wastes.

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TASK 2—LABORATORY PROGRAM FOR TRACE ELEMENTS CHARACTERIZATION

Subtask 2.1—Develop and Standardize Analytical Techniques and Methods

During the past year, a substantial effort was devoted to developing and standardizing methods for analyzing trace elements and mineral matter in coals and coal cleaning wastes. Evaluation of these techniques was based upon analyses of NBS-SRM and other standard coal and ash samples. The results obtained clearly demonstrate that the LASL analytical methods are both suitable and reliable for the analysis and characterization of coal and coal waste materials. The details of specific procedures and methods, and the results of the standard coal and ash analyses, are given in Appendix B, and are only briefly described in this section.

Procedures were established for reducing the considerable bulk of coal and waste materials collected from the field to a quantity suitable for laboratory work. This process, which involves a series of crushing, dividing, and blending steps, is based on the ASTM methods for preparing analytical samples from coals (D-2013) and aggregates (C-702).

Methods for both low- and high-temperature ashing of coal and waste samples were developed. Low-temperature ashing is particularly useful for concentrating the mineral matter in coals or coaly substances without significantly altering the character or structure of the minerals.

The extensive analytical capabilities at LASL were tapped to establish methods for identifying and characterizing trace elements and minerals in coals and coal cleaning wastes. For trace and minor element analyses, neutron activation analysis (NAA) is used extensively because raw coal and waste materials can be analyzed directly with a minimum of sample preparation, many elements can be observed simultaneously, and the method is reliable and accurate (Appendix B). A number of elements are not readily determined by NAA, and other techniques are used for these characterizations. These techniques include optical emission spectroscopy (OES), atomic absorption spectrophotometry (AA), x-ray fluorescence (XRF), electron microprobe (EM), ion microprobe (IM) and wet-chemical methods. Most of the remaining analyses are done by AA or OES. AA and OES methods have been widely used to analyze coals and mineral materials; the general usefulness, reliability, and precision of both methods are well established. A compilation of preferred LASL methods for analyzing various major and minor elements in coals and coal cleaning wastes appears in Table II. Where more than one technique can be applied to a specific analytical task, the method or combination of methods used will provide the necessary speed, sensitivity, and precision with the least expense.

The characterization of the crystalline mineral phases in the samples of interest is done largely by x-ray diffraction (XRD). Both qualitative and quantitative XRD analyses can be done directly on the highly mineralized coal-waste samples. However, because of dilution and interference from the organic components, quantitative results for most of the common minerals in raw coals are best obtained by examining the low-temperature ash. In some instances mineral phases are undetectable by XRD, particularly when they are amorphous or present in low concentrations. For this circumstance, the more sensitive electron microprobe may provide the necessary information.

Wet-chemical methods are used to determine the carbon, hydrogen, nitrogen, and sulfur contents of the coal and waste samples. Also, wet chemistry is used to prepare samples for chlorine and fluorine analyses using ion specific electrodes. Other properties of coals and wastes, such as moisture, volatile matter, and ash, are also determined using ASTM techniques.

TABLE II

PREFERRED LASL METHODS FOR ELEMENTAL ANALYSES
OF COALS AND COAL WASTES

Element	Method	Element	Method
Li	AA, OES	Br	NAA
Be	AA, OES	Rb	NAA, OES
B	OES	Sr	NAA
F	C	Y	OES
Na	NAA	Zr	OES
Mg	NAA, OES	Mo	OES
Al	NAA, OES	Ag	AA
Si	AA, OES, C	Cd	AA
P	AA, C	Sn	OES
S	C	Sb	NAA
Cl	NAA, C	I	NAA
K	NAA, OES	Cs	NAA
Ca	NAA	Ba	NAA
Sc	NAA, OES	La	NAA, OES
Ti	NAA, AA	Ce	NAA
V	NAA, AA, OES	Sm	NAA
Cr	NAA, AA, OES	Eu	NAA, OES
Mn	NAA, AA, OES	Tb	NAA
Fe	NAA, AA	Yb	NAA, OES
Co	NAA, AA, OES	Lu	NAA
Ni	AA, OES	Hf	NAA
Cu	AA, OES	Ta	NAA
Zn	NAA, AA	W	NAA
Ga	NAA, OES	Hg	NAA, AA
Ge	OES	Pb	AA, OES
As	NAA, AA	Th	NAA
Se	NAA	U	NAA

NAA—Neutron Activation Analysis.
AA—Atomic Absorption Spectrophotometry.
OES—Optical Emission Spectroscopy.
C—Chemical Methods.

Subtask 2.2—Collect Coal and Waste Samples

Samples of cleaning wastes from high-sulfur coals were collected from three coal preparation plants in the Illinois Basin and from a cleaning plant for a low-sulfur coal located in another

region. In addition to fresh waste materials, we also obtained samples of feed coal and cleaned coal from each plant. In two instances, we collected materials from aged and weathered gob (refuse) piles.

Gob and coal sampling procedures had to be improvised somewhat for each cleaning plant depending on the accessibility of the various coal and waste streams. However, in all cases, the procedures adopted were based on ASTM methods for collecting field samples of coal (D-2234) and aggregates (D-75). To reduce the possibility of sampling errors due to size segregation, whenever it was logistically possible, materials were collected from moving belts or streams.

A more complete description of the cleaning plants that were sampled, the materials collected, and the techniques and methods used, is given in Appendix C.

While collecting the samples from the Illinois Basin, we took a few photographs of waste dump areas, and particularly, weathered wastes. These photographs vividly illustrate what appears to us to be typical landscape in and around coal-waste disposal sites.

Figure 1 is a panorama of a coal-waste dump, which is similar to those we saw in many parts of the Illinois Basin. This is an area that has been used continuously for about the last 15 yr for the disposal of wastes from a coal preparation plant. The older waste material is at the lower level in the center of the picture. The photograph was taken from another newer waste pile which had just been graded. The edge of the graded area can be seen in the foreground of the figure.

Figure 1 illustrates an interesting aspect of waste dumps that we often observed in this coal region. Disposal sites are frequently located in low-lying areas, often in or near swamps and waterways. Although such sites are undoubtedly convenient to dump into, it would seem from the standpoint of water contamination to be the worst possible circumstance. Also noteworthy is the milky-looking consistency of the water immediately to the left of the older waste pile. This is a common occurrence in the drainage from coal refuse dumps, and is probably due to an acidic suspension of iron oxides and hydroxides called "yellow boy."

A view of freshly dumped coal cleaning waste is shown in Fig. 2. These are materials that had been deposited within the previous hour and each of the piles represents one truckload of waste. The larger pieces of waste in the foreground are about 15 cm (6 in.) across. It can be seen that the larger material is segregated at the lower edge of each pile, while the finer waste is found at the apex of the pile. This size-separation phenomenon, which is typical of aggregate materials, illustrates why it is so difficult to collect representative samples from accumulations dumped from trucks or hoppers. Another feature worthy of note is the general appearance and consistency of the new job. It looks much like fresh concrete that has been prepared with a broad distribution of aggregate.

Figure 3 depicts an active waste dump in which the recently deposited refuse has been graded and smoothed. More waste will be deposited on the graded surface.

The eroded face of an 8-yr-old coal refuse pile is shown in Fig. 4. Over the years, the consistency of the gob has been changed considerably. Very few distinct "hard" particles remain. Nearly all of the material has been degraded to a fine powder, and the remaining particles are very friable or weak. Undoubtedly, with time, the exposed waste will disintegrate completely to a sand or silt-like consistency.

Figure 5 is a photograph of the graded surface of an active disposal area. The white material dispersed on the surface is iron sulfate produced by the oxidation of pyrite or marcasite. The oxidation of iron sulfides to iron sulfate is the first step in the formation of sulfuric acid; the presence of water is necessary to complete acid formation. During and after rain storms, the iron sulfate is dissolved and carried away from the surface, again leaving fresh sulfide exposed. Rainfall had been sparse just previous to the time the photograph was taken; however, our discussions with people working in the area lead us to believe that the iron sulfate illustrated in the figure
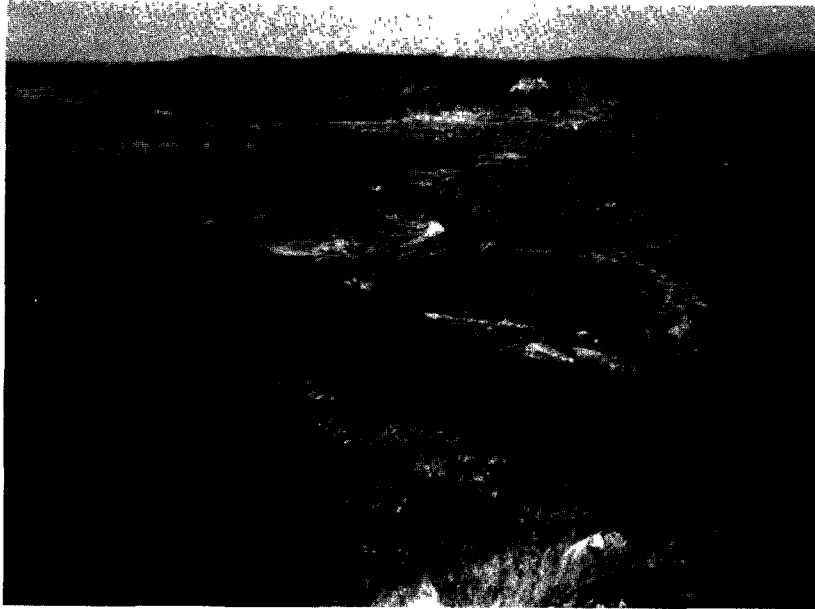
Fig. 1.
View of the landscape at an Illinois Basin coal-waste dump.

Fig. 2.
Freshly dumped coal cleaning waste.

Fig. 3.
Graded surface of an active coal refuse dump.
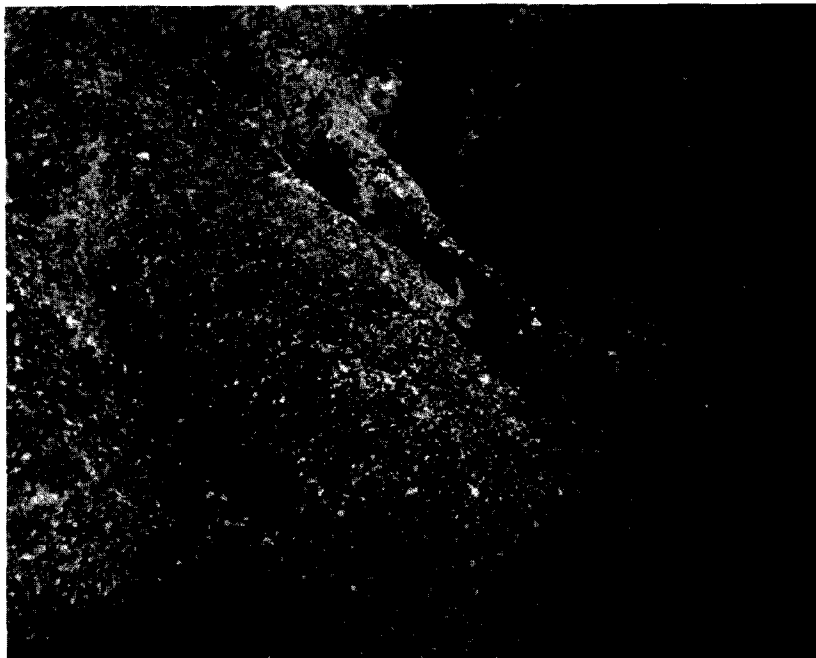
Fig. 4.
Eroded face of an 8-yr-old coal refuse pile.

was produced in a period of less than 3 months. Figure 6 shows how the sulfate concentrates in the natural drainage paths off the surface of the waste pile. Undoubtedly, much of the dissolved product is carried down into the waste pile by water seepage.

Finally, a drainage channel between two coal refuse banks is shown as Fig. 7. In this instance, the water is relatively static, so much of the suspended matter has settled out. Although it is difficult to detect from the photograph, the whole bottom of the watercourse is coated with a layer of yellow boy. As an aside, we have seen streams and waterways in the Illinois Basin that are located miles away from coal-waste dumps or mines, but are so clogged with yellow slime and mud that the rocks or debris on the stream bottom cannot be distinguished.

Subtask 2.3—Determine Trace Elements Disposition in Coal Cleaning Processes

We have begun to identify the trace elements in the feed coal, cleaned coal, and reject waste materials for the four coal cleaning plants under consideration. From these analyses, we will be able to ascertain, in a broad sense, the fate of trace elements in these commercial coal cleaning facilities. To maintain continuity in our reporting of waste analyses, the results obtained thus far in this endeavor are discussed below in the subtask on waste characterization (2.5). In addition, we are characterizing samples collected from each of the output streams of the three cells of a commercial jig or washing table; analytical results on these materials will appear in a future report.

Subtask 2.4—Identify Trace Elements of Concern

A preliminary identification of the trace elements of environmental concern in coal cleaning wastes will be made sometime in early FY 77, after the completion of the rather extensive initial waste characterization work now under way (see below). A more complete assessment of the trace elements in coal refuse, which may cause the greatest environmental problems, will be forthcoming near the end of the second year of this program.

Subtask 2.5—Characterization of Coal Preparation Wastes

We are now characterizing coal and waste samples from four different coal cleaning operations. Three of these, Plants A, B, and C, are from the Illinois Basin. The types of samples collected from these cleaning plants, and the procedures used, are described in Appendix C. In addition to the Illinois Basin samples, all of which are high-sulfur coal and wastes, we have collected some low-sulfur feed coal and waste from a cleaning plant located in another coal basin (Plant D). Because these latter materials represent a compositional contrast to the high-sulfur wastes from the Illinois Basin, we have included them in our initial studies. Samples of weathered coal refuse were also collected from two of the Illinois-Basin facilities.

Since we collected these samples, many of them have been divided according to particle size. We have 67 coal and waste samples in various stages of analysis. Quite obviously some of these materials will be characterized somewhat more extensively than others. A listing of these samples is given in Table III, together with information about the analyses which have, or will be, performed on each.
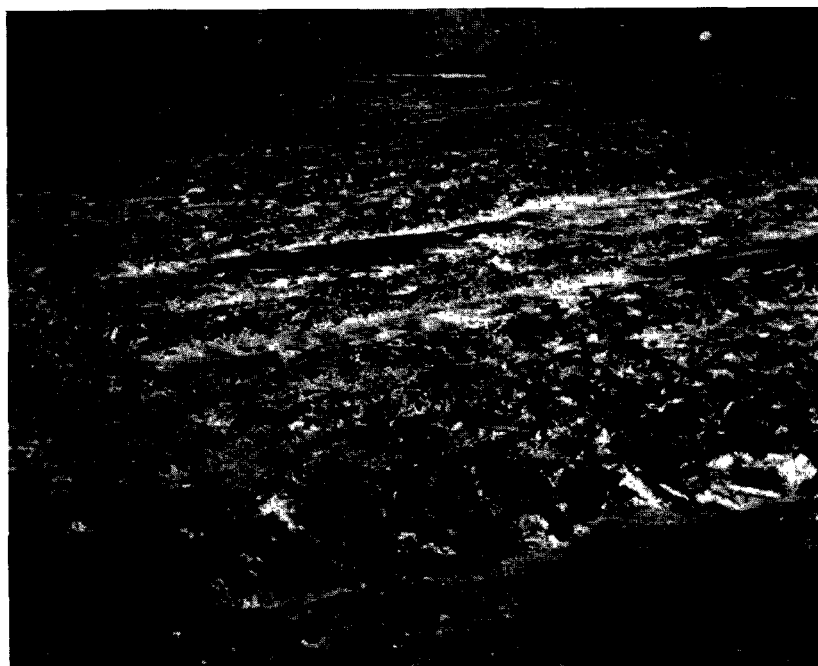
Fig. 5.
Graded surface of a coal-waste dump illustrating profuse formation of iron sulfate.
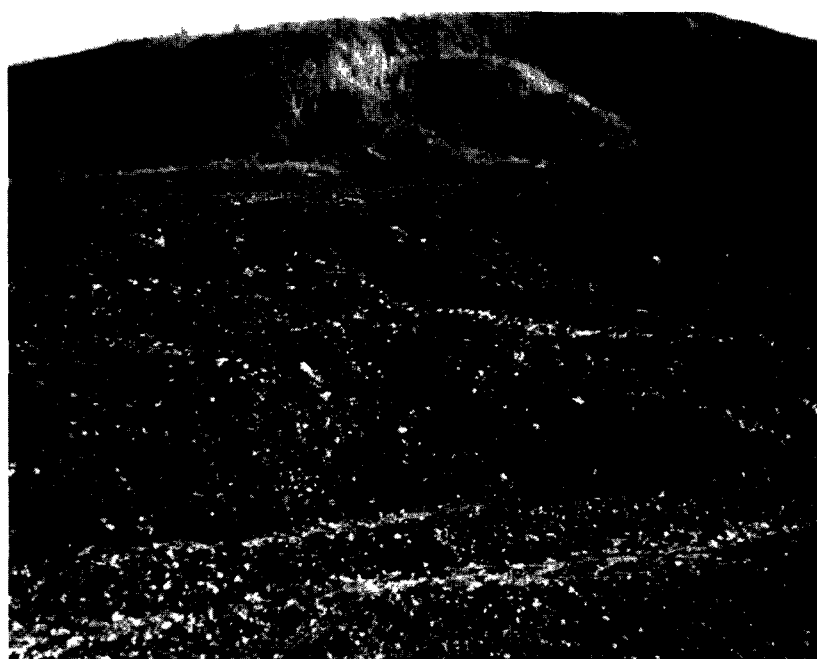
Fig. 6.
Concentration of iron sulfate in the drainage channels of a coal refuse pile.

