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ENVIRONMENTAL CONTAMINATION FROM TRACE ELEMENTS IN COAL PREPARATION WASTES

A Literature Review and Assessment

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by

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ENVIRONMENTAL CONTAMINATION FROM TRACE ELEMENTS IN COAL PREPARATION WASTES: A REVIEW AND ASSESSMENT OF THE LITERATURE

by

E. M. Wewerka, J. M. Williams,
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ABSTRACT

The purpose of this review of the literature is to collect and evaluate the available information on the chemistry and behavior of trace elements in coal processing wastes, and to utilize this information to assess the potential for environmental contamination from the trace elements in these wastes. Only limited attention has been given previously to the chemistry of trace elements in coal waste materials; however, most of the growing body of knowledge concerning trace elements and minerals in raw coals can be applied directly to coal wastes. The consensus from analytical studies is that nearly every naturally occurring element is likely to be present in coal and coal refuse. The fate of these elements during coal preparation is poorly defined; however, large concentrations of trace elements are discarded in the washing refuse. Toxic or harmful quantities of elements, such as Fe, Al, Mn, Co, Ni, and Zn, are released into the environment in the drainage from coal mineral wastes, but, in general, the behavior of trace elements during refuse weathering, leaching, and burning is not well understood. Although the mineral and inorganic matter in coal wastes is an acknowledged major contributor to both air and water pollution, without the benefit of further research, a comprehensive assessment of the full potential for environmental contamination from the trace elements in these wastes cannot be made.

---

1. INTRODUCTION

Coal, as mined, contains a great deal of extraneous rock and mineral matter. The inorganic constituents of coals often represent as much as 50% of run-of-the-mine products (Hanna et al. 1963). These rock and mineral impurities are expensive to ship, dilute the caloric content of the coal, and produce undesirable gaseous and particulate pollutants when the coal is burned or utilized. Consequently, much of the more highly mineralized coals—about one-half of the total mined in the U.S.—is cleaned or processed to remove some of the unwanted mineral and rock materials. The discarded rock, mineral, and coaly matter from coal processing, together with other coal mine refuse constitute the gob piles and culm banks, which are scattered over thousands of acres in coal-producing regions.

Recent estimates are that nearly 3 billion tons* of carbonaceous mineral wastes have accumulated in the U.S. as a result of coal processing and mine development (National Academy of Sciences 1975). Increased coal production, wider use of indiscriminate mining techniques, improved cleaning methods, and greater emphasis on clean fuels will undoubtedly increase the rate at which wastes accumulate. A vivid example of this trend—a 10-fold increase in the rate at which wastes have been produced since 1940—is shown in Fig. I-1a (National Academy of Sciences 1975). Although there has been a recent trend by utilities to use larger amounts of uncleaned coal, as detailed by Fig. I-1b, a committee studying the underground disposal of these wastes estimated that the current rate of waste production of 100 million tons per year will double by 1980 (National Academy of Sciences 1975). Added to the present accumulation, this material can no longer be merely discarded in convenient places. Indiscriminate disposal of coal wastes will not be accepted by a concerned populace.

Most of the current waste disposal areas are on private land (McNay 1971). Generally, the refuse is deposited in piles, in canyons, or stripped-out areas. The material is transported to the dumping areas primarily by truck, but aerial trams, mine cars, and conveyor belts are also used. Refuse piles can cover from one to over 100 acres, and may range from 20 to more than 300 feet in height or depth (McNay 1971). Most refuse piles are small, less than 500 000 cubic yards, but the bulk of the refuse, as shown in Table I-I, resides in the very large piles, those greater than 1.5 million cubic yards. The total number of sizeable active or abandoned refuse piles or impoundments is 3000-5000. Of the 961 refuse piles studied by the Department of Interior in 1968, over one-half posed some form of health, safety, or environmental problem (National Academy of Sciences 1975).

Most of the coal refuse is produced by cleaning or preparation facilities. These preparation plants generally crush the run-of-mine coal to minus 6-inch pieces prior to processing. The finer material, less than 1 mm, is often cleaned by froth-flotation techniques. The waste from this process is deposited in slurry ponds. The larger pieces of coal are separated from the heavier mineral matter by some form of density separation. This is accomplished primarily by oscillating water washers, jigs, cyclones, or baths with heavy-media solutions of magnetite or calcium

*Although it is the policy of EPA and ERDA to report measurements in the international system of metric units, for clarity of presentation, the units used in this report are given as they appear in the references. A conversion table is provided.

CONVERSION FACTORS: 1 lb = 0.45 kg, 1 ton = 0.91 metric ton, 1 ft = 0.30 m, 1 in = 2.54 cm and 1 cu yd = 1.31 m^3.

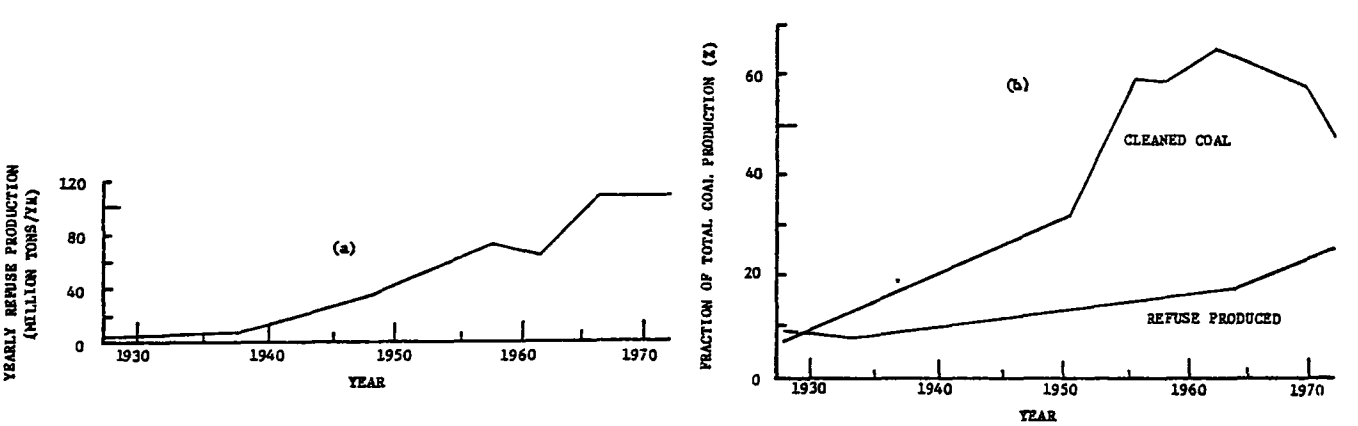

Fig. I-1.
(a) Annual production of coal refuse, (b) fraction of total coal production which is mechanically cleaned and fraction discarded as waste or refuse. Source: National Academy of Sciences 1975.

chloride (Deurbrouck and Jacobsen 1974). The fine residue obtained when the cleaned coal is dried, either by cyclones, centrifuges, or vacuum driers, also goes to the slurry pond. The bulk of the mineral refuse comes out of the plant looking like dark concrete which is deficient in cement and water, and whose rock filler is too big for adequate packing. This reject material constitutes about 25% of the run-of-mine coal and is the largest single contributor to coal waste piles (McNay 1971). (It is not uncommon also to find garbage, trash, abandoned equipment, tires, and other items in these piles.)

Coal-waste piles are generally formed from preparation (tipple) plant refuse and mine-development wastes by dumping them in a disposal area. The dumping may be down the side of an embankment, in which case the larger rocks roll to the bottom, and the finer refuse stays at the top, producing a segregated mass. Often refuse dumps are graded after disposal. The current trend is to use grading to produce a more uniform and compacted deposit. Frequently, in the past, refuse piles grew in a rather helter-skelter fashion (Harrington and East 1948). Wastes have been piled on vegetation near stream and residential areas, often on slopes having greater than 50% grades (Davies 1973; Coalgate et al. 1973). These conditions sometimes produced gob slides like those which caused the 1972 disaster at Buffalo Creek, WV (Busch et al. 1974), and the tragedy at Aberfan, Wales, a few years ago (Taylor 1973). Such haphazardly formed waste piles also create conditions which play havoc with water resources.