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Fig. 7.
Water-filled drainage channel between two coal refuse banks.

The results obtained thus far on the coal and waste samples have been compiled by a computer interactive method so that additional analytical information can be added as it is obtained. In addition, the use of a computer storage system facilitates the rapid retrieval of analytical results about any particular sample or set of samples. An attempt has been made to assemble the information in the tables into categories or groupings according to plant location or sample type. The symbols and abbreviations used in the tables are explained by footnotes which appear at the end of Table IV. A discussion and interpretation of the data for related waste samples follows.

Analysis of Coal Preparation Wastes from Illinois Basin Cleaning Plant B

Fresh coal refuse from Illinois Basin coal cleaning Plant B was collected from the dump itself where it was being deposited by trucks. Three 50-kg increments—designated in chronological order Gob A, B, and C—were successively collected over a 4-h period. About nine separate truckloads of refuse were sampled. The mineralogical and trace element analyses completed so far for these wastes appear in Table IV.

The data in Table IV reveal that the composition of the waste material was reasonably constant over the duration for which we collected the samples, although the later sample (Gob C) appears to contain a slightly greater amount of illite and lesser amount of pyrite than the earlier sample (Gob A). This trend is also reflected in the iron, aluminum, and silicon values.

This refuse, we believe, is fairly typical of the high-sulfur, mineral waste that is produced from the major coal types in the Illinois Basin. It contains about 20 wt% residual carbon and around 14 wt% sulfur. Typically, the bulk of the waste material is distributed among the clay minerals

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TABLE III

SUMMARY OF LASL COAL AND REFUSE SAMPLE ANALYSES (1)

5-15-76

LOCALE	(2) IDENTITY	(3) SIZE	SAMPLE	LTA	CHN ANAL	MINE-RALOGY	TRACE ELEMENTS	FLOAT SINK
STD VALUES	NBS 1632 COAL		STD	NA	NA	NA	YES	NA
LASL DATA	NBS 1632 COAL		STD	YES	YES	YES	YES	NA
PLANT A	FEED COAL A	28KG	13					
A	FEED COAL B	30KG	14					
A	CLEAN COAL	6KG	15					
A	GOB A-FRESH	65KG	25					
A	GOB B-FRESH	73KG	11					
A	GOB C-FRESH	71KG	12					
A	GOB D-FRESH	73KG	10					
A	GOB E-FRESH	70KG	28					
A	GOB A,C,E AVE	-1/4	25B					
A		-1	25C					
A		-1 1D	25D					
A		-2	25E					
A		+2	25F					
A	GOB OCCAS LG PC	20KG	16					
A	GOB 1Y TOP 3IN	31KG	8	YES	YES	YES	YES	
A	GOB 1Y 24IN BELO SURF	37KG	9	YES	YES	YES	YES	
PLANT B	FEED COAL	30KG	30					
B	PRODUCT COAL-FINE CUT	29KG	31					
B	PRODUCT COAL-COARSE CUT	29KG	29					
B	GOB A FRESH-DUMPED	47KG	24	YES	YES	YES	YES	
B	GOB B FRESH-DUMPED	49KG	17	YES	YES	YES	YES	
B	GOB C FRESH-DUMPED	51KG	23	YES	YES	YES	YES	
B	GOB A,B,C AVE	-1/4	24B	YES	YES	YES	YES	
B		-1	24C	YES	YES	YES	YES	
B		-1 1D	24D	YES	YES	YES	YES	
B		-2	24E	YES	YES	YES	YES	
B		+2	24F	YES	YES	YES	YES	
B	GOB A TYPE 2	61KG	26					
B	GOB B TYPE 2	54KG	27					
B	DRY STREAM AT 8Y GOB PILE	10KG	5	YES	YES	YES	YES	
B	GOB PILE-8Y AT FOOT	16KG	6	YES	YES	YES	YES	
B	GOB WHITE-1Y	-6	7A	NA	NA	NA	YES	NA
B		-10	7B	NA	NA	NA	YES	NA
B		-20	7C	NA	NA	NA	YES	NA
B		-35	7D	NA	NA	NA	YES	NA
B		-60	7E	NA	NA	NA	YES	NA
B		-115	7F	NA	NA	NA	YES	NA
B		-250	7G	NA	NA	YES	YES	NA
B		+6	7H	YES	YES	YES	YES	NA
B	SLURRY POND	10KG	4	YES	YES	YES	YES	
PLANT C	FEED COAL A	30KG	32					
C	FEED COAL B	34KG	33					
C	CLEAN COAL	27KG	34					
C	FEED COAL TYPE 2	33KG	35					
C	GOB A COARSE-FRESH	51KG	18					
C	GOB B COARSE-FRESH	59KG	21					
C	GOB C COARSE-FRESH	55KG	22					
C	GOB A,B,C, AVE	-1/4	18B					
C		-1	18C					
C		-1 1D	18D					
C		-2	18E					
C		+2	18F					
C	GOB FINE-FRESH	48KG	20					
C		-1/4	20B					
C		-1	20C					
C		-1 1D	20D					
C		-2	20E					
C	GOB VERY FINE-FRESH	24KG	19					
C		-1/4	19B					
C		-1	19C					
C		-1 1D	19D					
C		-2	19E					
PLANT D	FEED COAL	8KG	3	YES		YES	YES	
D	BREAKER REJECTS +6IN	11KG	1	YES		YES	YES	
D	FRESH GOB AT DUMP	10KG	2	YES	YES	YES	YES	

TOTAL NUMBER OF SAMPLES = 67

FOOTNOTES

(1) YES=ANALYSIS DONE, NA=NO ANALYSIS IS TO BE DONE, BLANK=ANAYLSIS YET TO BE DONE

(2) DESIGNATIONS A,B,C, ETC INDICATE THE ORDER IN WHICH SAMPLES WERE COLLECTED: A, FIRST; B, SECOND; ETC. Y=AGE OF MATERIALS IN YEARS

(3) SAMPLE WEIGHTS IN KILOGRAMS; SAMPLE PARTICLE SIZE IN MINUS(-) OR PLUS(+) MESH (SAMPLE 7) AND INCHES (ALL OTHERS); -1 1D INDICATES MINUS 1 INCH IN ONE DIRECTION AND -2 INCHES IN THE OTHERS

TABLE IV

TRACE ELEMENT AND MINERAL CONTENT OF COAL WASTE MATERIALS FROM ILLINOIS BASIN PLANT B

SAMPLE (1)	24	17	23	AVG
IDENTITY	GOB A	GOB B	GOB C	GOB
LOCALE	PLANT B	PLANT B	PLANT B	PLANT B
DATE OBTND	11-19-75	11-19-75	11-19-75	11-19-75
PCT H2O	9.62	10.35	10.38	10.12
PCT LTA	79.80	77.41	79.84	79.02
PCT HTA	64.20	61.30	65.20	63.57
PCT ORIGNL	100.00	100.00	100.00	100.00
SIZE,KG	46.60	49.10	50.60	48.77
CHNS ANAL	RAW BASIS	RAW BASIS	RAW BASIS	AVERAGED
CARBON	18.80	21.40	19.30	19.83
HYDROGEN	2.20	2.30	2.20	2.23
NITROGEN	.42	.45	.42	.43
SULFUR	14.30	14.70	11.40	13.47
MINERALOGY (2)	RAW BASIS	RAW BASIS	RAW BASIS	AVERAGED
KAOLINITE QUANT	MINOR 8.90	MINOR 9.00	MINOR 9.00	8.97
ILLITE QUANT	MAJOR 15.00	MAJOR 14.00	MAJOR 19.00	16.00
QUARTZ QUANT	MAJOR 10.20	MAJOR 11.40	MAJOR 11.70	11.10
PYRITE QUANT	MAJOR 26.80	MAJOR 28.40	MAJOR 21.90	25.70
SPHALERITE QUANT				
CALCITE QUANT	TRACE -.01	TRACE -.01	TRACE -.01	-.01
MIXED CLAY QUANT	MINOR	MINOR	MINOR	
MARCASITE QUANT	MINOR	TRACE	MINOR	
GYPSUM QUANT	TRACE	TRACE	TRACE	
ROZENITE QUANT				
ALBITE QUANT				
ELEMENT (3)	RAW BASIS	RAW BASIS	RAW BASIS	AVERAGED
LI PPM HA	111.00	92.00	103.00	102.00
BE PPM HA	2.80	2.40	3.10	2.77
B PPM LE	64.00	63.00	65.00	64.00
F PPM RO	620.00	420.00	670.00	.06
NA PCT RN	.07	.07	.09	.08
HA	.09	.08	.08	.08

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TABLE IV (cont)

SAMPLE	24	17	23	AVG
MG PCT H A	.21	.22	.27	.23
AL PCT H A	5.03	4.94	5.29	5.09
SI PCT R O	13.20	12.90	14.60	13.57
P PPM R O				
CL PPM R N	42.00	53.00	76.00	57.00
K PCT H A	1.07	1.07	1.21	1.12
CA PCT H A	.05	.07	.14	.09
SC PPM R N	13.00	11.00	12.00	12.00
TI PCT R N	.33	.36	.36	.35
V PPM R N	78.00	85.00	95.00	86.00
CR PPM R N	74.00	76.00	80.00	76.67
MN PPM H A	140.00	140.00	160.00	146.67
MN PPM R A	147.00	142.00	155.00	148.00
FE PCT H A	12.80	10.80	9.30	10.97
CO PPM R N	35.00	30.00	25.00	30.00
NI PPM L E	73.00	73.00	68.00	71.33
CU PPM H A	45.00	43.00	65.00	51.00
ZN PPM H A	108.00	140.00	124.00	124.00
GA PPM R N				
GE PPM L E	-8.00	-8.00	-8.00	-8.00
AS PPM R N	130.00	89.00	64.00	94.33
SE PPM R N	8.00	5.80	4.80	6.20
BR PPM R N	2.00	2.00	2.00	2.00
RB PPM R N	81.00	97.00	110.00	96.00
Y PPM L E	15.00	17.00	21.00	17.67
ZR PPM L E	82.00	80.00	100.00	87.33
MO PPM L E	57.00	53.00	47.00	52.33
AG PPM H A				
CD PPM H A	.40	.50	.60	.50
SN PPM L E	.80	.60	.60	.67
SB PPM R N	-8.00	-8.00	-8.00	-8.00
I PPM R N				
CS PPM R N	1.70	1.30	1.10	1.37
LA PPM R N	7.10	5.80	6.80	6.57
CE PPM R N	43.00	31.00	37.00	37.00
SM PPM R N	88.00	61.00	71.00	73.33
EU PPM R N	7.00	4.80	5.90	5.90
TB PPM R N	1.40	1.00	1.30	1.23
DY PPM R N	4.40	4.40	4.30	4.37
YB PPM R N	2.50	2.80	4.40	3.23
LU PPM R N	.47	.37	.38	.41
HF PPM R N	3.70	2.40	3.30	3.13
TA PPM R N	.94	.78	1.10	.94
W PPM R N				
HG PPM R N				
PB PPM H A	31.00	36.00	34.00	12.00
TH PPM R O	11.00	8.40	9.10	9.50
U PPM R O	2.70	2.70	2.70	2.70

FOOTNOTES

(1) PLUS OR MINUS INDICATES SIZE GREATER OR LESS THAN SIZE GIVEN.
NUMBERS 6 OR LARGER ARE MESH SIZES, OTHERS ARE IN INCHES

(2) MAJOR MINERALS, GREATER THAN ABOUT 10 WEIGHT PERCENT
MINOR MINERALS, FROM 1-10 WEIGHT PERCENT
TRACE MINERALS, LESS THAN 1 WEIGHT PERCENT
MINUS DESIGNATES A VALUE LESS THAN THAT GIVEN

(3) LETTERS INDICATE HOW SAMPLE WAS PREPARED AND ANALYZED
R= RAW SAMPLE
L= LOW TEMPERATURE ASH
B= HIGH TEMPERATURE ASH
N= NEUTRON ACTIVATION ANALYSIS
A= ATOMIC ABSORPTION
E= EMISSION SPECTROSCOPY
O= OTHER

TABLE V

TRACE ELEMENT AND MINERAL CONTENT
OF LOW-SULFUR COAL AND COAL
WASTE MATERIALS FROM PLANT D

SAMPLE (1)	3	1	2	3	1	2
IDENTITY	FEED COAL	BRAKR REJT	FRESH GOB	FEED COAL	BRAKR REJT	FRESH GOB
LOCALE	PLANT D	PLANT D	PLANT D	PLANT D	PLANT D	PLANT D
DATE OBTND	11- 5-75	11- 5-75	11- 5-75	11- 5-75	11- 5-75	11- 5-75
PCT H2O	3.38	.99	7.01	3.38	.99	7.01
PCT LTA	25.48	80.28	79.49	23.48	80.28	79.49
PCT HTA	18.90	68.80	67.60	18.90	68.80	67.60
PCT ORIGNL	100.00	100.00	100.00	100.00	100.00	100.00
SIZE,KG	7.80	10.80	10.50	7.80	10.80	10.50
CHNS ANAL		RAW BASIS	RAW BASIS			
CARBON			21.20			
HYDROGEN			1.83			
NITROGEN			.50			
SULFUR	.45	.18	.22			
MINERALOGY (2)	RAW BASIS	RAW BASIS	RAW BASIS	LTA BASIS	LTA BASIS	LTA BASIS
KAOLINITE QUANT	MAJOR	MAJOR	MAJOR	MAJOR	MAJOR	MAJOR
ILLITE QUANT		MINOR	MAJOR		MINOR	MAJOR
QUARTZ QUANT	MINOR	MAJOR	MAJOR	MINOR	MAJOR	MAJOR
PYRITE QUANT						
SPHALERITE QUANT						
CALCITE QUANT	MAJOR	MAJOR	MINOR	MAJOR	MAJOR	MINOR
MIXED CLAY QUANT		MINOR	MINOR		MINOR	MINOR
MARCASITE QUANT						
GYPSUM QUANT						
ROZENITE QUANT						
ALBITE QUANT						

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TABLE V (cont)

ELEMENT	RAW BASIS 3	RAW BASIS 1	RAW BASIS 2	LTA BASIS 3	LTA BASIS 1	LTA BASIS 2
LI PPM HA	11.00	23.00	29.00	43.17	28.65	36.48
BE PPM HA	1.30	3.20	4.10	5.10	3.99	5.16
B PPM LE	18.00	38.00	44.00	70.64	47.33	55.35
F PPM RO	1200.00	600.00	1900.00	.47	.07	.24
NA PCT RN	.13	.39	.41	.51	.49	.52
MG PCT HA	.16	.46	.40	.63	.57	.50
AL PCT HA	1.63	5.88	6.88	6.40	7.32	8.66
SI PCT RO	4.30	18.80	18.50	16.88	23.42	23.27
P PPM RO	458.00	380.00	268.00	1797.49	473.34	337.15
CL PPM RN	190.00			745.68		
K PCT HA	.27	1.08	1.28	1.06	1.35	1.61
CA PCT HA	1.09	2.74	1.20	4.28	3.41	1.51
SC PPM RN	3.70	9.40	11.60	14.52	11.71	14.59
TI PCT RN	.17	.35	.39	.67	.44	.49
V PPM RN	37.00	77.00	100.00	145.21	95.91	125.80
CR PPM HA	62.00	100.00	149.00	243.33	124.56	187.44
MN PPM RN	30.00	454.00	176.00	117.74	565.52	221.41
—	32.00	440.00	168.00	125.59	548.08	211.35
FE PCT HA	.66	3.30	2.50	2.59	4.11	3.15
CO PPM RN	3.60	6.30	8.90	14.13	7.85	11.20
NI PPM LE	7.00	13.00	17.00	27.47	16.19	21.39
CU PPM HA	18.00	33.00	39.00	70.64	41.11	49.06
ZN PPM HA	18.00	108.00	63.00	70.64	134.53	79.26
GA PPM RN	-3.00	-8.00	-8.00	-11.77	-9.97	-10.06
GE PPM LE	2.00	2.00			2.49	
AS PPM RN	8.00					
RB PPM LE	51.00	74.00	71.00	31.40	92.18	89.32
Y PPM LE	1.60	14.00	16.00	200.16	17.44	20.13
ZR PPM LE	.16	96.00	119.00	6.28	119.58	149.70
MO PPM LE	.15	7.60	9.00	.59	9.47	11.63
AG PPM RA	-3.00	.32	.37	-11.77	.40	.47
CD PPM HA	.56	.80	.62	2.20	1.00	.78
SN PPM LE		-8.00	-8.00		-9.97	-10.06
SB PPM RN		.65	1.50		.81	1.89
I PPM RN	1.70	4.80	6.30	6.67	5.98	7.93
CS PPM RN	13.00	39.00	40.00	51.02	48.58	50.32
LA PPM RN	23.00	67.00	69.00	90.27	83.46	86.80
CE PPM RN	1.70	5.30	4.90	6.67	6.63	6.16
SM PPM RN	.38	.64	1.30	1.49	.80	1.64
EU PPM RN	.20	.50	.50	.78	.62	.63
DY PPM RN			2.00			2.52
YB PPM RN	.10	.30	.40	.39	.37	.50
HF PPM RN	1.30	4.50	4.60	5.10	5.61	5.79
TA PPM RN	2.70			10.60		
W PPM RN	1.30		5.00	5.10		6.29
HG PPM RN		1.30			1.62	
PB PPM HA	10.00	22.00	28.00	51.02	23.67	27.68
TH PPM RO	5.20	12.60	14.50	20.41	15.70	18.24
U PPM RO	1.60	3.20	3.80	6.28	3.99	4.78

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(kaolinite, illite, mixed-layer clays), the sulfides (pyrite and marcasite), and quartz. In addition, small amounts of carbonate minerals and gypsum have been identified in this gob. There are also undoubtedly many minor or trace mineral phases present in this material as evidenced by the relatively high concentrations of such trace elements as lithium, sodium, manganese, zinc, arsenic, and cerium. From an environmental standpoint, there are disturbingly high quantities of the trace elements vanadium, chromium, zinc, arsenic, lead, and thorium distributed in this waste; however, the extent to which these elements are, or may be, released by environmental processes has not been determined. We believe that the behavior of the individual trace elements in coal preparation wastes will be dictated largely by the behavior of the major minerals in which the trace components reside. Labile or unstable minerals, such as pyrite or limestone, will undoubtedly release greater amounts of the associated trace elements into the environment at a faster rate than will the more stable minerals, such as quartz.

Analysis of Coal and Waste from Cleaning Plant D

Trace element and mineralogical analyses have been completed for samples of low-sulfur feed coal, breaker rejects, and fresh refuse from coal cleaning Plant D. The breaker reject is the rock and mineral matter that was too large (>15 cm) to be processed by the cleaning plant even after passing through a crusher. Results are given in Table V for both the raw or as-received coal and waste samples and for the residue produced by low-temperature ashing (LTA basis). The latter information provides a carbon-free direct basis on which to compare the trace elements and minerals in the various samples.

The major minerals present in the coal and refuse from cleaning Plant D are the clays, calcite, and quartz. The absence of pyrite or marcasite, and the relatively higher concentration of sulfur in the feed coal as compared to the waste, suggests that most of the sulfur present in the coal is organically bound. The waste materials from this coal cleaning plant contrast with those reported above for Plant B in that pyrite is a major consitituent in the latter refuse, but is absent altogether from Plant D waste.

The elemental composition of Plant D refuse reflects to a large degree the types of minerals present in the waste. The relatively high percentages of aluminum and silicon can, of course, be attributed to the high clay and quartz contents. Predictably, in the absence of pyrite, the iron content of Plant D coal and wastes is fairly low compared to the Illinois Basin waste discussed earlier. There are several toxic trace elements present in relatively high concentrations in the low-sulfur waste; notably iron, aluminum, manganese, copper, nickel, zinc, yttrium, and lead.

As we point out in Appendix C, only relatively small amounts of the coal and waste materials were collected from Cleaning Plant D. We were somewhat concerned about whether we had collected enough of each to provide statistically representative samples. The general correspondence and consistency between the relative quantities of each element present in the coal and refuse samples collected from this plant suggests that our samples are indeed representative of the short-term operation of the plant.

By comparing the trace element composition of the feed coal going into the preparation plant, and of the mineralized waste material discarded from the plant, we were able to categorize the elements according to their tendency to remain with the cleaned coal or to drop out with the heavier mineral matter during the washing operation. This information appears in Table VI. For comparison, we have included in the table corresponding data obtained by other laboratories from float/sink studies of high-sulfur coals. Table VI reveals some interesting differences between these two coal types. Cobalt, nickel, chromium, and copper, for example, tend to preferentially associate with the mineral matter in the high-sulfur coals; whereas, these elements in the

low-sulfur coals showed a positive tendency to remain with the coal fraction. This behavior may be due in part to the differences in pyrite contents of the two coal types. Copper, nickel, and cobalt are chalcophile elements that commonly occur as sulfide minerals, and perhaps these are present as sulfide phases or components in the dense pyrite fractions of the high-sulfur coals. In the absence of much pyrite in the low-sulfur coal, these elements must be present in some other mineral phase, and therefore, their behavior during density separation would be expected to deviate from that of the pyritic samples. Another possible factor, which could explain some of the deviations between the two sets of data in Table VI, is the scale-up factor between the laboratory float/sink studies used elsewhere and the commercial preparation plant products incorporated into our study.

An interesting comparison can be made between the relative concentrations of trace elements in the low-sulfur coal wastes and the high-sulfur Illinois Basin refuse considered earlier. It is seen from Table VII, perhaps as would be expected from the diverse geology of the two coal types, that only a few trace elements are present in both waste types in nearly equal amounts. Most of the elements found in the high-sulfur coal wastes in greatest relative abundance are those expected to form sulfides or to be associated with pyrite or marcasite, while those present in highest relative amounts in the low-sulfur coal refuse appear to be those most preferentially associated with the clay minerals, quartz, and the carbonates.

The characterization of the mineralogy and chemistry of trace elements in coals and coal wastes is one of the more important aspects of this project. At present, we are using both electron

TABLE VI

TENDENCY OF TRACE ELEMENTS TO REMAIN WITH COAL FRACTIONS DURING WASHING

LOW SULFUR COAL CLEANING PLANT D	HIGHER CONTENT IN COAL ASH ↑	HIGH SULFUR COALS OTHER STUDIES
F, P, S	>50%	Ge, Be
Li, B, Cr, Cu, Y, Zr Ti, V, Co, Ni, Ag, Sb, U	10–50%	Ga, B, Ti, V
Be, Na, Mg, Al, K, Ca Sc, Cs, La, Ce, Sm, Eu, Dy, Lu, Hf, Th	APPROXIMATELY EQUAL LEVELS IN BOTH ASHES	
Si, Fe, Zn, Mo, Cd	10–50%	Co, Ni, Cr, Cu, Mo
Mn	>50%	Hg, Zn, Cd, Pb, Mn
	HIGHER CONTENT IN WASTE ASH	
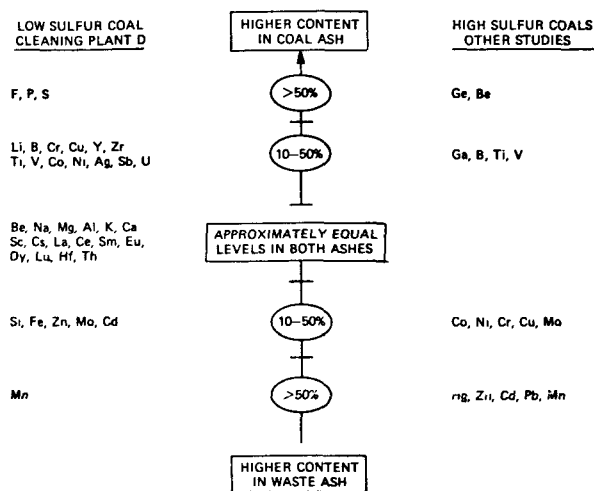
[a]Correlation based on data in Table V.

[b]Information collected from float/sink studies by Zubovic (Adv. in Chem. Ser. 55, 221-30, 1966), Gluskoter (Chap. 1, Adv. in Chem. Ser. 141, 1975), Duerbrouck ("Coal Cleaning: State of the Art," Conf. Coal and the Environment, Louisville, Kentucky, October 22, 1974), and Schultz (Chap. 11, Adv. in Chem. Ser. 141, 1975).

TABLE VII

RELATIVE CONCENTRATIONS OF TRACE ELEMENTS IN COAL PREPARATION WASTES OF DIFFERING SULFUR CONTENTS[a]

	↑	
HIGHER CONCENTRATION IN LOW-SULFUR WASTE	>100%	F, Na, Al, Si, P, Ca, Ta
	50–100%	Mg, Cr, Th
	10–50%	Be, K, Ti, V, Mn, Zr, Hf, U
APPROXIMATELY EQUAL IN BOTH WASTES		Sc, Y, Cd, Sb, Cs, La, Ce, Eu
	10–50%	B, Rb, Ag, Sm
	50–100%	Yb
HIGHER CONCENTRATION IN HIGH-SULFUR WASTE	>100%	Li, Fe, Co, Ni, Cu, Zn, Mo, Dy
	↓	

[a]Correlations based on data in Tables IV and V.

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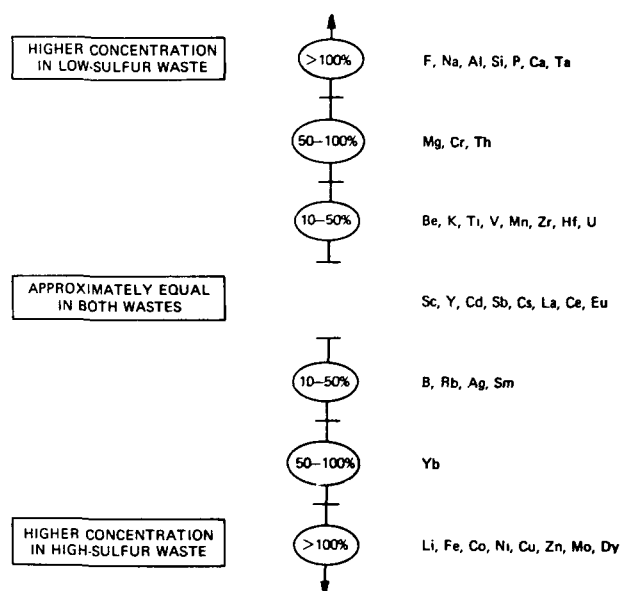
and ion microprobes as scanning devices to gain general information about the compositions of both the major and minor mineral phases present. Once we have more completely characterized the waste materials of interest, we will begin to use the microprobes to search for particular micromineral phases containing specific trace elements. This information is necessary to establish the spatial associations of trace elements within the waste structure.

Figure 8 is the photomicrograph of a sample of crushed refuse from Plant D that was examined with the electron microprobe. The elemental compositions of the particle at position A show evidence of three major phases: (1) calcium, carbon, and oxygen, probably as calcite; (2) aluminum, silicon, and oxygen with low concentrations of krypton, most likely a clay area; and (3) calcium, iron, magnesium, carbon, and oxygen, likely a dolomite or iron-rich dolomite. In area B, the large smooth particle near the top, which appears gray on the photograph, contains only silicon and oxygen, and is probably quartz. The black-appearing particle to its left contains silicon, aluminum, krypton, magnesium, iron, and oxygen, and is likely a mixture of clay minerals. The large particle at the bottom of area B, which appears to be much the same color as the mounting plastic, is residual coal because only carbon was detected. In the large gray particle labeled C, the light-gray part of the circular area at the lower left contains predominantly calcium, carbon, and oxygen, with some iron and magnesium, again defining a dolomitic or sideritic carbonate mineral, while the dark-gray portion contains aluminum, silicon, and oxygen (a clay?). In addition, this circular area contained carbon and trace amounts of sulfur, fluorine,
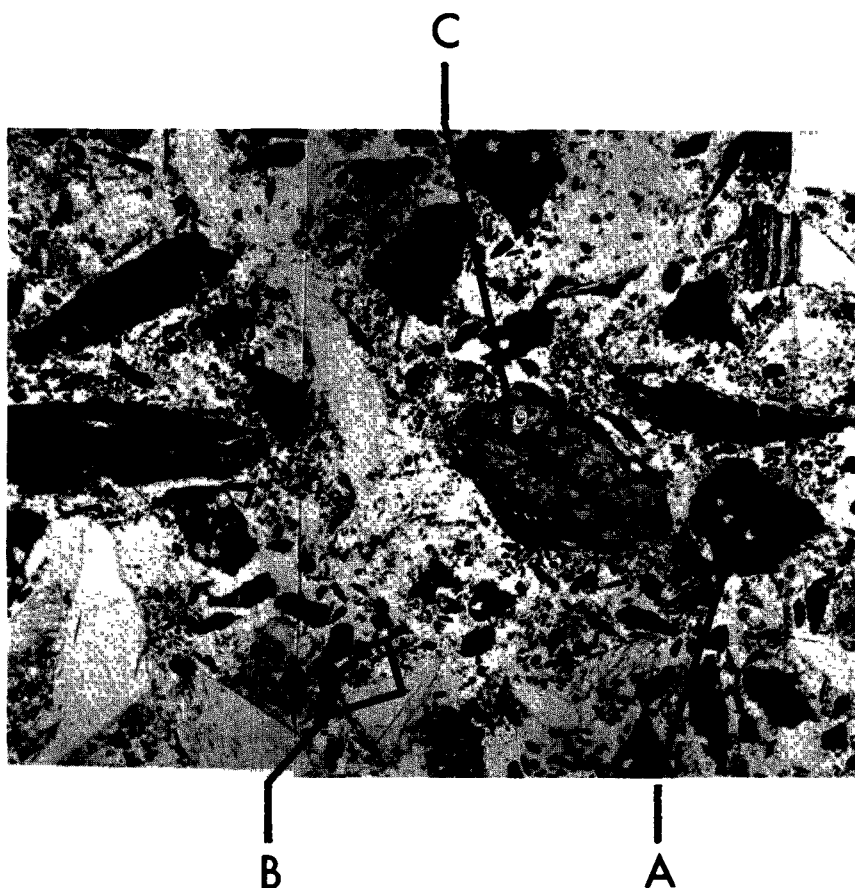
Fig. 8.