Water quality has always been a difficult problem where coal-mining activity is high. Water pollution from refuse piles arises from two main sources: siltation and acid drainage. Siltation is caused by finely divided coal ("blackwater"), minerals (silt), and disturbed soil (primarily from surface mining). This form of contamination is generally controllable in impoundment areas where the particles settle or are filtered as the water passes through a retaining barrier. Acid drainage is not so easily handled. In Appalachia alone, more than 10 500 miles of streams are affected by acid drainage from coal mines and refuse dumps (Appalachian Regional Commission 1969). It is estimated that 3.5 million tons of sulfuric acid entered the inland waterways in 1962 from coal-mine-related sources (Reid and Streebin 1973). The major portion of the acidity (75% in Appalachia) is supplied by inactive, underground mines (Foreman 1974). Coal-processing plants and refuse areas supply the remainder of the acid to stream systems. More than 2000 coal-waste piles are thought to be contributing to stream pollution (National Academy of Sciences 1975). Over half of the active refuse piles in Pennsylvania are within one-quarter mile of stream banks. The percentage of abandoned waste heaps this close to waterways is probably even higher.

Acid drainage occurs when iron sulfides (pyrite or marcasite) are exposed to air and water. The sulfur oxidizes to sulfuric acid and the iron is liberated as iron sulfate. Typically, 1.5 to 2 pounds of acid and 0.5 to 0.7 pounds of soluble iron are produced per acre of refuse per day, but, in some highly mineralized areas, acid has formed at a rate of more than 300 pounds per acre per day (National Academy of Sciences 1975). The acids formed in refuse dumps run off into drainage areas or percolate through the pile, where considerable mineral matter is dissolved. Some of the flow from refuse dumps eventually reaches subsurface water systems. Acid drainage lowers the pH of lakes and streams, making the growth of aquatic life, which functions best under slightly basic conditions, difficult (Kimmel and Sharpe 1976). The dissolved iron in refuse or mine drainage reduces the oxygen content in the water and forms ferric hydroxide, "yellow-boy," which settles out on the stream bottom. This material often covers wide swathes in drainage areas. Quite effective in smothering life-forms, yellow-boy leaves a desolate terrain of yellow-orange streams and soil.

Air pollution from refuse piles is also a major problem. Fires in gob piles have been occurring for more than 100 years (Sussman and Mulhern 1964). Some piles have burned continuously for over 20 years as timbers, clinging coal, and oxidizing sulfides provide fuel. This particular problem has received considerable attention in recent years, but as of 1968 it was estimated that there were still approximately 300 coal-waste piles burning (National Academy of Sciences

TABLE I-I

SIZES OF COAL-REFUSE PILES IN THE U.S.

Size of Refuse Pile (10^3 yd^3)	Fraction of Piles this Size[a] (%)	Fraction of Total Yd^3 [b] (%)
<100	33	2
100 - 500	29	10
500 - 1000	13	14
1000 - 2000	10	21
>2000	15	53

[a]Source: McNay 1971.
[b]Our estimate.

TABLE I-II

BURNING REFUSE PILES NEAR RESIDENTIAL AREAS

Number of Refuse Piles	% of Total	Population Near Refuse Bank
138	47	<1000
123	42	1 - 10 000
25	9	10 - 100 000
6	2	>100 000

Source: McNay 1971.

1975). Of the burning waste piles, 99% were on private land; 25% were in Pennsylvania. Also, 42% of the piles were less than half burned, 36% were more than three-quarters burned, and 28% were receiving new wastes at the time of the survey (McNay 1971). Burning waste piles are quite noxious and are generally located close to small communities (Spicer and Luckie 1970). Twenty-two sites were immediately adjacent to municipal, residential, or commercial lands and 89% were within 5 miles of a community with 200 or more people; 45%, within less than 1 mile (McNay 1971). Some were in an area populated by more than 100 000 people, as shown in Table I-II.

In recent years, attempts have been made to circumvent some of the major environmental problems associate with coal-refuse disposal (Boyer and Gleason 1972). To prevent exposure to water and air, waste materials have been crushed, carefully compacted, and then covered with top soil or sealed with sludge, clay, or other materials. Often coal debris is sealed into abandoned mines or placed in stripped-out areas. Substantial effort to stabilize waste piles and banks by revegetation has been undertaken, and much work has gone into methods of neutralizing acidic effluents. Although these measures appear to solve the immediate problem of stabilizing the structures of gob piles, and they seem to slow the environmental processes somewhat, it is not clear how effective they will prove to be in the long run.

In addition to these well-recognized problems, however, another potential environmental hazard is beginning to gain attention. Coals, and undoubtedly coal wastes, contain a broad array of trace or minor elements (Gluskoter 1975). Many of these trace elements, such as lead, cadmium, arsenic, selenium, mercury, etc., are of considerable concern because of the low tolerances of plants and animals for them (Piperno 1975). Undoubtedly many of these trace elements are carried into the environment by weathering, leaching, and burning of refuse. Although the relative amounts of these components per unit of waste is usually small, the total absolute amount of each available in a large waste bank could cause grave consequences in water, soil, or air if they were concentrated by natural processes.

The purpose of this review of the literature is to collect and evaluate the available information about the chemistry and behavior of trace elements in coal-processing wastes, and to assess the potential for environmental contamination from the trace elements in these wastes. Trace elements are defined here to include all elements except carbon, hydrogen, oxygen, nitrogen, and sulfur. For convenience, these trace elements have been subdivided into major (those forming the major minerals in coal) and minor classes. As a base, previous works on coal-cleaning processes and coal wastes were considered. Particular attention was focused on literature describing the

fate of trace elements during cleaning processes, and the chemical forms and associations of these trace elements in coal and coal-processing wastes. Information on specific trace-element/mineral correlations was sought. Literature on weathering, leaching, oxidation, or burning of coal refuse was also considered. And, finally, some insight into the economic utility of this material, which undergoes such considerable handling, was also sought. The details of the search and the results obtained are addressed in the following sections.

II. LITERATURE SEARCH FORMAT

An extensive and thorough search of the open literature on environmental pollution by trace elements in coal-processing wastes has been completed both by manual and computer searches of the literature.

The literature on coal and its related disciplines was found to be widely scattered and poorly catalogued. For example, many studies by state geological surveys and university research groups were picked up as secondary references from the bibliographies of more widely quoted articles. Nevertheless, it is believed that the search objectives have been achieved and that the references compiled accurately represent the available literature through mid-1975 on trace elements in coals and coal-processing wastes and trace-element contamination from these wastes.

The literature search was conducted in three phases:

1. All data bases were searched either electronically or manually.
2. All of the primary references from the data bases were examined through either their abstract or the complete article where available.
3. Secondary references found in the bibliographies of the primary articles, but not in the data base searches, were evaluated.

The three phases required about equal portions of a 6-month period.

The electronic search was carried out using the bases which are listed in Table II-I. These data bases were searched through CHEMCON (Chemical Abstracts), which is available through several commercial suppliers, and RECON (all others), which is available through ERDA from Oak Ridge National Laboratory. The number of references found in each data base is also included in Table II-I. An extensive list of key words was used to comb the data bases. This is given in Table II-II.

The electronic search of Chemical Abstracts was done somewhat differently. LASL had limited access to CHEMCON at the time of the search, so this part was restricted to literature on the chemistry and mineralogy of coal(s) for the period 1972 to mid-1975. However, as will be discussed, Chemical Abstracts was covered completely by the manual search. In addition, parts of a broad survey emphasizing the desulfurization of coal (CHEMCON, 1970 to early 1975) was made available by EPA-Research Triangle Park and Battelle, Columbus (see Table II-III). The references from the electronics searches were screened through their abstracts to give approximately 300 primary sources which were relevant to the subject at hand.

The manual search of the literature was made using several data bases—the major source being Chemical Abstracts, volumes 1 through 83 (1907 - mid-1975). Abstracts dealing with the subjects listed in Table II-II, but slanted toward coal wastes, were pulled from four major Chemical Abstracts listings: (1) coal, (2) lignite or brown coal, (3) waste and wastes, and (4) waste pollution. (The electronic search had already covered most of the articles from 1972 1975.) Other bases searched manually were ERDA Report Abstracts (1975), EPA Bibliography (1971 - 1973), EPA Report Abstracts (1975), and LASL's "What's New in Reports" (1974 1975), a weekly listing of reports mailed to LASL's library from throughout the country. This latter base listed several papers which had been too recently published to be covered by the abstracting services. In a final effort to secure primary references on trace elements in coal-processing wastes, the

TABLE II-I

ELECTRONIC DATA BASES SEARCHED[a]

Data Base	References	Comments
Chemical Abstracts	1678[b]	
Nuclear Science Abstracts (NSA)	387	
Water Resources Abstracts (WRA)	83	
Metals Abstracts (MEX)	0	
Energy R & D Projects (ER1)	356	Compendium of private and government projects compiled by ORNL from questionnaires sent to project authors.
Energy Data Base (ENG)	647	Subject matter covering the use, generation, distribution, environmental effects of energy as compiled by ORNL.
Energy Data Base (EDB)	804	Major ERDA energy data base: includes nonnuclear ERDA Research Abstracts (ERA), Energy Abstracts for Policy Analysis (EAPA), NSF-RANN Energy Abstracts, and other publications representing similar interests as compiled by ORNL.
Toxic Materials Data Base (TOX)	462	Subject matter includes effects on the environment of numerous toxic substances, including heavy metals, as compiled by ORNL.
Total references selected for visual review	4417[c]	

[a]Most of the data bases are restricted to post-1972 articles. Chemical Abstracts and NSA are relatively large, WRA, EDB and MEX are of moderate size (50 000-150 000 items) and ERI, TOX and ENN are small (< 10 000 items) in size.
[b]Includes 1511 items from Battelle (1970-early 1975 literature, see text) and 167 by LASL (1972-mid 1975) using a narrower scope.
[c]Estimate 20-30% duplicates as some articles were covered by nearly all data bases.