Photomicrograph showing areas analyzed on a sample of refuse from Cleaning Plant D (~100X).

chromium, rubidium, strontium, and barium. The strontium and barium are present in the carbonate phase.

Microprobe studies, such as that just described, amply demonstrate the structural and morphological complexity of the rocks and minerals present in these coals and coal wastes. These materials tend to be very fine grained and they are highly interspersed with each other. There are few pure mineral phases that extend over major areas of the waste particles. This, of course, makes it more difficult to sort out the mineralogy of the trace constituents.

Characterization of Weathered Coal Preparation Wastes

We have begun to characterize the trace elements and minerals in samples of aged or weathered coal cleaning wastes that we collected from the Illinois Basin. A description of the weathered waste material collected appears in Appendix C.

Refuse, which was about 1 yr old, was collected at a dump site near Cleaning Plant A. Some material was picked up near the surface and another increment was collected about 62 cm (24 in.) below the surface from a fresh cut. The analyses for these two weathered wastes are given in Table VIII.

A comparison of the data for the waste samples collected from the two depths reveals an interesting fact: certain minerals and trace elements are substantially depleted from the exposed or surface layer of waste material. This information is presented in Table IX. In particular, pyrite and marcasite (iron and sulfur values) are clearly less abundant in the surface material than in the interior of the pile. Also, as Table IX reveals, many of the trace elements which have strong tendencies to form sulfide minerals (cobalt, nickel, arsenic, copper, zinc, and cadmium) are also appreciably depleted from the surface layer. In fact, of all the elements studied, only phosphorus is present in the surface layer in substantially greater abundance than in the interior of the waste bank. A final judgment on this issue must be deferred until quantitative mineralogical analyses are completed; nonetheless, the behavior just described strongly implies that some of the labile minerals and many of the trace elements have been removed from the waste surface by the weathering and leaching processes.

Analysis of a Slurry Pond Residue

A sample of residue was collected at the inlet of the slurry pond near Cleaning Plant B. This material is composed of the very fine residual waste that is left in the process water from the cleaning operations. The sample we obtained is thought to represent the settled accumulation of 1 yr or more of plant operation. Analytical results for this material appear in Table VIII.

A listing of the relative abundances of trace elements in the slurry sample as compared to the fresh gob from the same cleaning plant is given in Table X. This information reveals a strong tendency of certain trace elements to segregate by particle size. Particularly interesting is that many of the sulfide-forming elements, such as zinc, cadmium, and copper, are found in greater relative amounts in the finer slurry particles, while the iron and sulfur analyses indicate that pyritic materials in general do not exhibit much of a bias toward either coarse or fine waste.

TABLE VIII

TRACE ELEMENT AND MINERAL CONTENT OF WEATHERED COAL-WASTE MATERIALS FROM ILLINOIS BASIN PLANTS A AND B

SAMPLE (1)	8	9	4	5	6
IDENTITY	GOB TP3 1Y	GOB D24 1Y	SLURY POND	DRY STM 8Y	GOB PIL 8Y
LOCALE	PLANT A	PLANT A	PLANT B	PLANT B	PLANT B
DATE OBTND	11-18-75	11-18-75	11-19-75	11-19-75	11-19-75
PCT H2O	12.24	6.43	22.10	7.83	7.83
PCT LTA	85.20	83.90	69.37	68.58	79.90
PCT HTA	71.50	74.10	58.10	56.50	67.40
PCT ORIGNL	100.00	100.00	100.00	100.00	100.00
SIZE, KG	31.20	37.40	9.70	9.50	16.30
CHNS ANAL	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS
CARBON	12.61	13.55	22.54	17.00	13.70
HYDROGEN	1.42	1.40	1.88	2.12	1.34
NITROGEN	.28	.28	.47	.56	.31
SULFUR	6.99	10.60	11.10	3.95	14.10
MINERALOGY (2)	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS
KAOLINITE QUANT	MAJOR	MAJOR	MAJOR	MAJOR	MAJOR
ILLITE QUANT	MAJOR	MAJOR	MAJOR	MINOR	MINOR
QUARTZ QUANT	MAJOR	MAJOR	MAJOR	MAJOR	MAJOR
PYRITE QUANT	MINOR	MAJOR	MAJOR	MAJOR	MAJOR
SPHALERITE QUANT					
CALCITE QUANT	MINOR	MAJOR			
MIXED CLAY QUANT	MINOR	MINOR	MINOR	MINOR	TRACE
MARCASITE QUANT					
GYPSUM QUANT	MAJOR	MAJOR	MINOR	TRACE	TRACE
ROZENITE QUANT					
ALBITE QUANT					MINOR

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TABLE VIII (cont)

SAMPLE	4	5	6	8	9
ELEMENT (3)	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS
LI PPM H A	67.00	64.00	61.00	63.00	69.00
BE PPM H A	1.90	1.60	1.90	1.70	1.30
B PPM L E	57.00	83.00	80.00	63.00	65.00
F PPM R O	450.00	440.00	480.00	540.00	560.00
NA PCT R N A	.06	.10	.09	.14	.14
MG PCT H A	.20	.14	.14	.36	.44
AL PCT H A	5.18	6.34	5.63	6.61	6.54
SI PCT R O	11.30	15.80	15.20	16.30	15.80
P PPM R O	10.00	410.00	12.00	970.00	12.00
CL PPM R N A	57.00	59.00			24.00
K PCT H A	.94	.96	.99	1.42	1.29
CA PCT H A	.29	.08	.72	1.22	1.32
SC PPM R N	7.40	6.90	6.40	9.10	10.00
TI PCT R N	.26	.41	.40	.35	.42
V PPM R N A	61.00	54.00	46.00	72.00	72.00
CR PPM H A	62.00	75.00	67.00	87.00	85.00
MN PPM R N A	190.00	27.00	100.00	230.00	430.00
FE PCT H A	10.10	2.84	2.10	6.84	8.91
CO PPM R N	21.00	.94	13.00	3.40	13.00
NI PPM L E	80.00	9.40	27.00	20.00	46.00
CU PPM H A	102.00	26.00	38.00	31.00	45.00
ZN PPM H A	342.00	36.00	6.60	83.00	146.00
GA PPM L E	18.00	16.00	15.00	18.00	20.00
GE PPM R N	-7.00	-7.00	-8.00	-9.00	-8.00
AS PPM R N	72.00	15.00	5.80	16.00	35.00
SE PPM R N	7.50	6.00		10.00	6.80
BR PPM R N A	2.50	.86			
RB PPM R N	150.00	93.00	110.00	64.00	100.00
Y PPM L E	15.00	11.00	12.00	18.00	23.00
ZR PPM L E	78.00	64.00	77.00	95.00	100.00
MO PPM L E	27.00	24.00	39.00	29.00	35.00
AG PPM H A	3.90	1.40	5.80	1.40	2.70
CD PPM L E	2.60	.50	.30	.60	.80
SN PPM R N	-7.00	-7.00	-8.00	-9.00	-8.00
SB PPM R N	2.40	1.70	1.50	1.40	2.70
I PPM R N					
CS PPM R N	4.00	5.60	3.70	5.30	5.10
LA PPM R N	25.00	45.00	49.00	46.00	39.00
CE PPM R N	55.00	80.00	81.00	86.00	77.00
SM PPM R N	4.40	4.40	4.60	4.70	7.30
EU PPM R N	.88	.78	.79	.99	1.10
TB PPM R N					
DY PPM R N	3.30	2.20	2.50	4.10	4.90
YB PPM R N	1.40	1.70	1.60	1.80	2.30
LU PPM R N	.27	.30	.31	.47	.41
HF PPM R N	3.40	3.90	3.40	3.20	3.10
TA PPM R N	.44	.60	.60	.40	.75
W PPM R N A	4.00	8.00		6.00	
HG PPM H A					
PB PPM H A	37.00	20.00	22.00	32.00	36.00
TH PPM R O	7.90	7.00	8.63	10.00	10.00
U PPM R O	3.90	2.60	4.80	9.80	5.40

TABLE IX

RELATIVE TRACE ELEMENT CONTENTS IN COAL PREPARATION WASTES AS A FUNCTION OF WASTE DUMP DEPTH[a]

HIGHER CONTENT IN TOP 3 INCHES	>100%	P
	50–100%	U
	10–50%	Be, K, Se, La, Ce, Lu
APPROXIMATELY EQUAL CONTENT AT BOTH LEVELS		B, F, Na, Al, Si, Ca, Sc, V, Ga, Cr, Zr, Cs, Eu, Hf, Th
	10–50%	Li, Mg, Ti, Fe, Cu, Y, Mo, Cd, Dy, Yb
	50–100%	S, Mn, Zn, Rb, Ag, Sb, Sm, Ta
HIGHER CONTENT 25 in BELOW SURFACE	>100%	Co, Ni, As
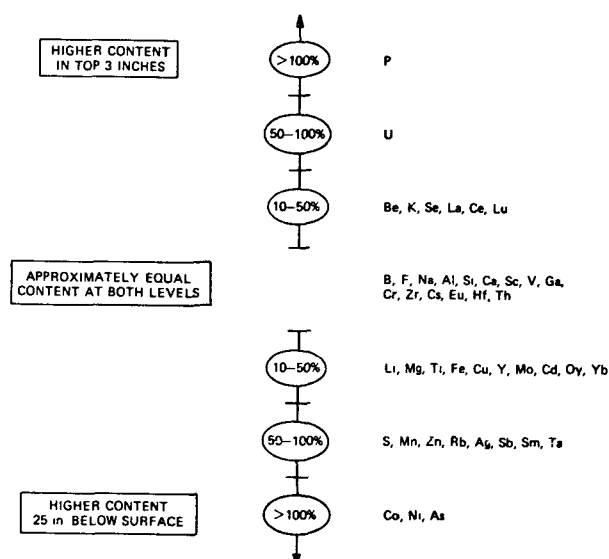
[a]Correlations based on data in Table VIII.

TABLE X

DISTRIBUTION OF TRACE ELEMENTS AND MINERALS BETWEEN SLURRY AND GOB FOR ILLINOIS BASIN CLEANING PLANT B[a]

HIGHER CONCENTRATION IN SLURRY	>100%	Ca, Zn, Br, Ag, Cd
	50–100%	Al, Cu, Rb, Sb
	10–50%	Mn, Si, U
APPROXIMATELY EQUAL LEVELS IN BOTH		B, Na, Mg, Cl, K, Fe, Ni, Y Zr, Cs, Hf
	10–50%	F, Si, S, V, Cr, As, Ce, Sm, Eu, Dy, Th
	50–100%	Li, Be, Sc, Ti, Co, Mo, La, Lu
HIGHER CONCENTRATION IN GOB (WASTE)	>100%	Yb
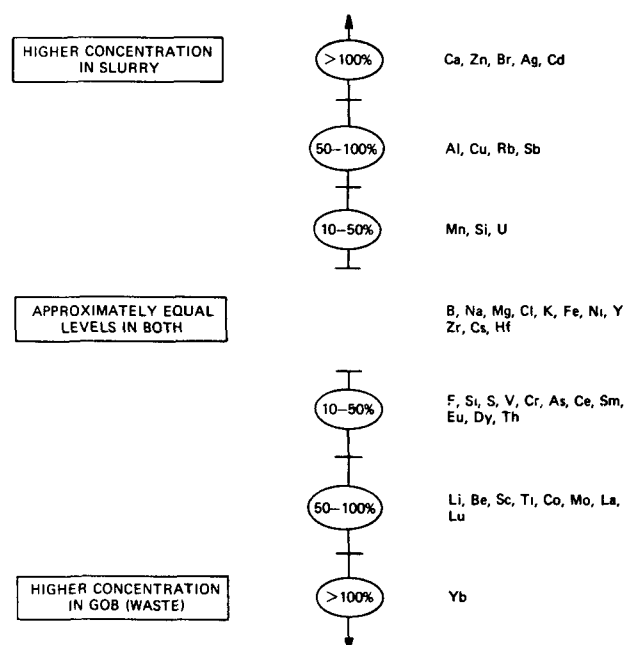
[a]Correlations based on data in Tables IV and VIII.

Characterization of Refuse From a Highly Weathered Waste Dump

Samples of coal refuse were collected from the base of an 8-yr-old waste bank, and along a dry stream bed located immediately adjacent to the bank at Plant B. The stream is apparently active only during periods of heavy precipitation, carrying surface water away from the dump area. The elemental and mineralogical analyses for these two weathered waste materials appear in Table VIII.

The results for the two sample locations are compared in Table XI. Most of the elements are fairly equally distributed between the weathered waste bank and the stream sediment. However, the higher content of carbon, hydrogen, and nitrogen in the stream samples suggests that the lighter coal particles have been preferentially washed out of the waste pile. Based on the elemental composition of the samples, the waste bank appears to have a relatively higher content of the denser pyritic material than the stream bed. Elements such as aluminum, sodium, krypton, and silicon, associated primarily with the medium-density clays and quartz, are found about equally distributed in both the waste bank and stream sediment samples. These observations suggest that the mechanical action of running water, rather than dissolution/precipitation phenomena, is the prime force for moving material from the waste bank into this stream bed.

TABLE XI

DISTRIBUTION OF TRACE ELEMENTS
BETWEEN AN EIGHT-YEAR-OLD GOB PILE
AND AN ADJACENT DRY STREAM BED[a]

HIGHER CONCENTRATION IN STREAM BED	(>100%)	P, Ga
	(50–100%)	Be, Cd, Cs, (C,H,N)
	(10–50%)	V, Cr, Sb
APPROXIMATELY SAME LEVEL IN BOTH		Li, B, Na, Mg, Al, Si, K, Sc, Ti, Cu, Zn, As, Se, Y, La, Ce, Sm, Eu, Dy, Yb, Lu, Hf, Ta
	(10–50%)	Ni, Rb, Zr, Mo, Th
	(50–100%)	U
HIGHER CONCENTRATION IN WASTE PILE	(>100%)	S, Ca, Mn, Fe, Co, Ag
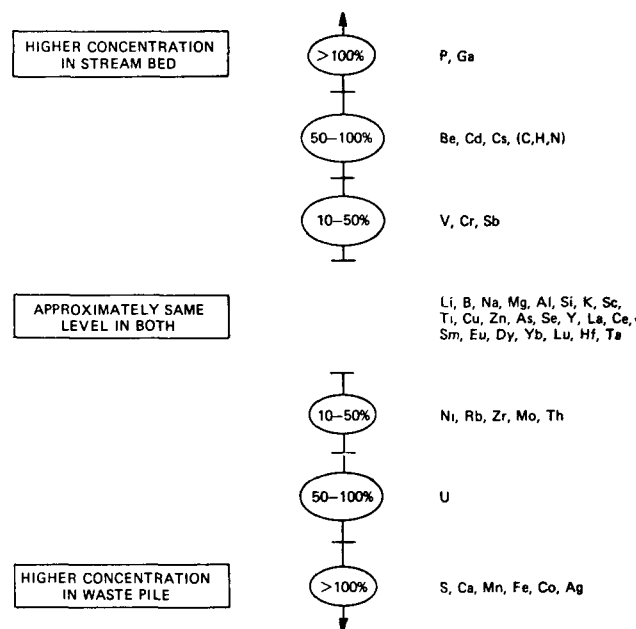
[a]Correlations based on data in Table VIII.

Analysis of Oxidized Pyritic Coal Refuse

Samples of oxidized pyritic waste were collected from the surface of a refuse dump in the Illinois Basin. The exterior surfaces of these samples were coated with a white crystalline material, which was later determined to be iron sulfate.

During shipment of these samples from the field to our laboratory, much of the white crystalline material fell off the sample surfaces and accumulated at the bottom of the shipping container. Subsequently, these waste materials were graded according to particle size in the range of +6 to −250 mesh in an attempt to recover the fine powder. The coarsest sample was found to be relatively rich in matrix material (unoxidized pyrite and marcasite), and the finest particle fraction was mostly iron sulfate (rozenite) as demonstrated by the mineralogical data presented in Table XII.

A comparison of the elemental analyses for the various samples of oxidized and unoxidized materials reveals an interesting and perhaps important trend. As Table XIII illustrates, most of the trace elements investigated were present in higher concentrations in the sulfate when compared to their original abundance in the pyritic matrix. At present, we don't have an explanation for this rather startling phenomenon. However, it will be important to delineate the mechanism by which the concentration of trace elements is increased in the highly soluble, surface layers.

Because of our particular interest in these oxidized pyritic wastes, we examined them further with SEM to observe their microstructures and the growth patterns of the white surface layers.

TABLE XII

TRACE ELEMENT AND MINERAL CONTENT OF WEATHERED AND SIZED COAL-WASTE MATERIALS FROM ILLINOIS BASIN PLANT B

SAMPLE	7H	7A	7B	7C	7D	7E	7F	7G
IDENTITY (1)	GOB/WH +6	GOB/WH -6	GOB/WH -10	GOB/WH -20	GOB/WH -35	GOB/WH -60	GOB/WH-115	GOB/WH-250
LOCALE	PLANT B	PLANT B	PLANT B	PLANT B	PLANT B	PLANT B	PLANT B	PLANT B
DATE OBTND	11-19-75	11-19-75	11-19-75	11-19-75	11-19-75	11-19 75	11-19-75	11-19-75
PCT H2O	90.50							
PCT LTA	60.90							
PCT HTA	93.70							
PCT ORIGNL	25.10	1.60	1.50	1.10	.70	.70	.40	.40
SIZE,KG		.40	.40	.30	.20	.20	.10	.10
CHNS ANAL	RAW BASIS	OMIT	OMIT	OMIT	OMIT	OMIT	OMIT	OMIT
CARBON	7.40							
HYDROGEN	.86							
NITROGEN	.12							
SULFUR	50.00							
MINERALOGY (2)	RAW BASIS	OMIT	OMIT	OMIT	OMIT	OMIT	OMIT	RAW BASIS
KAOLINITE QUANT								TRACE
ILLITE QUANT								MINOR
QUARTZ QUANT	TRACE							MAJOR
PYRITE QUANT	MAJOR							TRACE
SPHALERITE QUANT								
CALCITE QUANT								
MIXED CLAY QUANT								
MARCASITE QUANT	MAJOR							
GYPSUM QUANT								
ROZENITE QUANT								TRACE
ALBITE QUANT								MAJOR

TABLE XII (cont)

SAMPLE ELEMENT (3)	7H RAW BASIS	7A RAW BASIS	7B RAW BASIS	7C RAW BASIS	7D RAW BASIS	7E RAW BASIS	7F RAW BASIS	7G RAW BASIS
LI PPM HA	10.00							
BE PPM HA	-.10							
B PPM LE	40.00							
F PPM RO	190.00							
NA PCT HA	.02	.04	.06	.07	.09	.09	.09	.09
MG PCT HA	.40							
AL PCT HA	.90							3.20
SI PCT RO	1.96							
P PPM RO	10.00							
CL PPM RN	30.00	39.00	17.00		22.00	21.00	34.00	30.00
K PCT HA	.21							.55
CA PCT HA	.05							
SC PPM RN	1.70	3.80	5.10	5.40	6.10	5.90	5.10	4.80
TI PCT RN	.08	.13	.17	.21	.23	.23	.22	.21
V PPM RN	9.00	22.00	28.00	35.00	38.00	37.00	34.00	32.00
CR PPM HA	30.00							
MN PPM RN	200.00	77.00	88.00	100.00	120.00	140.00	160.00	150.00
FE PCT HA	159.00							14.00
CO PPM RN	33.90	6.40	8.00	8.40	11.00	14.00	17.00	19.00
NI PPM LE	7.80							
CU PPM RN	26.00							
ZN PPM HA	43.00							
GA PPM RN	228.00	9.70	16.00		17.00	10.00		8.20
GE PPM LE	26.00							
AS PPM RN	-9.00	76.00	73.00	67.00	55.00	51.00	43.00	35.00
SE PPM RN	125.00	6.10	5.80	6.10	4.80	3.70	4.40	3.40
BR PPM RN								
RB PPM LE	-10.00	150.00	46.00	49.00	130.00	120.00	150.00	140.00
Y PPM LE	67.00							
ZR PPM LE	96.00							
MO PPM RN	1.50							
AG PPM HA	1.20							
CD PPM HA	-9.00							
SN PPM LE	1.10							
SB PPM RN		2.20	1.40	1.70	6.10	3.50	2.10	2.10
I PPM RN	5.60		1.60	1.70	3.00	2.80		2.50
CS PPM RN							17.00	
LA PPM RN		12.00	15.00	19.00	16.00	16.00	32.00	17.00
CE PPM RN		23.00	30.00	31.00	35.00	31.00	3.60	34.00
SM PPM RN	.90	2.00	3.00	3.80	3.50	3.50	.57	3.50
EU PPM RN	.24	.35	.48	.48	.70	.62		.41
TB PPM RN	.60	1.60	1.80	2.20	2.70	2.50	2.40	2.30
DY PPM RN		.70	1.40	1.40	.88	1.60	.82	1.00
YB PPM RN	.15	.21	.24	.26	.28	.21	.24	.24
LU PPM RN	.36	.89	1.10	1.20	1.70	1.90	1.70	2.40
HF PPM RN	.17	.11	.19	.20	.19	.06	.26	.26
TA PPM RN								
W PPM RN				2.00		4.00	4.00	
HG PPM HA	12.00							
PB PPM HA	1.80							
TH PPM RO	.50	3.50	4.20	4.40	4.00	4.00	4.00	3.60
U PPM RO		1.60	1.90	2.40	2.30	2.20	2.20	2.00

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This material appeared as fine whiskers or fibers deposited on the surfaces of the sample. Typical fibers are shown in the photomicrograph, Fig. 9. All the fibers that were examined contained iron, sulfur, aluminum, and oxygen, although the aluminum was present only in minor quantities. The interior of the matrix material was composed principally of pyrite, but narrow channels were found within the pyrite that contained iron, sulfur, oxygen, and a small amount of aluminum, and these may be the source from which the sulfate whiskers grew.

Subtask 2.6—Characterize Environmental Behavior of Coal Preparation Wastes
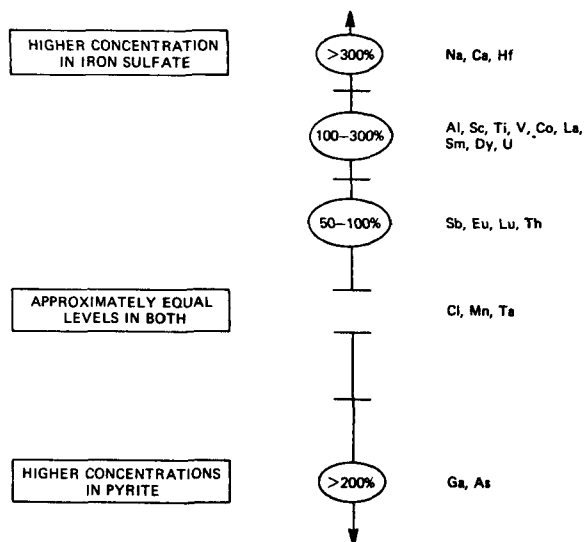
Studies of the effects of aqueous leaching on the trace elements and minerals in Illinois Basin coal refuse have been started. Several waste materials have been leached for various times with neutral and acidic solutions, but so far, the analyses have been completed for only one sample.

A 10-g sample of crushed coal refuse (−20 mesh) from Cleaning Plant B was leached with 100 ml of 0.01 M sulfuric acid solution for 5 days at ambient temperature. During the experiment, the waste sample and leachate were contained in a sealed Pyrex flask and agitated with a horizontal shaker. After the completion of the experiment, the acidic leachate (pH 2.3) was removed from the residue by filtration and analyzed for a core group of 13 trace elements.

The concentration of the trace elements in solution, and the percentage of each extracted (based on the content in the original sample) are reported in Table XIV. The high percentage of

TABLE XIII

PYRITE OXIDATION: RELATIVE CONCENTRATIONS OF TRACE ELEMENTS IN PYRITE AND IRON SULFATE[a]

HIGHER CONCENTRATION IN IRON SULFATE	>300%	Na, Ca, Hf
	100–300%	Al, Sc, Ti, V, Co, La, Sm, Dy, U
	50–100%	Sb, Eu, Lu, Th
APPROXIMATELY EQUAL LEVELS IN BOTH		Cl, Mn, Ta
HIGHER CONCENTRATIONS IN PYRITE	>200%	Ga, As

[a]Correlations based on data in Table XII.

TABLE XIV

TRACE ELEMENTS LEACHED FROM COAL REFUSE COLLECTED FROM PLANT B

Trace Element	ppm in Solution	Per Cent Extracted[a]
Ca	71	83
Co	1.8	60
Ni	3.2	45
Zn	4.7	38
Cd	0.02	35
Mn	4.0	29
Fe	1650	15
Mg	22	9
As	0.67	8
Cu	0.27	5
Cr	0.10	1.4
Al	58	1.2
K	8.8	0.7

[a]Based on the original content of each element in the refuse sample.

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(500X)

(1000X)

(2000X)

Fig. 9.
Scanning electron micrograph showing typical fibers from the surface of oxidized pyrite.

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some of the elements that were removed from the waste material by dissolution is indeed striking. Based on the available information, it can be surmised that the carbonate and sulfide minerals were leached to the greatest degree. Although the experiment involved a relatively high concentration of leachate, and relatively small particles of waste, the other conditions (pH, temperature, and time) were not greatly out of line with conditions often encountered in nature.

Subtask 2.7—Development of Procedures for Trace Element Separations

A major goal of this program is to begin to identify methods for removing or separating trace elements of environmental concern from coal processing wastes. Toward this end, one of the areas we are considering is whether specific mineral or trace element types concentrate in certain of the various size fractions produced by coal cleaning operations. The removal or treatment of a specific range of particle sizes to control toxic or harmful trace elements in coal wastes would be one of the easiest and most convenient operations to perform. Therefore, each of the Illinois Basin refuse materials (Plants A, B, and C) was classified according to size, both to characterize the distributions of sizes present and to determine whether mineral or trace element separations could possibly be made by this technique.

After drying, the samples were screened and hand separated into five size categories: −1/4 in., −1 in., −1 x 2 in., −2 in., and +2 in. Representative samples of waste in each of these size ranges is shown in Figs. 10a through e. Occasionally, pieces larger than 15 cm (6 in.) in width or length appear; these were included in the +2 in. material, but are shown separately in Fig. 10f. The relative amount of each size fraction was determined by weighing. The particle size distributions for each of the three Illinois Basin coal refuse types are shown in Fig. 11. Two of the plants (A and C) have similar size materials, whereas the other (B) has a finer blend.

Following size analyses, each fraction was crushed, blended, and further reduced in preparation for further characterization. While doing the sample size separations, we noted visually that certain mineral types had tendencies to accumulate in certain size ranges. For example, the clays were very friable and showed a marked tendency to disintegrate into small particles. On the other hand, much of the heavier mineral matter, presumed at the time to be pyritic material, congregated in the larger size fractions. The analytical results obtained thus far on the size fractions, for the most part, substantiate these observations. The mineralogical data are incomplete, but referral to the iron and sulfur values for Plant B wastes, found in Table XV, confirms that the largest waste particles (>1 in.) contain substantially greater proportions of pyrite and marcasite than the smaller fractions. Consideration of the aluminum values suggests that the clay minerals are more uniformly spread over all the size ranges, but there does appear to be some bias toward greater aluminum (clay mineral) content in the smaller size ranges. A clearer picture of this situation will be provided when the quantitative mineral analyses are completed.

A very interesting picture emerges from a consideration of the tendencies of some of the trace elements to preferentially segregate in the various particle sizes. The relatively high contents of iron, sulfur, arsenic, and molybdenum in the largest waste fragments is rather striking, as are the enriched concentrations of such elements as lithium, phosphorus, copper, zinc, and lead in the smaller size fractions. A compilation of the trace element compositions as a function of waste particle size appears in Table XVI.

Although it is not yet clear why certain trace elements are preferentially found in certain waste size ranges, nor is it yet certain that this phenomenon is universal, the implication of such behavior is important because it suggests that it may be possible to separate or remove certain trace elements from coal preparation waste solely on the basis of waste particle size.
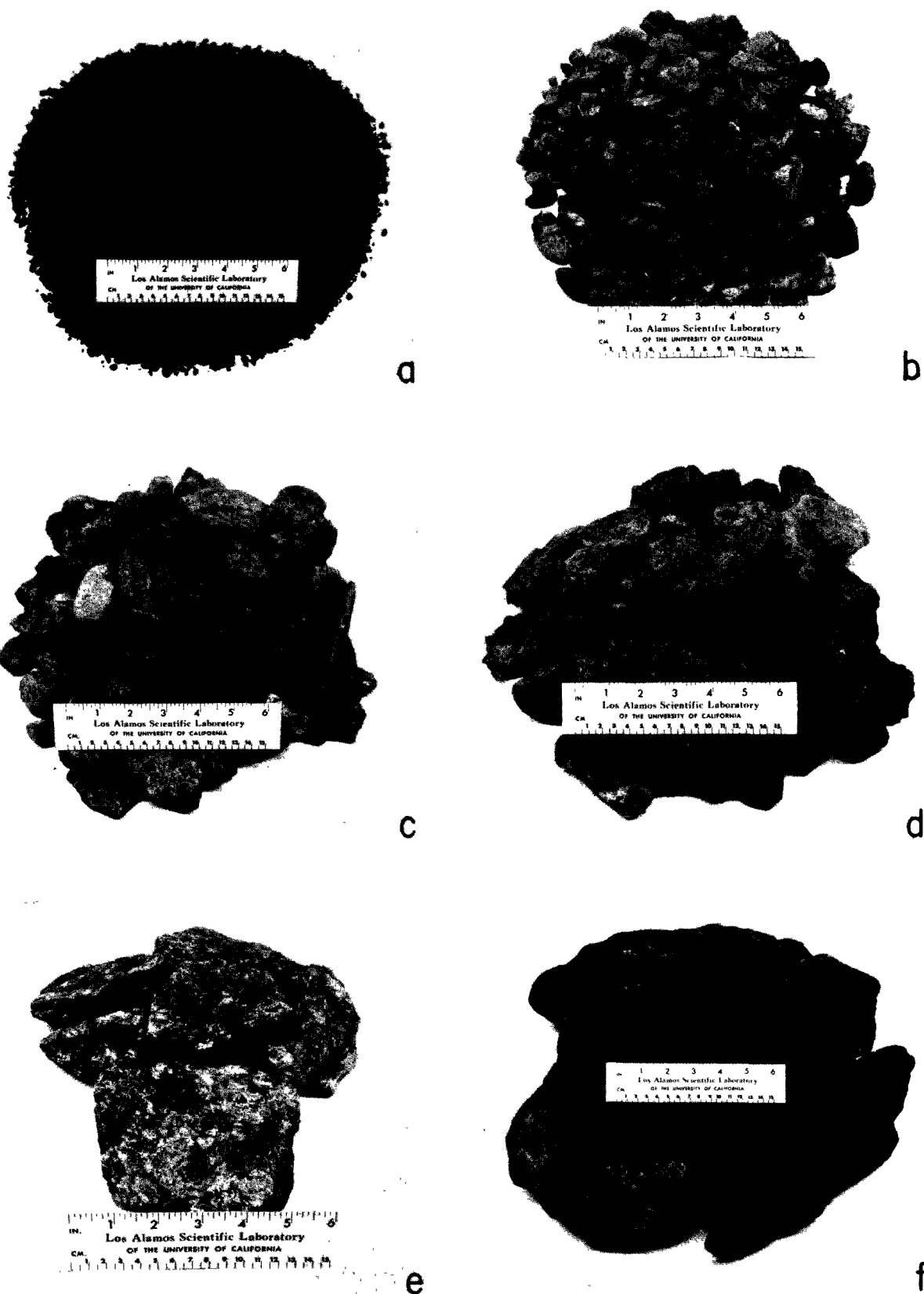
Fig. 10.