TABLE II-II

KEYWORDS FOR LASL'S ELECTRONIC LITERATURE SEARCH

File 1	Coal
	Coals
File 2	Pollution
	Environment
	Environmental Impact
	Environmental Effects
	Environmental Quality
	Geology
	Geochemistry
	Land Reclamation
	Ecology
	Revegetation
File 3	Solid Wastes
	Residues
	Waste Disposal
	Wastes
	Waste Water
	Liquid Wastes
	Mining Wastes
File 4	Chemical Composition
	Chemical Analysis Minerals
	Minerals
	Trace Amounts
	Trace Elements
	Metals
File 5	Mining
	Processing
	Chemical Preparation
	Cleaning
	Crushing
	Preparation
	Flotation
	Enrichment
	Extraction
	Washing
	Sampling
	Separation Processes
	Roasting
	Demineralization

TABLE II-III

KEYWORDS IN EPA/BATTELLE'S ELECTRONIC SEARCH

File 1	Coal
File 2	Cleaning
	Washing
	Leaching
	Chemical Treatment
	Hydrogenation
	Desulfurization
	Hydrodesulfurization
	Sulfur Removal
	Preparation
	Beneficiation
	Liquefaction

agenda of recent meetings of regularly scheduled symposia, such as the Symposium of Coal Mine Drainage Research and the Symposium on Mine and Preparation Plant Refuse Disposal were considered. A few references did not show up in any of the standard places but were obtained by word of mouth from colleagues working at several other institutions. The manual search produced about 300 relevant, primary sources—a number equal to that of the electronic search.

The second phase of the search involved an extensive review of the primary sources. For this review the list was reduced to include only those articles dealing with studies of U.S. coal or coal refuse. This substantially reduced the number to be given closer scrutiny, since both the English and Russians have published widely on these topics. (Some foreign references are considered in Sec. X, however.) The selected sources were obtained in full form from numerous libraries. With these in hand, the bibliographic section of each article was searched for references related to relevant works, which had not previously appeared.

The final phase of the search was devoted to obtaining and reviewing the secondary references—approximately 50 in number. These were mostly publications from state geological surveys and universities, which appeared well known to the authors of the primary sources, but not to the public at large. The time needed to secure these secondary references was generally much longer than that needed to secure the primary sources.

The net result of this search is the list of 200 references which appears at the end of this review. Although selective, it represents the state of the art concerning trace elements and minerals in coal wastes—their identities, problems of disposal, and possible uses. Frequently, when a subject or author appeared in several related references, only the most pertinent one was listed in the bibliography. When references were part of a continuing or updated series, only the final article was usually listed.

An adjunct to this endeavor is the establishment of a computer-interactive storage system which includes all of the pertinent references pulled in the search. Presently there are about 650 references in this data base, and the list will be updated periodically. A computer search and retrieval system, based on key word identification, will be used to comb the file. This data base will be available upon request.

III. TRACE ELEMENTS AND MINERALS IN COAL-PROCESSING WASTES

Only a few studies of the minerals and trace elements in coal-processing wastes have been reported. Most of this work has concerned the composition and structure of the major minerals; only limited attention has been given to identifying or characterizing the minor or trace elements in these wastes. This is not to say that information about the character of the trace elements in coal wastes is nonexistent, however. There is an ever-expanding base of knowledge about the trace elements and minerals in raw coals, and, considering that coal refuse is primarily concentrated mineral wastes derived from coals, it is reasonable to assume that most of the pertinent information from studies of raw coals can be applied directly to coal refuse. Undoubtedly, the small number of direct studies of the composition of coal refuse stems from this emphasis on raw coals.

Several reviews concerning the structure and composition of coal-refuse materials have appeared in recent years (Coalgate 1975; Moulton et al. 1974; Coalgate et al. 1973; Sun et al. 1971). These included information about the engineering properties of the material, and about well-recognized problems such as acid drainage from the wastes, but there was little reported about trace elements and minerals in these wastes. Nonetheless, the few studies which have touched upon the subject of the mineralogy of coal refuse are of interest and are reviewed first.

TABLE III-I

MINERALS IDENTIFIED IN COAL REFUSE FROM SEVERAL WEST VIRGINIA SITES

Quartz[a]	Calcite
Chlorite	Feldspar
Illite	Pyrite
Kaolinite	Muscovite

[a]Predominant species.

Source. Busch et al. 1974, 1975.

One of the more detailed investigations of coal-refuse composition was completed recently under the sponsorship of the U.S. Bureau of Mines (Busch et al. 1975; 1974). Since this work was initiated in the aftermath of the Buffalo Creek disaster, the main purpose of the study was to collect engineering and physical-properties data, which could be applied to waste-bank construction. As part of the study, however, the major minerals and some of the trace elements were identified in samples of both fine and coarse bituminous-coal refuse from several sites in West Virginia. Quartz was the predominant mineral species identified in these refuse samples, as seen from the data in Table III-I.

Emission spectroscopy and atomic absorption spectrometry were utilized to determine the elemental composition of the waste samples. A compilation of the elements identified and the probable composition ranges appear in Table III-II. The data show that many of the minor elements in the coal-refuse samples can be attributed to the major minerals. For example, Al and Si are the main components in clays, Si is found in quartz, Fe in pyrite, and Ca and Mg compose much of the structure of calcite and chlorite, respectively. The specific sources or mineral associations of the less abundant elements, however, are more difficult to surmise.

In another study, Barnhisel and Massey (1969) examined the mineralogy of spoil-bank materials from three locations in eastern Kentucky. Qualitative analyses were obtained by x-ray diffraction and other techniques. Clay minerals (kaolinite and illite) and quartz were the most abundant constituents of these wastes. Lesser quantities of chlorite and pyrite were present, also.

The character of the mineral matter in anthracite coal refuse was studied by Augenstein and Sun (1974) of Penn State University. X-ray diffraction and infrared techniques were used to identify the minerals in samples of weathered refuse from inactive disposal sites as well as samples of fresh materials from active operations. All of these wastes were found to have similar mineralogical compositions. The clay minerals, kaolinite, illite, and pyrophyllite, made up about 70 to 80% of the rock in these samples; quartz made up 10 to 30%, while rutile and pyrite were generally present at less than 2% each. Waste composition did not vary greatly with the size of the material.

This small, but impressive, group of studies is the total extent of what was found in the literature from direct studies of trace elements and minerals in coal refuse. However, as discussed earlier, the relatively large volume of information on the inorganic constituents of raw coals can ordinarily be applied directly to coal wastes. The available information on trace elements and minerals in raw coals is reviewed in the next section.

TABLE III-II

ELEMENTAL ANALYSES OF WEST VIRGINIA COAL REFUSE[a]

Element	Min Value	Max Value
Be	0.2	3
Na	150	375
Mg	500	8000
Al (%)	>2.5	---
Si (%)	>2.5	---
K	500	1200
Ca	50	2000
Sc	3	25
Ti	300	3000
V	25	250
Cr	3	25
Mn	65	1300
Fe (%)	0.75	4.1
Co	3	25
Ni	25	250
Cu	12	50
Zn	30	85
Ga	3	25
Y	3	25
Zr	3	25
Ag	0.3	2.5
Cd	0.25	1.0
Pb	20	150

[a]All values ppm unless otherwise indicated.
Source: Bush et al. 1974, 1975.

IV. TRACE ELEMENTS AND MINERALS IN RAW COALS

While there is a paucity of data dealing with the composition and mineralogy of coal refuse, an abundance of information is available from many studies of the trace elements and minerals in raw coals. Coal-refuse piles are simply accumulations of the rock and inorganic debris separated from the coals during mining or preparation, hence, most of the data about coal mineralogy can be directly extrapolated to coal-refuse materials.

Knowledge of coal mineralogy has generally kept pace with the development of modern analytical instrumentation and techniques, but recent concern about environmental contamination resulting from coal production or utilization has sparked a new flurry of interest in the chemistry of the inorganic coal constituents. The identities of the major minerals and many of the trace elements in coals are now fairly well established. The more recent studies have begun to concentrate on elucidating the associations among trace elements and major minerals in coals, and understanding the details of the chemistry and behavior of these constituents during mining, processing, or utilization.

A comprehensive review of the available information concerning trace elements and minerals in raw coals, of course, is outside the scope of this endeavor. However, the following information,

culled from some of the more prominent works on this subject, will serve to illustrate the present state of knowledge in this area.

Mineral and Trace-Element Analyses

To identify the minerals and trace elements in coals or coal refuse, it is usually necessary first to separate the inorganic components from the carbonaceous matrix. This is done to concentrate the mineral matter and remove background interferences from the organic fractions. Removal of the organic material can be accomplished in several ways, which include heavy-media separation (float-sink) and oxidation by high- or low-temperature methods. Low-temperature oxidation or ashing (LTA) is now almost universally used for this purpose, because the reaction temperature is low enough (<150°C) that the minerals and inorganic compounds in most cases are not significantly altered or lost (Gluskoter 1975). In the LTA method, oxygen is passed through a radiofrequency discharge to produce active species at low temperature, which then pass over the coal to oxidize the organic material.

Following the separation of the mineral matter from the coal or refuse, the minerals and minor elements can be more readily identified (Babu 1975). X-ray diffraction, electron microprobe, infrared spectroscopy, and differential thermal analysis are among the useful techniques used to identify major-mineral phases in coaly materials. Neutron activation analysis, emission spectroscopy, and atomic absorption spectrometry are the most widely used techniques for identifying coal-associated trace elements, although spark-source mass spectrometry, x-ray spectroscopy, and electron spectroscopy are becoming increasingly popular for certain applications.

Major Minerals in Coals

Many distinct types of rocks and minerals have been identified in close association with coals and coaly deposits. In spite of some variations from locality to locality and even within individual seams, certain classes of major minerals are present in nearly all coals. These are the aluminosilicates or clay minerals, silica, carbonates, sulfides, and sulfates.

The clay minerals are present in coals in greatest abundance. The principal ones are kaolinite, illite, and mixed-layer illite/montmorillonite. It is not unusual for more than 90% of the coal-associated mineral matter to be composed of these clay mineral types (Thiessen et al. 1936). Rao and Gluskoter (1973) report an average of 52% clays in the mineral matter of 65 Illinoin Basin coals. The mineral matter in 57 coal samples of various ranks and from many parts of the country were studied by O'Gorman and Walker (1972; 1971). They report that clay-mineral contents ranged from about 10 to more than 70% in these coals.

The main sulfide and sulfate minerals in coals are pyrite and its dimorph marcasite, and gypsum. These minerals compose about 25% of the mineral matter in Illinois coals (Rao and Gluskoter 1973). For American coals, in general, pyrite and marcasite will range from essentially none to as high as 40% of the total inorganic matter (O'Gorman and Walker 1972). Gypsum may represent as much as 60% of the minerals in some coals, although such high quantities are unusual (O'Gorman and Walker 1972).

Carbonate minerals are found in coals in a wide range of compositions, usually as mixtures of calcite, dolomite, and siderite. These average about 9% of the mineral matter in Illinois coals (Rao and Gluskoter 1973), and when present, do not often exceed 10% of the total inorganic material of most American coals (O'Gorman and Walker 1972; 1971).

Quartz (silica) is very seldom found in coals in large amounts. Generally, about 20% of the mineral constituents is the maximum present (O'Gorman and Walker 1972). Rao and Gluskoter (1973) report that quartz represents about 15% of the minerals in Illinois coals.

In addition to these major minerals, there have been various other less abundant minerals identified in coals. The range of the mineral types identified in coals and coal deposits is illustrated by the list of major and minor coal minerals presented as Table IV-I.

Trace Elements in Coals

Studies of trace elements in coals have been conducted for more than 100 years (Gluskoter 1975). However, the advent of modern work in the field is attributed to Goldschmidt, who first applied instrumental techniques to the problem in the mid-1930s.

Many trace or minor elements are present in coals; in all about 40 such elements have been identified and undoubtedly others are present. Several excellent studies have been conducted in recent years on this subject.

Zubovic and his coworkers at USGS have studied selected trace elements in coals on a regional basis (1967, 1966, 1964, and 1961). These investigations included coals from the Appalachian, Eastern Interior, Western and Southwestern Interior, and Northern Great Plains regions. Emission spectroscopic analyses were used to determine the concentrations of 15 minor elements in these coals. The average trace-element contents for the variety of coals studied appear in Table IV-II.

A group at Penn State University, headed by O'Gorman and Walker, considered the trace-element contents of coals by ASTM rank (1972, 1971). A total of 57 samples ranging from lignite to anthracite was analyzed by atomic absorption spectrometry and emission spectroscopy. The average trace-element concentrations of the ashes obtained from the various coals are given in Table IV-III.

Work conducted at ISGS has resulted in the identification of many of the elements present in Illinois coals (Gluskoter 1975; Ruch et al. 1974). The trace elements in over 80 Illinois Basin coals were analyzed by neutron activation analysis, emission spectroscopy, atomic absorption spectroscopy, x-ray spectroscopy, and ion-selective electrode. The averages for the elements found in these coals are reported in Table IV-IV.

In addition to these efforts, there have been several other excellent studies or reviews about trace elements in coals (Averitt et al. 1976; Sather et al. 1975; Ayer 1974; Magee et al. 1973; Sun et al. 1971; Zubovic 1966; Abernethy and Gibson 1962; Headlee and Hunter 1953; Gibson and Selvig 1944). Information from these sources and those discussed earlier was compiled into listings of the ranges of concentration of the various trace elements found in American coals and the ashes from these coals. These lists appear in Tables IV-V and IV-VI.

Except for a few elements, which are thought to be almost exclusively associated with the organic coal components, most of the trace elements in coals are distributed among or within the major-mineral constituents (Gluskoter 1975; Ruch et al. 1974; Zubovic 1966). The actual associations or relationships among the various trace elements and coal minerals have been explored in only a few instances. Miller (1974) has studied the distribution of certain trace elements and minerals in 15 Illinois coals. As illustrated in Table IV-VII, a positive correlation was found between some of the trace elements in the coals and specific mineral types. Ruch and his coworkers (1974) statistically analyzed a large volume of data on trace elements in coals. They noted positive geochemical associations among groups of trace elements which have common tendencies to associate with or form certain mineral types. Results from washability studies also suggest preferred associations among certain minerals and trace elements (Ruch et al. 1974; Deurbrouck and Jacobsen 1974; Schultz et al. 1975). Si, Ti, Al and K were found in clay-rich

TABLE IV-I

MINERALS IDENTIFIED IN AMERICAN COALS

Major Minerals

Aluminosilicates	Silica	Sulfates	Sulfides	Carbonates
Illites	Quartz	Gypsum	Pyrite	Calcite
Kaolinite			Marcasite	Dolomite
Illite/montmorillonite				Siderite

Minor Minerals

Sulfides	Oxides	Micas	Sulfates	Feldspar	Alunites	Carbonates
Sphalerite	Hematite	Muscovite	Thenardite	Plagioclase	Jarosite	Aragonite
Galena	Rutile	Chlorites				Ankerite

Source: Rao and Gluskoter, 1973.
Source: O'Gorman and Walker 1971, 1972.

TABLE IV-II

AVERAGE TRACE-ELEMENTS CONTENTS FOR COALS FROM VARIOUS REGIONS OF THE U.S.[a]

Element	SWI[b]	EI[c]	NGP[d]	APP[e]
B	33	96	116	25
Be	1.1	2.5	1.5	2.5
Co	4.6	3.8	2.7	5.1
Cr	13	20	7	13
Cu	11	11	15	15
Ga	2.0	4.1	5.5	4.9
Ge	5.9	13	1.6	5.8
La	6.5	5.1	9.5	9.4
Mo	3.1	4.3	1.7	3.5
Ni	14	15	7.2	14
Sn	1.3	1.5	0.9	0.4
Ti	250	450	591	350
V	18	35	16	21
Y	7.4	7.7	13	14
Zn	108	44	59	7.6

[a]ppm.
[b]SWI = Forty-eight coals from Western and Southwestern Interior Region.
[c]EI = Eastern Interior Region, 53 coals.
[d]NGP = Northern Great Plains Region, 51 samples.
[e]APP = Seventy-three coals from Appalachian region.
Source: Zubovic et al. 1961, 1964, 1966, 1967.