Size fractions of Illinois Basin coal refuse. a, −1/4 in.; b, −1 in.; c, −1 x 2 in.; d, −2 in.; e, +2 in.; f, +6 in.

31
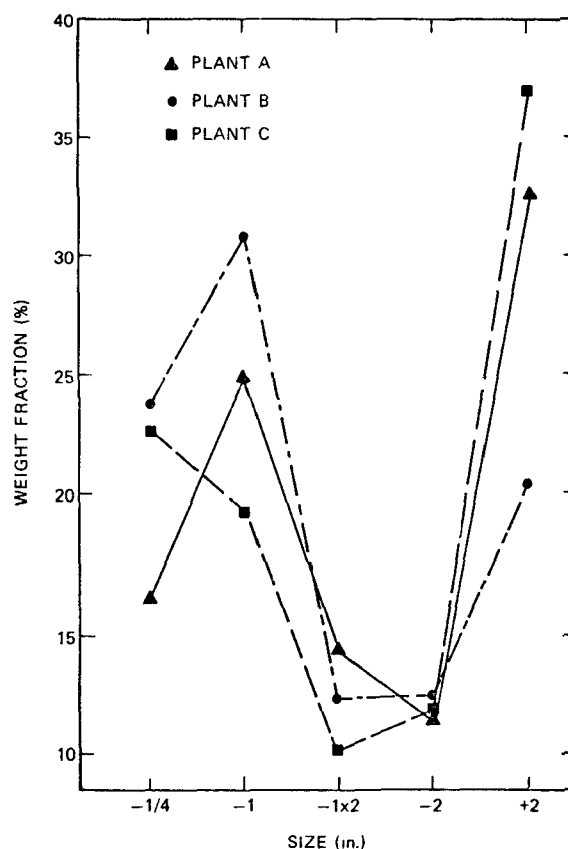
Fig. 11.
Size distribution of coal cleaning wastes from the Illinois Basin.

TASK 3—LABORATORY PROGRAM FOR TRACE ELEMENTS REMOVAL/RECOVERY

Work on this task was begun as scheduled during the second half of the fiscal year. Progress in this area has been slow, however, due to the necessity of having first to identify specific environmental problems from trace elements in coal wastes before control or removal measures can be defined. Nonetheless, some of the activities described above, for example, the separation of trace elements according to waste particle size and the removal or recovery of trace elements by aqueous leaching, apply directly to the goals of this task. Greater emphasis can be given to Task 3 after we are further along with our studies of coal refuse composition and environmental behavior.

Personnel

A large number of LASL personnel contributed to the programmatic effort during the past year. Their work and continued interest is essential to the success of this program and is deeply appreciated.

Advisors: R. D. Baker, R. J. Bard, and R. C. Feber

Analytical Advisors: G. R. Waterbury, M. E. Bunker, and N. E. Vanderborgh

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Neutron Activation Analyses: E. S. Gladney, W. K. Hensley, J. Bubernak, and G. M. Matlack

Spectrochemical Analyses: O. R. Simi, J. V. Pena, and D. W. Steinhaus

Atomic Absorption Spectrophotometry and Wet Chemistry: R. D. Gardner, J. E. Troxel, and W. H. Ashley

X-ray Fluorescence, Electron Microprobe, and Ion Microprobe: E. A. Hakkila, J. M. Hansel, W. B. Hutchinson, and N. E. Elliot

X-ray Diffraction/Mineralogy: J. A. O'Rourke

Mass Spectrometry: E. D. Loughran

Literature Search: E. M. Wewerka, J. M. Williams, P. L. Wanek, and J. D. Olsen

TABLE XV

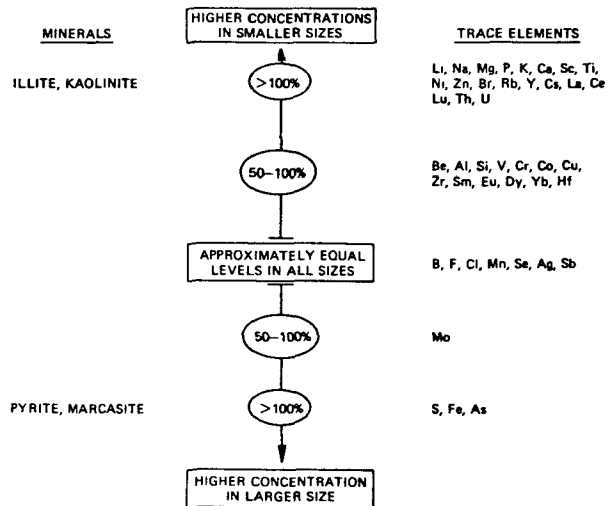### TRACE ELEMENT AND MINERAL CONTENT OF SIZED COAL-WASTE MATERIALS FROM ILLINOIS BASIN PLANT B

SAMPLE (1)	AVG	24B	24C	24D	24E	24F
IDENTITY	GOB	AVE -1/4	AVE -1	AVE -1D	AVE -2	AVE +2
LOCALE	PLANT B	PLANT B	PLANT B	PLANT B	PLANT B	PLANT B
DATE OBTND	1-19-75	11-19-75	11-19-75	11-19-75	11-19-75	11-19-75
PCT H2O	10.12					
PCT LTA	79.02	86.30	78.90	80.20	68.80	81.30
PCT HTA	63.57	72.30	65.20	64.60	49.80	60.00
PCT ORIGNL	100.00	23.80	30.90	12.40	12.50	20.30
SIZE,KG	48.77					
CHNS ANAL	AVERAGED	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS
CARBON	19.83	13.80	20.70	19.60	27.60	17.30
HYDROGEN	2.23	2.00	2.20	2.20	2.50	1.70
NITROGEN	.43	.30	.45	.43	.56	.38
SULFUR	13.47	8.60	8.50	8.60	13.90	24.40
MINERALOGY (2)	AVERAGED	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS	RAW BASIS
KAOLINITE QUANT	8.97	MAJOR	MAJOR	MAJOR	MINOR	MINOR
ILLITE QUANT	16.00	MAJOR	MAJOR	MAJOR	MINOR	
QUARTZ QUANT	11.10	MAJOR	MAJOR	MAJOR	MAJOR	MINOR
PYRITE QUANT	25.70	MAJOR	MAJOR	MAJOR	MAJOR	MAJOR
SPHALERITE QUANT						
CALCITE QUANT	-.01					
MIXED CLAY QUANT		MINOR	MINOR	MINOR	MINOR	
MARCASITE QUANT			TRACE		MINOR	MAJOR
GYPSUM QUANT		TRACE			TRACE	
ROZENITE QUANT						
ALBITE QUANT						

TABLE XV (cont)

SAMPLE / ELEMENT	AVG AVERAGED (3)	24B RAW BASIS	24C RAW BASIS	24D RAW BASIS	24E RAW BASIS	24F RAW BASIS
LI PPM HA	102.00	125.00	119.00	126.00	79.00	54.00
BE PPM HA	2.77	3.50	2.80	3.50	2.50	1.70
B PPM LE	64.00	67.00	68.00	65.00	57.00	57.00
F PPM RO		730.00	580.00	660.00	740.00	520.00
NA PCT HA	.06	.10	.08	.09	.05	.04
	.08	.09	.06	.09	.07	.05
MG PCT HA	.23	.32	.26	.28	.18	.13
AL PCT HA	5.09	5.92	5.47	5.26	4.12	3.17
SI PCT RO	13.57	17.10	14.60	15.90	9.70	8.90
P PPM RO	57.00	600.00	210.00	480.00	200.00	-10.00
CL PPM RA		37.00	39.00	31.00	55.00	40.00
K PCT HA	1.12	1.48	1.22	1.40	.97	.71
CA PCT HA	.09	.12	.09	.08	.06	.07
SC PPM RA	12.00	18.00	15.00	12.00	10.00	6.80
TI PCT RA	.35	.45	.41	.42	.26	.21
V PPM RN	86.00	120.00	100.00	92.00	61.00	51.00
CR PPM HA	76.67	82.00	73.00	79.00	64.00	47.00
MN PPM RN	146.67	190.00	160.00	130.00	130.00	120.00
	148.00	202.00	150.00	156.00	92.00	125.00
FE PCT HA	10.97	9.00	8.50	9.50	11.20	16.20
CO PPM RN	30.00	44.00	34.00	24.00	26.00	24.00
NI PPM LE	71.33	110.00	70.00	70.00	43.00	50.00
CU PPM HA	51.00	69.00	53.00	61.00	35.00	34.00
ZN PPM RA	124.00	178.00	106.00	111.00	78.00	58.00
GA PPM HA	-8.00	-9.00	-8.00	-8.00	-7.00	-8.00
GE PPM LE	94.33	64.00	64.00	54.00	88.00	200.00
AS PPM RN	6.20	5.70	5.70	6.00	6.60	7.40
SE PPM RN	2.00				3.30	1.30
BR PPM RN						
RB PPM LE	96.00	210.00	160.00	120.00	80.00	190.00
Y PPM LE	17.67	20.00	22.00	19.00	12.00	12.00
ZR PPM LE	87.33	100.00	84.00	79.00	63.00	65.00
MO PPM LE	52.33	46.00	40.00	42.00	53.00	87.00
AG PPM HA	.50	.80	.40	.60	.70	.40
CD PPM HA	.67	.50	.30	.20	.30	.90
SN PPM LE	-8.00	-9.00	-8.00	-8.00	-7.00	-8.00
SB PPM RN	1.37	1.70	1.10	1.10	1.20	1.10
I PPM RN	6.57	9.10	7.70	5.90	4.90	2.70
CS PPM RN	37.00	50.00	45.00	35.00	25.00	24.00
LA PPM RN	73.33	110.00	91.00	70.00	55.00	50.00
CE PPM RN	5.90	8.70	7.40	5.70	4.50	4.30
SM PPM RN	1.23	1.80	1.50	1.20	.96	1.00
EU PPM RN	4.37	6.70	5.60	5.40	3.20	3.30
TB PPM RN	3.23	3.90	3.60	3.10	2.33	2.10
DY PPM RN	.41	.56	.51	.38		.20
YB PPM RN	3.13	4.70	3.70	3.20	3.20	2.20
LU PPM RN	.94	1.20	.98	.90	1.40	1.40
HF PPM RN						
TA PPM RN						
W PPM RN						
HG PPM HA	12.00	39.00	30.00	38.00	25.00	35.00
PB PPM RA	9.50	14.00	12.00	9.60	7.80	5.10
TH PPM RO	2.70	3.70	3.20	3.10	2.00	1.60
U PPM RO						

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TABLE XVI

**SEGREGATION OF TRACE ELEMENTS
AND MINERALS ACCORDING TO
PARTICLE SIZE OF ILLINOIS
BASIN COAL WASTE[a]**

MINERALS		TRACE ELEMENTS
	HIGHER CONCENTRATIONS IN SMALLER SIZES	
ILLITE, KAOLINITE	(>100%)	Li, Na, Mg, P, K, Ca, Sc, Ti, Ni, Zn, Br, Rb, Y, Cs, La, Ce Lu, Th, U
	(50–100%)	Be, Al, Si, V, Cr, Co, Cu, Zr, Sm, Eu, Dy, Yb, Hf
	APPROXIMATELY EQUAL LEVELS IN ALL SIZES	B, F, Cl, Mn, Se, Ag, Sb
	(50–100%)	Mo
PYRITE, MARCASITE	(>100%)	S, Fe, As
	HIGHER CONCENTRATION IN LARGER SIZE	

[a]Correlations based on samples 24B, C, and F in Table XV.

APPENDIX A

SUMMARY AND CONCLUSIONS FROM LITERATURE SURVEY

The major conclusions from the review of the literature are that

• Few studies of the trace elements in coal preparation wastes have been conducted.

• There is a considerable body of knowledge about trace elements and minerals in raw coals, which, in most instances, can be applied directly to coal wastes.

• The fate of trace elements during coal washing or preparation is poorly defined.

• The drainage and runoff from coal refuse is a serious polluter of waterways, but neither the contributions nor the effects of trace elements to this form of environmental contamination is well understood.

• Combustion of coal-waste materials is a major source of air pollution; however, the fate of trace elements during waste-dump burning is unknown.

• Based on the available information, a comprehensive assessment of the seriousness of environmental contamination from trace elements in coal preparation wastes cannot be made.

• Some of the methods used to prevent or treat acidic effluents from coal wastes may also be useful for controlling trace element releases, but these may lead to undesirable secondary effects in some cases.

• Significant quantities of important minerals and materials are present in coal refuse, but methods for recovering them have not been extensively investigated within the context of today's economics.

The following paragraphs provide brief summaries of the highlights of each of the major sections included in the review.

Introduction

The mineral wastes from coal preparation and mine development constitute a major environmental problem. Over 3-billion metric tons of these materials have accumulated in the U.S., and the current annual rate of waste production (100-million metric tons per year) is expected to double within a decade. The total number of active and abandoned refuse dumps is estimated to be between 3000 and 5000. About one-half of these pose some type of health, environmental, or safety problem. Structural weaknesses in coal refuse banks have led to tragic landslides. Coal waste piles are also the source of highly mineralized, often acidic drainage, which affects more than 10 000 miles of streams and waterways, and the 300 or so burning refuse dumps are a major source of air pollution. In addition to these problems, there is growing concern about possible environmental contamination from the trace elements in coal mineral wastes. The purpose of this review is to use the available information to assess the potential of this latter possibility.

Literature Search Format

An extensive search of the open literature on trace elements in coal preparation wastes and environmental contamination from these elements was completed both by computer- and manual-search techniques. Over 4400 references on the general topics of coal, coal wastes, the elemental and mineralogical composition of coal and its wastes, and the environmental behavior of these materials, were reviewed. This major collection of background information was culled to 200 of the most pertinent references, on which this review is based.

Trace Elements and Minerals in Coal Preparation Wastes

Only a few studies of the minerals and trace elements in coal preparation wastes have been reported. Most of these have concerned the identification and structures of the major minerals; only limited attention has been given to the trace elements present in these wastes.

Trace Elements and Minerals in Raw Coals

Much information on this subject is available, and most of it can be applied to coal preparation wastes. Clay minerals, silica, carbonates, sulfides, and sulfates constitute the major minerals in most coals. Nearly all of the naturally occurring elements have been identified in coals—most in trace or minor amounts. With few exceptions, the less-abundant elements are associated with the major mineral phases. This leads to the conclusion that the behavior of many of the trace elements in coal wastes during weathering, leaching, or burning will be dictated by the behavior of the major minerals.

Trace Element Behavior During Coal Preparation

The fate of trace elements during coal preparation has received only limited attention, and still is not well defined. Laboratory investigations of elemental behavior using float-sink techniques have been conducted. These studies reveal that trace elements differ in their susceptibilities to be removed from coals by density separation, but significant reductions of these elements in coals can be achieved. Therefore, large quantities of trace elements are discarded in the washing refuse.

Water Contamination from Trace Elements in Coal Preparation Wastes

The aqueous drainage from coal refuse is usually contaminated by acids and dissolved or suspended mineral matter. The higher concentrations of dissolved species are found in the more highly acidic solutions. Typically, the acid drainage from coal refuse contains high concentrations of Fe, Al, Ca, Mg, and SO_4 ions, which are derived from the major minerals. Little is known about the minor or less abundant trace elements in coal waste drainage. Some of these elements have been identified in the drainage or leachates from coal refuse or spoils, but a thorough assessment of this subject has not been made. There is considerable evidence that coal refuse dumps will continue to produce significant quantities of water-borne contaminants for many years after their disposal.

Trace Element Emissions from Burning Coal Refuse

The gaseous products from the combustion of residual carbon and minerals in coal refuse are significant atmospheric contaminants. Approximately 300 to 500 of these waste piles are now burning. The causes of refuse fires are varied, but once started they can burn for many years. By analogy with other coal-combustion systems, volatile trace elements are undoubtedly released by burning refuse, but this problem has not been addressed.

Trace Elements of Environmental Concern in Coal Preparation Wastes

There are numerous potentially toxic trace elements in coal wastes, and many of these find their way into the environment. Ions, such as iron, aluminum, and manganese, which leach out of coal refuse in large amounts, can be harmful to soils, waterways, and plant and animal life. Little information exists on the behaviors of toxic heavy metals in coal refuse banks. The possibility that toxic elements can accumulate or concentrate within the waste pile, or in the surrounding environment, warrants attention. Based on the available information, an adequate assessment of the total potential for environmental contamination from trace elements in coal preparation wastes cannot be made.

Prevention and Treatment of Contamination from Coal Preparation Wastes

Much attention has been given to methods for preventing or controlling contamination from coal refuse materials. These techniques have been directed primarily at preventing or neutralizing acidic effluents and reducing the dissolved or suspended mineral matter in waste waters. Preventive measures include grading, compacting, and sealing of wastes to reduce the influx of air and water. Treatment of acid drainage is done by alkaline neutralization, ion exchange, reverse osmosis, or flash distillation. Some of the methods for preventing or treating acid drainage may also be useful for controlling or reducing environmentally harmful trace elements.

Recovery of Trace Elements and Minerals from Coal Waste Materials

Some work has been reported on the use of coal refuse materials. Of primary interest is the recovery of residual coal, but the use of these wastes for building and construction products and as a source of metals or minerals has also been reported. Among the major materials that have been sought from coal wastes are sulfur and aluminum. Processes for recovering minor elements such as gallium, germanium, manganese, and molybdenum have been developed. Magnetic separation, ion exchange, and roasting and leaching methods are among the most promising techniques for recovering useful materials from coal refuse. Coal mineral wastes could supply much of the U.S. demand for certain metals and minerals if the economic and technological problems of recovery could be solved.

APPENDIX B

SAMPLE PREPARATION, ANALYTICAL PROCEDURES, AND ANALYTICAL RESULTS FOR STANDARD COAL AND ASH SAMPLES

Sample Preparation and Reduction

Raw coal and waste samples are crushed to less than 2 in. with a hammer. The material is spread thinly in ceramic-coated pans and dried for 24 h at 60°C in a forced-draft oven. The dried

sample is further crushed to −3/8 in. with a jaw crusher, and then is reduced to a 0.5-kg lot with a cone or riffle splitter. In the final step, the reduced coal or waste samples are pulverized to −20 mesh with a rotary grinder (equipped with ceramic plates).

Low- and High-Temperature Ashing

Low-temperature ashing (LTA) is done in an oxygen-plasma asher according to the following procedure.

Five powdered (−20 mesh) and blended samples of coal or waste material (0.7-g each) are dried for 24 h at 60°C after having been placed into ceramic boats. Then the dried samples are ashed at 75°C until all of the organic matter has been removed (constant weight). This usually requires 72 to 96 h to complete. During ashing, the samples are stirred frequently to expose new material to the oxygen plasma. The three sample boats with ash values closest to the mean of all five samples are selected for analytical work.

High-temperature ashing (HTA) is done by a procedure similar to that used for LTA, except that the ashing step is done at 500°C in an electric muffle furnace. About 2 h is required to completely ash a sample at high temperature.

Neutron Activation Analysis

Neutron activation analysis (NAA) is one of the most accurate and reliable methods of assaying for trace elements in natural materials. The method relies on the production of radioactive nuclides in a sample and the subsequent detection and measurement of the associated gamma radiation with a Ge(Li) detector. It is a nondestructive technique in most applications, and has the advantage that many elements can be observed simultaneously. Although the method is "blind" to a number of elements, this is often advantageous. Among those that cannot be observed (or are very difficult to observe) are carbon, oxygen, silicon, and lead.

The present program involves the trace element assay of large numbers of samples of coal and waste residues. For this work, we have developed a computer code that will scan the gamma-ray spectrum of a neutron-bombarded sample and produce a list of all elements identified and their concentrations (in ppm). The method involves matching each gamma-ray energy against a computer "library" of possible gamma rays that can result from neutron capture. The library contains the principal gamma rays from 67 elements, involving 124 separate isotopes. However, it should be recognized that in routine NAA analyses of natural materials (coal, rock, soil, etc.), it is unusual to observe more than about 30 elements unless postbombardment chemistry is employed.

We have tested our system by assaying several standard NBS materials. Table B-I includes the NAA results for NBS coal (SRM-1632), and Table B-II contains the NAA results on the NBS standard fly ash (SRM-1633). Eight elements (titanium, manganese, magnesium, vanadium, aluminum, sodium, calcium, and barium) were determined using 15-mg samples which were irradiated for 20 s in a thermal neutron flux of 7×10^{12} n/cm^2 s. These samples were permitted to decay for 10 min following the irradiation and were then counted for 10 min with a 55-cm^3 Ge(Li) detector. The remaining elements were determined using 3-g samples and an irradiation time of 5 min. These samples were permitted to decay for 10-14 days and were then counted for 10 min. Additional elements could be determined, if deemed necessary, by lengthening the counting periods or by modifying the decay times. Based on the two-count procedure described above, the

TABLE B-I

ANALYTICAL RESULTS FOR COAL SRM 1632

Element	SRM-1632 Coal[a,b] Elemental Concentrations	Emission[a,c] Spectroscopy	Atomic[a,d] Absorption and Wet Chemistry	Neutron[a] Activation
Li		24 ± 1.1	25	
Be	1.5	1.2 ± 0.07	1.5	
B		30 ± 1.1		
F			100	
Na	414 ± 20	1200*		415 ± 42
Mg	0.20 ± 0.05%	0.16%*		0.20 ± 0.04%
Al	1.85 ± 0.13%	2.1%		1.80 ± 0.18%
Si	3.2%	2.1%*	3.2%	
P			71	
K	0.28 ± 0.03%	0.31%*		0.28 ± 0.05%
Ca	0.43 ± 0.05%	0.51%*		0.44 ± 0.09%
Sc	3.7 ± 0.3	3.6 ± 0.08		3.8 ± 0.4
Ti	1040 ± 110	900*	800	1100 ± 110
V	[35 ± 3]	32 ± 1.3	36	36 ± 4
Cr	[20.2 ± 0.5]	16 ± 1.2	19	21.6 ± 2
Mn	[40 ± 3]	36 ± 1.8	40	40 ± 4
Fe	[8700 ± 300]	6500*	8730	9800 ± 1000
Co	5.7 ± 0.4	4.7 ± 0.32	7	5.8 ± 0.6
Ni	[15 ± 1]	15 ± 1.1	15	
Cu	[18 ± 2]	17 ± 7.5	21	
Zn	[37 ± 4]	45 ± 17	37	34
Ga		6.2 ± 0.3		
Ge		2.7 ± 0.22		
As	[5.9 ± 0.6]		7	6.6 ± 1.3
Se	[2.9 ± 0.3]			3.1
Rb	21 ± 2	22 ± 2.9		19 ± 6
Sr	161 ± 16	280*		170 ± 17
Y		7.6 ± 0.81		
Zr		25 ± 3	46	
Nb		<15		
Mo		3.6 ± 0.16		
Ru		<5		
Rh		<5		
Ag	0.06 ± 0.03	<0.15	0.08	
Cd	[0.19 ± 0.03]	0.7	0.31	
Sn		2-10		
Sb	3.9 ± 1.3			4.1 ± 1.2
Cs	1.4 ± 0.1			1.4 ± 0.3
Ba	352 ± 20	410*		345 ± 70
La	10.7 ± 1.2	6.0 ± 0.17		
Ce	19.5 ± 1	30		19.7 ± 0.2
Pr		<15		

TABLE B-I (cont)

Element	SRM-1632 Coal[a,b] Elemental Concentrations	Emission[a,c] Spectroscopy	Atomic[a,d] Absorption and Wet Chemistry	Neutron[a] Activation
Nd		<15		
Sm	1.7 ± 0.2	<15		
Eu	0.33 ± 0.04	0.41 ± 0.06		0.37 ± 0.04
Gd		<15		
Tb	0.23 ± 0.05	<15		0.20 ± 0.04
Dy		<5		
Ho		<1.5		
Er		<15		
Tm		<5		
Yb	0.7 ± 0.1	0.91 ± 0.07		0.55 ± 0.08
Lu	0.14 ± 0.01	<7		0.15 ± 0.02
Hf	0.96 ± 0.05			1.15 ± 0.12
Ir		<50		
Pt		<15		
Au		<5		
Hg	[0.12 ± 0.02]			0.16
Tl	[0.59 ± 0.03]	<5	<1	
Pb	[30 ± 9]	12-120	30	
Bi		<1.5	<1	
Th	3.2 ± 0.2	<15		3.2 ± 0.3
U	[1.4 ± 0.1]		6	

[a]All values are expressed in ppm unless otherwise indicated.

[b]Values in brackets are certified NBS results. Other values are NBS uncertified or from J. M. Ondov et al., Anal. Chem. 47, 1102 (1975).

[c]Emission spectrochemical results followed by an asterisk have an estimated precision of ±20% RSD (relative standard deviation), otherwise the precision is estimated to be ±50% RSD. A result with a standard deviation indicates the average of six replicate analyses.

[d]Atomic absorption values have an estimated precision of ±2.0% RSD unless the value is at the detection limit of the method.

sensitivity of our NAA counting setup for selected elements is as shown in Table B-III. As an example, if a 3-g sample containing 0.5 ppm arsenic were analyzed, the strongest arsenic gamma ray would produce a peak with an area of ~100 counts, which is about as small a peak as we have confidence in measuring.

Spectrochemical Analysis (Optical Emission Spectroscopy)

Three spectrochemical methods were used for the analysis of coal and coal ash samples: (1) a high-temperature ashing (HTA) method for trace elements, (2) an improved low-temperature ashing (LTA) method for trace elements, and (3) a method for major and minor elements. In the

TABLE B-II

ANALYTICAL RESULTS FOR COAL ASH SRM 1633

Element	SRM-1633[a,b] Coal Ash Elemental Concentrations	Emission[a,c] Spectroscopy	Atomic[a,d] Absorption and Wet Chemistry	Neutron[a] Activation	X-ray[a] Fluorescence
Li		140 ± 9	80		
Be	12	14 ± 0.95	12		
B		500 ± 29			
F			20		
Na	0.32 ± 0.04%	0.97%*		0.34 ± 0.03%	
Mg	1.8 ± 0.4%	1.6%*		1.5 ± 0.3%	
Al	12.7 ± 0.5%	13%*		12.3 ± 0.5%	
Si	21 ± 2%	17%*			
P			880		
K	1.61 ± 0.15%	3.3%*			
Ca	4.7 ± 0.6%	4.8%		5.1 ± 0.6%	3.5%
Sc	27 ± 1	23 ± 2.3		24 ± 1	
Ti	0.74 ± 0.03%	0.72%*	0.87%	0.70 ± 0.07%	0.30%
V	[214 ± 8]	230 ± 12	410	225 ± 20	
Cr	[131 ± 2]	150 ± 13	130	118 ± 8	
Mn	[493 ± 7]	460 ± 26	506	504 ± 25	
Fe	6.2 ± 0.3%	5.6%	7.0%	5.6 ± 0.2%	6.0%
Co	41.5 ± 1.2	38 ± 0.96	39	41 ± 3	
Ni	[98 ± 3]	120 ± 7.5	78		
Cu	[128 ± 5]	110 ± 11	129		
Zn	[210 ± 20]	210 ± 36	250	308 ± 75	
Ga		68 ± 14			
Ge		25 ± 1.4			
As	[61 ± 6]			68 ± 15	
Se	[9.4 ± 0.5]			10.1 ± 2.2	
Rb	125 ± 10	110 ± 22		112 ± 20	
Sr	0.17 ± 0.03%	0.23%			0.8%
Y	62 ± 10	44 ± 4.2			
Zr	301 ± 20	160 ± 34			
Nb		<100			
Mo		37 ± 1.3			
Ru		<30			
Rh		<30			
Ag		<1	0.35		
Cd	[1.45 ± 0.06]	<5	1.53	1.0	
Sn		10			
Sb	6.9 ± 0.6	<100		9.8 ± 2.1	
Cs	8.6 ± 1.1			7.7 ± 1.3	
Ba	0.27 ± 0.02%	0.30%*		0.25 ± 0.03%	0.18%
La	82 ± 2	45 ± 4.5		86 ± 2	
Ce	146 ± 15	200		145 ± 6	
Pr		<100			

Element	SRM-1633[a,b] Coal Ash Elemental Concentrations	Emission[a,c] Spectroscopy	Atomic[a,d] Absorption and Wet Chemistry	Neutron[a] Activation	X-ray[a] Fluorescence
Nd		<100			
Sm	12.4 ± 0.9	<100		12.8 ± 0.6	
Eu	2.5 ± 0.4	2.8 ± 0.13		2.6 ± 0.2	
Gd		<100			
Tb	1.9 ± 0.3	<100			
Dy		<30			
Ho		<10			
Er		<100			
Tm		<30			
Yb	7 ± 3	5.7 ± 0.56		4.8 ± 0.6	
Lu	1.0 ± 0.1	<50		1.0 ± 0.2	
Hf	7.9 ± 0.4			6.5 ± 0.7	
Er		<300			
Pt		<90			
Au		<30			
Hg	[0.14 ± 0.01]				0.55
Tl	4	<30	5		
Pb	[70 ± 4]	74 ± 9	82		
Bi		<10			
Th	24.8 ± 2.2	<100		22.5 ± 0.6	
U	[11.6 ± 0.2]				

[a]All values are expressed in ppm unless otherwise indicated.

[b]Values in brackets are certified NBS results. Other values are NBS uncertified or from J. M. Ondov et al., Anal. Chem. 47, 1102 (1975).

[c]Emission spectrochemical results followed by an asterisk have an estimated precision of ±20% RSD (relative standard deviation) otherwise the precision is estimated to be ±50% RSD. A result with a standard deviation indicates the average of six replicate analyses.

[d]Atomic absorption values have an estimated precision of ±2.0% RSD unless the value is at the detection limit of the method.

HTA method for trace elements, the coal is ignited at a high temperature (~750°V), the ash is mixed with an equal weight of high-quality graphite powder, and precisely weighed portions of the mixture are analyzed by dc-arc excitation. In the LTA method, the sample is ignited at <100°C in an oxygen plasma, the ash is mixed with four parts of sodium carbonate-graphite powder buffer, and weighed portions of the mixture are excited by dc arc. When the method for major and minor elements (sodium, magnesium, aluminum, silicon, krypton, calcium, titanium, iron, strontium, barium) is applied, HTA or LTA is mixed with 40 parts of copper oxide-graphite powder buffer and weighed portions are analyzed by dc-arc excitation.