TABLE IV-III

AVERAGE TRACE-ELEMENT CONTENTS OF THE ASH FROM U.S. COALS OF VARIOUS RANK[a]

Element	Anth[b]	LVB[c]	MVB[d]	HVB[e]	L(SB)[f]
Ag	<1	<1	<1	<1	<1
B	90	123	218	770	1010
Ba	866	740	896	1253	5027
Be	9	16	13	17	6
Co	81	172	105	64	45
Cr	304	221	169	193	54
Cu	405	379	313	293	655
Ga	42	41		40	23
Ge	<20	<20			
La	142	110	83	111	62
Mn	270	280	1432	120	688
Ni	220	141	263	154	129
Pb	81	89	96	183	60
Sc	61	50	56	32	18
Sn	962	92	75	171	156
Sr	177	818	668	1987	4660
V	248	278	390	249	125
Y	106	152	151	102	51
Yb	8	10	9	10	4
Zn		231	195	310	
Zr	688	458	326	411	245

[a]ppm.
[b]Anth = Anthracite.
[c]LVB = low-volatile bituminous.
[d]MVB = medium-volatile bituminous.
[e]HVB = high-volatile bituminous.
[f]L(SB) = lignite (subbituminous)
Source: O'Gorman and Walker 1971, 1972.

specific gravity fractions; whereas, Fe, As, Hg, Mo, Pb, Cd, and Zn were concentrated in the highest density washing fractions, and were likely present in, or as, sulfide minerals. Ruch et al. (1974) have observed that certain trace elements occur as discrete micromineral phases in coals. Among these are Cd and Zn (sphalerite), Pb (galena), and F (apatite). Caruccio (1972) also has observed that certain trace elements frequently occur in the various forms of pyrite present in coals.

Thus, as these studies demonstrate, there is considerable evidence that not only are trace elements in coals associated in the main with the inorganic matter, but that many of these elements are likely to be found in conjunction with specific minerals, as opposed to being uniformly or randomly dispersed throughout the inorganic phases.

The main purpose of the foregoing sections was to establish an understanding of the types of minerals and trace elements which are likely to be found in coal-processing wastes. There have been relatively few investigations of the mineralogy of coal wastes themselves; however, the large volume of information about minerals and trace elements in raw coals can be applied directly to this subject.

TABLE IV-IV

TRACE-ELEMENT CONTENTS OF EIGHTY-TWO COALS FROM THE ILLINOIS BASIN[a]

Element	Average	Element	Average
As	14.9	K (%)	0.16
Al (%)	1.22	Mn	53.2
B	113.8	Mg (%)	0.05
Be	1.7	Mo	8.0
Br	15.3	Na (%)	0.05
Ca (%)	0.74	Ni	22.4
Cd	2.9	P	62.8
Cl (%)	0.15	Pb	39.8
Co	9.2	Sb	1.4
Cr	14.1	Se	2.0
Cu	14.1	Si (%)	2.4
F	59.3	Sn	4.6
Fe (%)	2.06	Ti (%)	0.06
Ga	3.0	V	33.1
Ge	7.5	Zn	313.0
Hg	0.2	Zr	72.1

[a]All values in ppm unless otherwise indicated.
Source: Gluskoter 1975.
Source: Ruch et al. 1974.

Although there are variations in composition, it must be concluded from considering the available information that most coal-refuse materials will be composed mainly of clay minerals, pyrite, quartz, carbonate minerals, and gypsum. Some of these minerals, such as quartz and the clays, are chemically quite resistant to weathering and other natural processes, whereas, the pyrites and carbonates notably lack such resistance.

Another major conclusion from the studies referenced is that a great many inorganic elements are present in coals. In all, about 40 elements have been identified in coal and coal refuse, and undoubtedly others are present. With few exceptions, most of the trace or minor elements in coals reside in or among the inorganic constituents as discrete mineral phases, solid solutions, or polymorphs of other minerals. This intimate and recurring association of specific trace elements with specific mineral components leads to the conclusion that the behavior of many trace elements in coal-waste materials during weathering, leaching, or burning will be linked directly to the behavior of the major-mineral phases. Therefore, it is anticipated that the trace elements associated with the more labile minerals in the refuse will be those most likely to be released into the environment by weathering or burning. This suggests that an understanding of the relationships among minerals and trace elements will be a key factor in developing control methods for environmental contamination from trace elements in coal refuse.

The next topics of interest concern the fate of trace elements during coal washing or preparation, and how the minerals and trace elements in coal-refuse materials are affected by the processes occurring in waste dumps. These subjects are addressed in the following sections.

TABLE IV-V

RANGE OF TRACE ELEMENTS IN U.S. COALS[a]

Major Elements[b]			Minor Elements		
Element	Range (%)		Element	Range (ppm)	
Na	0	- 0.20	Be	0	31
Mg	0.1	- 0.25	B	1.2	356
Al	0.43	- 3.04	F	10	295
Si	0.58	- 6.09	P	5	1430
Cl	0	- 0.56	Sc	10	100
K	0.02	- 0.43	V	0	- 1281
Ca	0.05	- 2.67	Cr	0	610
Ti	0.002	- 0.32	Mn	6	181
Fe	0.32	- 4.32	Co	0	43
Zn[c]	0	- 0.56	Ni	0.4	104
			Cu	1.8	185
			Ga	0	61
			Ge	0	819
			As	0.5	106
			Se	0.4	8
			Br	4	52
			Y	<0.1	59
			Zr	8	133
			Mo	0	73
			Cd	0.1	65
			Sn	0	51
			Sb	0.2	9
			La	0	98
			Hg	0.01 -	1.6
			Pb	4	218
			U	<10	- 1000

[a]References used were Ruch et al. (1974, Abernethy and Gibson (1962), Zubovic et al. (1961-1967), Sun et al. (1971) and Magee et al. (1973). (Data by Deul and Annell in these references have been omitted.)
[b]Elements present in .0.2% in coals.
[c]Zinc is not normally considered a major element in coals.

TABLE IV-VI

RANGE OF TRACE-ELEMENT CONCENTRATIONS IN ASHES FROM U.S. COALS[a]

Major Elements[b]		Minor Elements	
Element	**Range (%)**	**Element**	**Range (ppm)**
Na	0.71 2.72	Li	<20 - 3100
Mg	0. 2.4	Be	0 - 1100
Al	5.3 - 21.2	B	30 - 6500
Si	9.3 - 28	P	<440 - 3360
K	0.66 1.32	Sc	2 - 155
Ca	0.58 14	V	6 - 3800
Ti	0.1 2.6	Cr	<1 - 1800
Fe	2.09 - 24.4	Mn	30 - 1800
Zn[c]	0. 1.6	Co	0 - 600
Sr	0.009 - 0.96	Ni	0 - 1200
Ba	0.01 1.39	Cu	10 - °0'0
		Ga	0 - 540
		Ge	0 - 1500
		As	21 570
		Rb	<91 - 1100
		Y	0 - 620
		Zr	100 - 1450
		Mo	0 - 2900
		Ag	<1 84
		Sn	0 - 4250
		Sb	<40 - 230
		La	0 - 820
		Yb	<2 - 23
		W	<10 - 182
		Hg	<70 259
		Pb	10 - 1420
		Bi	1 900

[a]References used were O'Gorman and Walker (1971 & 1972), Sun et al. (1971), Magee et al. (1973), Abernethy and Gibson (1962), Headlee and Hunter (1953) and Zubovic et al. (1961-1967). (Data by Deul and Annell in these references have been omitted.)
[b]Elements present in ≥0.7%.
[c]Zinc is not normally considered a major element in coals.

TABLE IV-VII

TRACE ELEMENTS - MINERAL CORRELATIONS[a]

As, Be, Cu, Sb	Pyrite
B, Cd, Zn, Hg	Sphalerite
B, Cd, Mn, Se, Mo, V	Calcite
B, Cr, Mn, Cd, Mo, Se, V, Zn	Quartz
B, Cu, F, Hg, Sn, V	Clays

[a]Correlation coefficients >0.5.
Source: Miller 1974.

V. TRACE-ELEMENT BEHAVIOR DURING COAL PREPARATION

Cleaning of run-of-the-mine coals to remove some of the unwanted mineral matter has been done for more than a half-century (Deurbrouck 1961). Environmental concern about air pollution from sulfur dioxide has focused attention on the removal of sulfur from the coal. Indeed, many of the recent studies on the washability of coals have centered on this aspect: notable are the reports from the Illinois State Geological Survey (Helfinstine et al. 1974), the Bureau of Mines at Pittsburgh (Deurbrouck and Jacobsen 1974), Bituminous Coal Research, Inc. (1972), and Mitre Corporation (Hoffman et al. 1974). The general conclusion from these studies is that coal cleaning represents a viable short-term solution to providing a low-ash and low-sulfur coal. The newer preparation plants can recover about 90% of the BTU content of coals, while reducing medium-sulfur (1-3%) coal to less than 1% sulfur (Deurbrouck and Jacobsen 1974).

The fate of trace elements during coal preparation has received limited, but dedicated, attention in recent years. Concern for the environment has increased efforts to insure that toxic materials will not spew out of power plants in sufficient quantities to contaminate the environment. More recently, the catalytic and corrosive properties of these chemicals have received attention, as new coal conversion processes are being developed. At every turn, the emphasis is on reducing the metal (ash) content of the coal before use. Granting that coal is full of undesirables (See Sec. IV), the next few paragraphs will briefly describe what is known about the behavior of trace elements during coal washing, and to what extent trace elements are likely to be removed by this process and, consequently, concentrated in the discarded refuse.

The most widely used washing techniques (representing 75% of the total commercial production) utilizing density separation methods, as Table V-I reveals. Production equipment is generally too large and the feedstock too variable to easily determine what happens to trace elements during large-scale cleaning of coal. To simulate these processes on a laboratory scale, investigators use static vats of organic solvents with varying densities. The float portion of a sample in a solvent of some given density is scooped out and the sink fraction is drained and subjected to the next solvent mixture. When analyzed, these float-sink samples provide a histogram which depicts the behavior of the property measured as the density of the sample (washing medium) changes.

Histograms illustrating the float-sink behavior of B, P, Se, and Zn are shown in Fig. V-1 (Ruch et al. 1974). Some elements, such as B, are not readily removed from coal by density gradient means. Other elements, Zn, for example, are more completely removed from the lighter coal. Many elements (P and Se) show intermediate behavior. The tendency of specific trace elements

TABLE V-I

COAL-CLEANING METHODS

Washer Type	Fraction of coal cleaned by equipment type (%)			
	1942	1952	1962	1972
Jigs	47.0	42.8	50.2	43.6
Dense-medium processes	8.8	13.8	25.2	31.4
Concentrating tables	2.2	1.6	11.7	13.7
Flotation	---	---	1.5	4.4
Pneumatic	14.2	8.2	6.9	4.0
Classifiers	7.4	8.5	2.1	1.0
Launders	13.1	5.2	2.2	1.0

Source: Deubrouck and Jacobsen 1974.

to concentrate in the sink fraction has been the subject of studies at USGS (Zubovic 1966), ISGS (Gluskoter 1975), and the Bureau of Mines at Pittsburgh (Deurbrouck and Jacobsen 1974). A list of the findings from these investigations is given in Table V-II.

A completely satisfactory picture of trace-element behavior during washing is still not available. A wide array of variables complicate the problem. For example, trace elements almost certainly do not exist as pure minerals on a macroscale, especially those elements present at the ppm level. Also some minerals, such as pyrite, are present in a wide array of particle sizes in the coal matrix, ranging from lenses greater than 6 inches in diameter to microscopic fragments deposited in the tiny cells of carbonized plant life. Very fine grinding is required to release these minute particles (Deubrouck and Jacobsen 1974; Sun and Savage 1968). Another point to consider is the possibility that certain elements are intricately interwoven as polymorphs or solid solutions through one of the major-mineral phases. Considering these and other questions, it must be concluded that more definitive work is needed.

Some semiquantitative data on trace-element removal during float-sink washing is tabulated in Table V-III. From these data it is seen that significant reductions in the trace-element content of coals are achieved by washing. Likewise, significant quantities of these elements will be discarded by a washing plant. If these data are representative, then, the refuse will contain greater than 2.5 times the trace-element level present in the raw coal. A similar conclusion can be drawn from the following list of elements which are reduced in Illinois coals by more than 50% when 20% of the raw coal is removed by float-sink (Miller 1974).

Al	As	Ca	Cd	Co	Cr	Cu
Fe	Ga	Hg	K	Mn	Mo	Ni
Pb	Sb	Se	Si	Ti	Zn	Zr

In summary, the understanding of trace-element removal from coal by washing or preparation is in its infancy, but several things are clear. Trace elements differ in their susceptibility to be removed from coal by density separation. While the reasons for this phenomenon are not entirely clear, one can draw from the reported data the fact that significant amounts of these elements will be discarded in the washing refuse and that this refuse will have a higher concentration of these elements than was present in the feed coal.

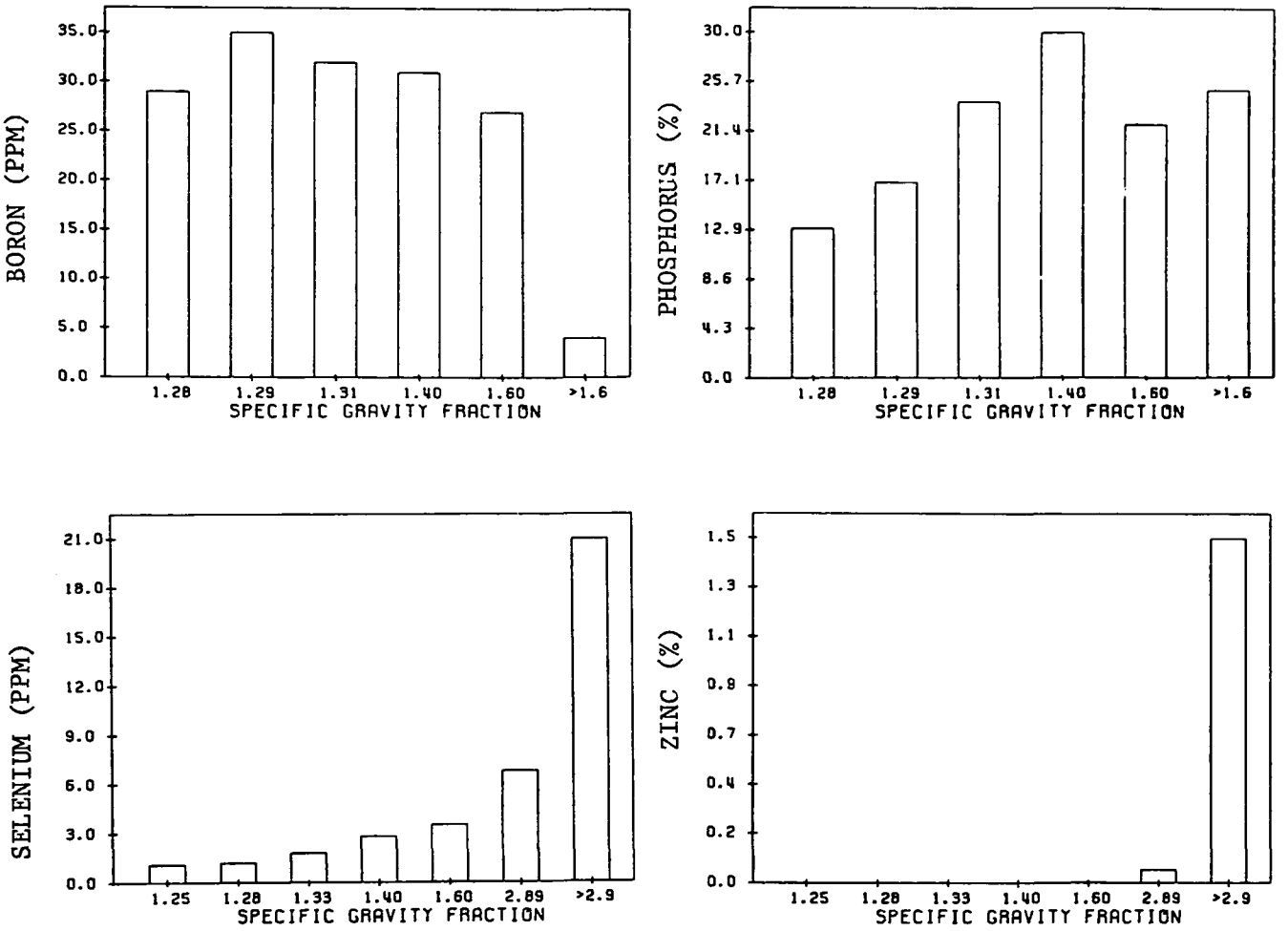

Fig. V-1.
Histograms showing the concentrations of boron, phosphorus, selenium, and zinc in the floating portion versus the solvent specific gravity used in a float-sink test. Source: Ruch et al. 1972.