Results were obtained by visual comparison of standards and samples exposed on the same spectrographic plate or by photometry of those plates. A visual comparison result has a precision estimated at ±50% relative standard deviation (RSD). A result obtained by photometry has an estimated precision of ±20% RSD.

TABLE B-III

ESTIMATED 100-COUNT PEAK-AREA
DETECTION LIMITS IN TYPICAL
NAA ANALYSIS OF 3-g SAMPLES

Element	ppm	Element	ppm
Ba	45	Lu	0.04
Sr	45	Th	0.5
Cu	2	Cr	5
K	450	Hf	0.7
As	0.5	La	2
Ti	500	Sb	1
Mn	4	Cs	2
Mg	6000	Sc	0.09
Na	100	Fe	900
V	6	Zn	10
Al	300	Co	2
Ca	5000	Eu	0.3
W	0.5	Yb	0.5
Sm	0.07	Rb	50
Ce	2	Ta	0.5

The emission spectrochemical results for the coal (NBS SRM-1632) and the coal ash (NBS SRM-1633) are presented in Tables B-I and B-II, respectively, with the results obtained by other methods. The spectrochemical results agree very favorably with the NBS certified values.

Atomic Absorption Spectrophotometry

One of the main techniques used for determining trace elements and minor constituents in the NBS coal and fly ash samples was atomic absorption spectrophotometry with a carbon-rod atomizer.

The coal samples were dry-ashed at a high temperature ($\sim$500°C). The resulting ash and the NBS fly ash were dissolved in 5 ml 12M Hcl at 300°C in a sealed quartz tube. The SiO_2 was filtered for gravimetric determination, and the solutions were analyzed for specific trace elements by atomic absorption spectrophotometry. The results of these analyses are also given in Tables B-I and B-II.

Two wet-ashing techniques were investigated: one using a HNO_3-$HClO_4$ mixture and one using HF. Both techniques left a slight amount of insoluble residue indicating incomplete dissolution.

A small sample of low-temperature ash from the NBS coal was analyzed, and the results were compared with the high-temperature ash results. Zinc, lead, copper, cadmium, and silver gave higher results (10-30%) on the low-temperature ash with the titanium result being lower.

X-Ray Fluorescence and Ion Microprobe

X-ray spectroscopy, electron microprobe, and ion microprobe techniques were evaluated for examination of coal and fly ash. In x-ray spectrographic analysis, the powdered samples were examined using an energy dispersive spectrograph without sample dissolution or separation procedures.

Energy dispersive x-ray spectroscopy was evaluated for determining major constituents in the ash sample, NBS SRM-1633. Zinc was used as an internal standard, but only linear background corrections and no correction for absorption or fluorescence were employed. Results (Table B-II) were in fair agreement with other methods, but probably could be improved with better excitation of the sample and with a mathematical treatment of the data.

The NBS coal ash sample also was analyzed with the ion microprobe (IMMA) using a computer program CHARISMA for quantitative data reduction (Table B-IV). Data were uncorrected for overlapping oxide peaks. A mathematical correction for overlapping peaks is being developed as time permits, and application of corrections should improve results and enable determination of more elements.

X-Ray Diffraction

Both qualitative and quantitative x-ray studies are under way on raw coals and ash. It now appears that quantitative results can be obtained for most of the common mineral constituents in the raw coals by examining the low-temperature ash fractions.

The method used is essentially that developed at the Mellon Institute by Klug, et al.[1-3] for the analysis of quartz in industrial and community dusts, which was subsequently extended by Rao[4] and Miller[5] to the evaluation of mineral constituents in coals. For this purpose 1 μ α-Al$_2$O$_3$, of high purity, is being used as an internal standard. The values of the proportional constants, the R-factors, given by Miller for such components as illite, kaolinite, and pyrite are being reexamined and various methods of preparing truly unoriented samples are being explored. Hopefully the R-factors for the unoriented or reproducibly oriented clay minerals will soon be known with greater accuracy.

In an initial application of the quantitative method, a sample of the standard NBS coal, SRM-1632, was evaluated. In the raw coal sample only "illite," kaolinite, and α-quartz were detected above the high background radiation, but after 75°C ashing (LTA) most of the expected mineral constituents were observed. Using the Miller R-factors, quantitative analysis of the LTA fraction gave the following percentages of minerals as present in the raw coal:

4.46% Kaolinite

7.9% Illite Group Minerals

2.08% α-Quartz

<0.1% Sphalerite

1.59% Pyrite

0.52% Calcite

The percentages listed for the clay minerals must be considered at present as only approximate. It would appear however, that once good R-factors are available, and with isotropic samples, the kaolinite content can be established with appreciably better accuracy. The illite indicial peak appeared to be from a composite of two or more illite-group minerals, therefore any measurements assuming pure illite can only be relative. Separation of the minerals of this group by methods developed at the USBM[6] seems feasible, thus permitting analysis of the individual components; however, the accuracy of such analyses will probably never be as great as with the other components.

TABLE B-IV

COMPARISON OF IMMA VALUES FOR
SRM-1633 COAL ASH WITH OTHER TECHNIQUES[a]

Element	NBS Value Certified	Round Robin Anal. Chem. 47, 1102 (1975)	IMMA
H			1.25%
Li			1.4
Be			5
B			180
C			1%
N			20
O			10.8%
F			60
Na		0.32 ± 0.04%	0.44%
Mg		1.8 ± 0.4%	1.2%
Al		12.7 ± 0.5%	10.2%
Si		21 ± 2%	22.9%
P			325
Ca		4.7 ± 0.6%	Interference
K		1.61 ± 0.15%	4.9%
Sc		27	Interference
Ti		0.74 ± 0.03%	0.75%
V	214 ± 8	235 ± 15	370
Cr	131 ± 2	127 ± 6	361
Mn	493 ± 7	496 ± 19	480
Fe		6.2 ± 0.3%	Interference
Co		41.5 ± 1.2	Interference
Ni	98 ± 3	98 ± 9	Interference
Cu	128 ± 5		230
Zn	210 ± 20	216 ± 25	Interference
As	61 ± 6	58 ± 4	87
Sr		0.17 ± 0.03%	0.19%
Ba		0.27 ± 0.5%	0.48%
U	11.6 ± 0.2	12 ± 0.5	

[a]All values are given in ppm unless otherwise specified.

Wet-Chemical Analyses

Several standard ASTM methods were used to characterize the SRM-1632 coal and SRM-1633 fly ash for moisture, volatile matter, ash, fixed carbon, hydrogen, total carbon, and nitrogen. Total sulfur, pyritic sulfur, carbonate carbon, chloride, and fluoride were measured using methods not available as ASTM procedures.

These analyses were performed on a 125-g sample that was pulverized in a diamond mortar to pass a No. 60 sieve. The material was allowed to equilibrate, and weighed portions were taken for

the following analyses by ASTM (D-271) methods. The precision valves are based on these replicate analyses.

Moisture: A 10-g portion was heated for 1 h at 110°C, and the weight loss calculated as moisture. Estimated precision was about 0.02%.

Volatile matter: A 1-g portion of sample was heated for 6 min at 600°C, then for 6 min at 950°C, excluding air. After correcting for moisture, the weight loss was calculated as volatile matter. Precision was about 0.05%.

Ash: The residue from the moisture determination was heated in air at 750°C to constant weight and the residue calculated as ash. Precision was about 0.02%.

Fixed carbon: Fixed carbon was calculated by subtracting from 100 the sum of moisture, volatile matter, and ash.

Hydrogen: A 50-mg sample was burned in O_2 at 900°C. The weight of water formed was calculated as H_2. The precision was about 2% relative.

Total carbon: Total carbon was determined by igniting a 25-mg sample in O_2 at 900°C. Carbon was calculated from the weight of CO_2 obtained. The precision was about 0.3%.

Nitrogen: Nitrogen was determined by the Kjeldahl procedure. After dissolving the sample in $18M$ H_2SO_4 with suitable catalysts, the solution was made basic, and the nitrogen was distilled as ammonia and titrated. Precision was about 1% relative.

ASTM methods were not available for the following analyses that were made by established LASL methods:

Total sulfur: Sulfur was determined with a LECO Titrimetric Sulfur Analyzer. A 50-mg sample was burned in O_2 and the combustion gases bubbled through a solution of HCl. The SO_2 was titrated with a KIO_3-KI solution as evolution occurred, using a starch indicator. Precision was about 2% relative.

Pyritic sulfur: Pyritic sulfur was determined by leaching first with HCl to dissolve readily soluble iron; then with HNO_3 to dissolve FeS_2. In the latter solution, iron was determined by atomic adsorption and the sulfur was calculated.

Carbonate carbon: The sample was treated with acid and the evolved CO_2 absorbed and weighed for calculation of carbon.

Chloride and fluoride: The sample was pyrohydrolyzed, and chloride and fluoride were determined in the distillate using specific ion electrodes.

The analytical results for the SRM-1632 and -1633 samples are presented in Table B-V for future reference and standardization. The analyses of the lignite coal from the Beulah Mine in North Dakota, which had been analyzed by the Bureau of Mines, are shown in Table B-VI.

TABLE B-V

WET-CHEMICAL ANALYSES OF STANDARD REFERENCE
MATERIALS 1632 AND 1633

| | SRM-1632 | | SRM-1633 |
	As Received	H₂O/Mineral-Free Basis	As Received
Moisture	2.74%		0.17%
Ash	13.41%		96.10%
Total C	68.9%	82.4%	3.05%
Fixed C	55.2%	66.1%	1.07%
Organic C	13.6%	16.3%	1.92%
CO₃ carbon	0.07%	0.08%	0.06%
H₂	4.46%	5.34%	0.10%
Total S	1.43%	1.71%	0.29%
Pyritic S	0.51%	0.61%	0.20%
O₂—diff.	8.03%	9.69%	0.25%
Volatile Matter	28.62%	34.25%	2.66%
Organic S	0.92%	1.10%	0.09%
N₂	1.03%	1.23%	0.04%
Cl	3.8%		0.08%
F	100 ppm		20 ppm

TABLE B-VI

ANALYSIS OF LIGNITE FROM BEULAH MINE, MERCER COUNTY, NORTH DAKOTA

| | LASL Analyses | | | Bureau of Mines Analyses | |
	As Received	(Calculated) Dry Basis	Dry Sample	As Received	Dry Sample
Moisture	13.6%	---	---	25.30%	---
Vol. Matter	38.0	44.0	43.7	33.02	44.21
Fixed C	39.8	46.0	46.2	34.29	45.89
Ash	8.6	10.0	10.1	7.39	9.90
Total	100.0	100.0	100.0	100.00	100.00
Hydrogen	4.5%	3.5%	4.1%	6.18%	4.51%
Carbon	54.4	63.0	62.0	46.55	62.32
Nitrogen	1.7	2.0	1.8	0.64	0.86
Oxygen	29.9	20.5	21.0	38.47	21.33
Sulfur	0.87	1.01	0.96	0.77	1.03
Ash	8.6	10.0	10.1	7.39	9.90
Total	100.00	100.00	100.00	100.00	100.00

APPENDIX C

PROCEDURES FOR COLLECTION OF COAL CLEANING WASTE SAMPLES

Illinois Basin Coal Cleaning Plant A

The first coal preparation plant that we sampled has a throughput of about 20 x 10³ tons of raw coal per day. The feed coal, which is a mixture of strip-mined varieties, is highly mineralized. The coal washing is done with a battery of six-cell McNally jigs. The coarse coal product is screen dried, and the finer coal is dewatered in a series of cyclones and is further dried in a rotary drier. The washing plant removes about 40% of the input material, and produces a cleaned coal containing approximately 10 wt% ash.

Fresh gob samples were obtained from a moving conveyor belt at the outlet of the washing plant. An approximately 11-kg sample was taken with a shovel every 600 s until a total of 30 increments (340 kg) were collected. As much as possible, a complete cross-belt sample was removed each time.

Four separate samples of feed coal, each weighing about 14 kg were collected at 1-h intervals from a stopped conveyor belt at the inlet of the plant. Also, 6 kg of cleaned coal, representative of an 8-h plant output, was obtained. This was collected from an automated sampling device located at the exit of the plant.

Finally, about 70 kg of weathered gob was retrieved from a waste pile which was approximately 1 yr old. Samples were collected at the surface and from a fresh cut about 24 in. deep produced by a bulldozer.

The samples collected at this plant, like all others gathered elsewhere, were sealed in plastic-lined drums for shipping and storage.

Illinois Basin Coal Cleaning Plant B

The input coal for this cleaning plant is also a mixture of strip-mined types. The coal is cleaned with one of two McNally jig boxes. The coarser coal (>0.25 cm) is screen-dried after passing through the jig table. Drying of the fine product is accomplished by a succession of screens, dewatering cyclones, and centrifugal driers. This plant produces about 4 x 10³ tons of clean coal (~10 wt% ash)/day.

There was no convenient place to collect the waste material at this cleaning plant, so we obtained the gob samples from the dump where they were being continuously deposited by trucks. Nine separate truckloads of waste, representing about 4 h of plant output, were sampled. Three separate 7-kg samples were taken from each truckload: one at the top, one at midside and one at the bottom-side of the pile. This procedure was used to obtain representative materials from each size range.

Five samples of feed coal ~7 kg each were collected from a moving belt at the entrance to the plant. These were taken at random over a 3-h period. The cleaned coal was sampled randomly eight times over the same 3-h period. About 60 kg total of this material was collected.

In addition to the fresh gob dump, we were given access to several older waste disposal areas. These ranged in age from about 2 to 10 yr old. We collected a quantity of weathered rocks, minerals, and finely divided materials from the surfaces and drainage areas of these waste heaps.

Illinois Basin Coal Cleaning Plant C

The day we visited this Illinois-Basin preparation plant, coal from a single underground seam was being washed. The plant contains two 3-cell jig boxes, although only one was operating when we were there. The cleaned coals are dried before shipping by techniques similar to those used in the other plants we visited: that is, by the use of screens, centrifugal dewatering devices, and rotary driers. The daily output of the washing plant is about 8 x 10^3 tons of coal containing about 11 wt% ash.

At this plant, we collected waste samples from the output streams of each of the cells of the jig box. By collecting the samples in this way, we were able to obtain unmixed quantities of fine, medium, and coarse gob. Eighteen total increments of each waste size were collected at 450-s intervals over 4 h. The amount of each size collected was in proportion to the relative output of each cell. A total of about 225 kg of wastes were obtained, of which ~90% was coarse material. It should be noted that our sampling sequence was interrupted several times because of a lack of coal.

About 70 kg of feed coal was collected semi-randomly from a moving belt over a 4-h period. The cleaned coal was collected during the same time in a random manner from railroad hopper cars. A total of about 27 kg of this material was obtained.

Low-Sulfur Coal Cleaning Plant D

The feed coal for this plant was furnished equally by an underground mine and a strip mine using the same coal seam. The major portion of the coal (>0.12 cm) is cleaned by heavy media flotation and hydrocyclones, while the finer material is cleaned by froth flotation. After the mineral matter is reduced from 20 to 7 wt% at an output of 2 x 10^3 tons of cleaned coal per day, the product is mechanically dewatered before storage to await shipping. The coarse waste is dumped by truck to form a dam behind which the slurry is drained.

Samples of approximately 10 kg each were collected at this coal cleaning plant. These included the feed coal, breaker rejects (+15 cm), and fresh gob, which had just been dumped at the disposal site. This material was collected over a short period of time from available storage piles.

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16. ABSTRACT The report gives the status of a program to assess the potential for environmental pollution by trace elements discharged from coal storage piles and coal cleaning wastes. Mineralogic and trace element analyses on raw coal and wastes from three Illinois Basin preparation plants are nearly complete. Aqueous leaching studies are in progress to determine the release potential of pollutants from coals and coal wastes. The work will lead to the recommendation of removal/recovery methods for controlling trace element release to the environment.

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