TABLE V-II

DISTRIBUTION OF TRACE ELEMENTS DURING FLOAT-SINK WASHING

Source	Increasing Concentration in Sink Fraction →			
USGS[a]	Ge Be	Ga Ti B V	Ni Cr Co Y Mo Cu	Sn La Zn
ISGS[b]	Ge Be B	P Ga Sb Ti V	Co Ni Cr Se Cu	Hg Zr Zn As Cd Pb Mn Mo
PERC[c]			Ni Cu S Cr	F Hg Cd Pb Mn
Summary[d]	Ge Be	Ga B Ti V	Co Ni Cr Cu Mo	Hg Zn Cd Pb Mn

[a]Zubovic (1966).
[b]Gluskoter (1975).
[c]Schultz et al. (1975) and Deurbrouck and Jacobsen (1974).
[d]Based on observations from at least two laboratories.

TABLE V-III

REDUCTION OF TRACE ELEMENTS IN COALS BY FLOAT-SINK WASHING

	Source A[a]			Source B[b]	
Trace Element	Level Remaining in Coal (ppm)	No Samples Tested	Level of Reduction (%)[c]	Level of Reduction (%)	No Samples Tested
Mn	7 - 68	2	50 - 78	50 - 75	2
Pb	3 - 8	3	42 - 53	56	1
Cd	0.02 - 0.10	3	0 - 97	0	1
Hg	0.17	1	47	24 - 47	3
F	26 - 65	3	14 77	6 - 42	3
Cr	10 - 20	2	28 - 60	29 - 56	2
S				18 - 50	7
Cu	10 - 22	2	24 - 41	29 - 43	2
Ni	11 - 27	2	20 - 27	28 - 30	2

[a]Duerbrouck and Jacobsen (1974).
[b]Schultz et al. (1975).
[c]12.5-23% of total sample removed as sink fraction.
Solution densities for both studies = 1.60 g/ml.

VI. WATER CONTAMINATION FROM TRACE ELEMENTS IN COAL-PROCESSING WASTES

The contaminated runoff from coal-processing wastes and mining activities is one of the most serious water-pollution problems in many parts of the country. Often the drainage is highly acidic and will contain large quantities of dissolved or suspended materials. The actual magnitude of the pollution problem from acid runoff and drainage from coal mineral wastes can only be estimated, but the total amount is staggering. The U.S. Fish and Wildlife Service reports that some 10 000 miles of waterways, located mainly in the eastern half of the country, are being degraded by acid drainage (Appalachian Regional Commission 1969). Under the worst of circumstances, such waters are nearly devoid of aquatic life, but even slightly acidic waters are far less productive than neutral or alkaline streams or lakes (Kimmel and Sharpe 1976; Sykora et al. 1972; Rehwoldt et al. 1971; Boccardy and Spaulding 1968; Morgan 1942). In addition to waterway damage, some 200 x 10^3 acres of land lay barren or noticeably infertile as a result of refuse disposal and acid runoff (National Academy of Sciences 1975).

The major source of acid from coal mineral materials is thought to be abandoned or neglected mines. About 70% of the total of this type of contamination is attributed to mines; the other 30% results from coal-refuse materials (National Academy of Sciences 1975; Foreman 1974). This information is somewhat misleading, however. The bulk of acid drainage comes from coal mines only because there are more of them than there are refuse piles (National Academy of Sciences 1975). (There are approximately 70 000 abandoned or inactive underground coal mines in the U.S. versus about 5 000 abandoned waste piles.) Taken on a local level, a single refuse pile of major proportions has far more potential for producing acid and mineral contaminants than does an abandoned mine. Because coal refuse is relatively finely divided and well exposed, the weathering and leaching processes that produce acid drainage and mineral dissolution can work more effectively (Good et al. 1970). For these reasons, refuse-pile drainage is often considered to be a more serious pollution hazard than mine drainage.

Acid drainage either from coal refuse or from coal mines—both of which are lumped under the generic term acid mine drainage (AMD)—typically contains substantial amounts of dissolved and suspended mineral matter (see below). In the ensuing paragraphs, it will be shown that the major part of the water-borne contaminants in AMD results from the dissolution and degradation of the major coal minerals. Considering the high degree of mineral dissolution, many of the trace elements associated with the minerals in coals must also be present in the contaminated runoff from coal wastes. Not a great deal is known about this latter topic, but enough analytical work has been done on the character of waste pile runoff to establish that a significant potential exists for pollution by trace elements from waste runoff or drainage.

Before getting into a discussion of the available literature on the composition of refuse drainage, it will be informative to consider first some of the factors responsible for the formation of sulfuric acid in coal mineral wastes.

Formation of Sulfuric Acid in Coal-Processing Wastes

The chemistry of the formation of acids in coal-processing wastes has been studied extensively (Williams 1975; Porges et al. 1966; Hanna et al. 1963; Lorenz 1962; Hoffert 1947). The initial step in acid production is the air oxidation of pyritic substances (pyrite, marcasite) in the wastes to form $FeSO_4$ and SO_2,

$$FeS_2 + 3O_2 \rightarrow FeSO_4 + SO_2 \quad . \tag{1}$$

Further oxidation in the presence of water results in the formation of sulfuric acid,

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \quad . \tag{2}$$

Under some circumstances, the acid concentration in the drainage from coal mineral wastes can run as high as 5 wt% (Hoffert 1947). The most facile formation of sulfuric acid occurs where the pyrites are very finely divided (Caruccio 1970; Barnes and Romberger 1968; Nelson et al. 1933), and where waste pile structure and climatic conditions are conducive to a good flow of air and water through the waste materials (Moebs 1966; Hanna et al. 1963).

Overall, the stoichiometry of the formation of sulfuric acid from pyritic wastes can be written as Eq. (3). Actually, this situation,

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad , \tag{3}$$

is much more complex than it appears; accordingly Eq. (3) is very simplified, and it does not reflect the mechanism of the reaction. There is strong evidence, for example, that iron- or sulfur-oxidizing bacteria are involved in the process (Smith et al. 1968; Lorenz and Tarpley 1963; Hebley 1953; Temple and Colmer 1951) and, although the chemical dynamics of the acid-forming reactions have been studied by many researchers, the details of the rate-determining step are still not known with certainty (Singer and Stumm 1970; 1969; 1968; Morth et al. 1970; Lau et al. 1970; Shumate et al. 1969; Smith et al. 1968; Burke and Downs 1937). There is some evidence that marcasite is more easily oxidized than pyrite (Barnes and Romberger 1968; Hoffert 1947), and that certain inhibitors or accelerators affect the acid-forming reactions (Hanna et al. 1963). Some of the other variables which have been found to influence the rates of the acid-forming processes include: pH, presence of water, oxygen partial pressure, and Fe^{+++} concentration (Caruccio 1968). Because of the enormous complexity of the pyrite oxidation/acid-forming reactions, it is extremely difficult to sort out the essential steps from the subsidiary reactions.

Unfortunately, time alone does little to help alleviate the intensity of acid formation in coal mineral wastes. In fact, the older materials seem to be far more prolific acid producers than newly worked materials (Hoffert 1947). Perhaps this is due to the accelerative effects of bacterial agents, which have not had sufficient time to flourish in the newer wastes. Rate differences for pyrite oxidation of more than 10^6 have been observed between sterile laboratory conditions and field conditions where bacteria readily multiply (Singer and Stumm 1970).

The complete story of acid drainage does not end with its formation, however. The acidic solutions produced by the weathering of pyrites will affect many of the other minerals present in the waste piles (Grube et al. 1971; Lorenz 1962). Certain of the clay minerals will be dissolved by the acidic agents (Barnhisel and Rotromel 1974; Grim 1968). This will add Al and other ions to the solution, along with the Fe and So_4 ions already present from pyrite degradation (Struthers 1964). In addition, calcites and dolomites are known to be readily attacked by acids, with the resultant production of Ca and Mg ions. Undoubtedly, the trace elements associated with these acid-soluble mineral phases will also be brought into solution. The net effect of all this is the production of waste drainage or runoff that contains high concentrations of both dissolved salts and sulfuric acid (Jasinski and Gaines 1972; Dugan 1970).

Trace Elements in Coal-Waste Drainage

The present state of knowledge concerning the major and minor elements present in coal-waste drainage is amply illustrated by the studies detailed in the following text. For the purposes of

completeness, drainage from coal mines, coal-mine-development wastes (spoil heaps) and coal-preparation wastes (gob piles) are all considered in this section. As pointed out earlier, the latter two materials compose the bulk of what is known as coal-processing wastes. There is no apparent difference in the composition of the drainage from these sources, as all involve the same minerals; and hence, no attempt is made by workers in the field to differentiate among the various drainage sources.

The effects of drainage from coal-mining activity on surface and ground water in Pennsylvania was the subject of a recently reported study (Gang and Langmuir 1974). The mineral and trace-element contents of the water from several springs and a number of surface waters were analyzed. Among the constituents considered were Fe, Mn, Al, Zn, Co, Ni, Cu, Cr, Cd, Ag, and Pb. Fe and Mn were found to be greatly in excess of local drinking water standards for all of the water samples; the contents of Zn, Cr, and Cd exceeded these standards in some of the ground waters. Generally, the trace-metals concentrations were higher in ground-water samples than in the surface waters. A compilation of the ranges of concentrations of dissolved species for all of the water samples studied is given in Table VI-I.

Blevins and his coworkers (1970) at the University of Kentucky studied the effects of acid drainage from coal-mining activities on the soils in the flood plains below the mined areas. As part of this study water samples were collected from various places along the flood plain and analyzed. These results appear in Table VI-II. In all instances significant quantities of dissolved ions are present in the water samples; however, particularly noteworthy are the relatively high concentrations of the plant-toxic ions Fe and Mn in the soil water table.

Massey (1972) has studied the dissolved components in drainage solutions from eastern Kentucky coal spoils. He found that the concentrations of Fe, Al, and Mn in leachates from the coal wastes are roughly a function of the pH of the solution. Under the most acidic conditions Fe is the dominant dissolved ion. Concentrations of Zn, Cu, and Ni as high as 145, 85, and 122 ppm, respectively, were found in aqueous extracts from the spoil materials. Massey could not determine whether these heavy elements were originally present in the sulphide minerals or if they resulted from secondary dissolution of some of the other mineral types present in the wastes. The concentrations of Zn and Cu in spoil leachates decreased significantly with increasing pH, but Ni concentrations were not greatly affected by the solution acidity.

Results similar to Massey's were obtained in another study of weathered coal spoils from six eastern Kentucky areas (Cummins et al. 1965). The pH of aqueous extracts of these materials ranged from 2.2 to 5.7. The concentrations of some specific elements detected in the extracts are reported in Table VI-III. The highest concentrations of dissolved ions were found in the extracts from the most highly acidic spoils.

In a similar study, Massey and Barnhisel (1972) investigated the character of the dissolved mineral matter in aqueous solutions extracted from samples of acid spoil materials from eastern Kentucky coals. Successive extractions with water were made over a 35-week period. Listed in Table VI-IV are the maximum concentrations observed for selected ions from each of the spoil materials. These results are a startling illustration of the potential for water contamination from acid coal refuse. Of particular interest in this study were the concentrations of Ni, Zn, and Cu ions, as there is some indication that these elements can be geochemically enriched in certain rocks or soils. In one case, concentrations as high as 5000 ppm Zn, 700 ppm Ni, and 200 ppm Cu were reported in a shale commonly associated with coal beds (Vine).

Lowry (1961) investigated the identities of some of the leachable components from 19 different Ohio coal spoils, which had been subjected to various degrees of weathering. The content of total soluble salts in aqueous leaching solutions, which in one case was 7 wt%, was found to be a function of the pH of the leachate. High concentrations of Fe, Al, Mn, Ca, and Mg ions and lesser amounts of Na and K ions were detected in the more highly acidic solutions.

A research group from West Virginia University determined the concentrations of several trace elements in the drainage from a number of West Virginia coal-mining areas (Corbett et al. 1967).

TABLE VI-I

QUALITY OF SURFACE AND GROUND WATER IN A PENNSYLVANIA COAL-MINING REGION

Variable	Mean[a] PPM	Mean[a] PPB	Range[b]		Water Standard[c]
*pH	4.24[d]		2.69	- 6.78	6.0 - 8.5
*μ	1625[e]		222	7000	<625
Monovalent Cations					
Na	15.9		0.8	70	
K	4.8		1.5	11.4	
Ag		0.54	0.0	3.1	<50
Divalent Cations					
Mg	120		5.8	985	
Ca	104		3.0	312	
*Fe(II)	61.5		0	510	<0.3
*Mn	29		0	281	<0.05
Zn	1		0.001 -	14.5	<5
Ni	0.69		0.04	7.5	
Co	0.5		0.01	4.98	
Cu		29.6	1.5	410	<1000
Cr		10.8	0	120	<50
Cd		3.6	0.3	13.1	<10
Pb		1.8	0	7.0	<50
Trivalent Cations					
*Fe(III)	19.7		0	102	<0.3
Al	13.2		0	201	
Neutral					
SiO_2	10.3		2.9	70	
Monovalent Anions					
Cl	204		0	129	<250
HCO^3	13.9		0	122	
Divalent Anion					
*SO_4[f]	985		28	- 6230	<250

*The average of this variable exceeds the water standard.
[a]PPM = parts per million, PPB = parts per billion.
[b]Range units same as for mean.
[c]Recommended local drinking water standards (units same as for mean).
[d]pH units.
[e]Micromhos at 25 C.
[f]Much as HSO_4.
Source: Gang and Langmuir 1974.

TABLE VI-II

WATER QUALITY ALONG A FLOODPLAIN BELOW A MINED AREA[a]

Sample	Source	pH	Fe	Al	Mn	Ca	Mg
1	Stream Channel	3.7	1	22	5	152	56
2	Soil Water Table	3.7	137	11	26	104	32
3	Pond (middle)	3.8	1	17	21	156	88
5	Pond (bottom)	3.9	9	1	3	52	20

[a]Concentrations in ppm.
Source: Blevins et al. 1970.

TABLE VI-III

TRACE ELEMENTS IN EXTRACTS OF LABORATORY LEACHED KENTUCKY COAL SPOILS[a]

Elements	SO_4	Fe	Al	Mn	Cu	Zn	P	B	Mo	Cl
Mean	1313	104	6.1	37	18.2	14.2	32	0.17	0.058	2.3
High	6500	619	26.6	205	27.8	18.1	170	0.20	0.188	33.2
Low	50	13	0.2	2	1.3	9.0	1	0.15	0.005	0.2

[a]Concentrations listed in ppm.
Source: Cummins et al. 1965.

TABLE VI-IV

LEACHABILITY OF EASTERN KENTUCKY COAL REFUSE[a,b]

Sample	pH	Fe	Al	Mn	Ca	Mg	Na	K	Zn	Ni	Cu
1	1.0	37500	29700	375	1100	800	55	50	59	122	85
2	1.6	19500	15200	220	1000	595	95	62	46	28	10
3	2.2	11000	16000	1800	650	2050	355	320	145	97	11
4	2.2	2800	11600	324	1075	615	83	65	55	16	11
5	2.4	86	200	80	670	300	91	170	44	17	15
6	2.8	15	470	95	1325	530	91	165	24	10	3
7	5.2	7	1	47	1800	700	130	225	1	1	1

[a]Concentration in ppm.
[b]Maximum observed concentrations.
Source: Massey and Barnhisel 1972.

Most of the water samples were acidic but a few were nonacidic. B, Ba, Cr, Mn, and Sr were detected in all of the samples, while Be, Cd, Co, Cu, Ni, Ag, Pb, and V were found only in the acid waters. Unfortunately the concentrations of these elements were not reported. These researchers attributed the greater number of trace elements in the acidic samples to the much higher solvating power of the acid solutions.

In a 1974 report, Martin summarized a large accumulation of data on the quality of aqueous effluents from coal-refuse piles located in many of the coal-producing regions of the country. Samples were collected and analyzed from direct runoff, seeps, ponds, and swamps in or near refuse disposal sites. The results from Martin's report are reproduced here (as Tables VI-V to VI-IX) almost in their entirety because they represent one of the most comprehensive assessments of the quality of the natural drainage waters from coal-refuse materials.

From the tables, it is seen that the total acidity (free acid, acid salts, and dissolved CO_2) of these refuse effluents varied from alkaline to an acid equivalent (as $CaCO_3$) of 34 x 10^3 mg/ℓ. The pH values (free hydrogen ions) of the samples ran between 2.1 and 6.9. The most general observation that can be made from this valuable collection of information is that the concentrations of metals and sulfate ions generally relate to the acidity of the effluents. Surprisingly, however, total acidity and total ion concentration are only casually related. This observation implies that the total amount of materials dissolved from refuse piles is dependent on local conditions such as particle sizes, mineralogy and waste composition, and disposal area drainage patterns, and that relatively high concentrations of dissolved species can accumulate in the effluents from nonacidic waste materials.

There are obvious variations in the amounts of contaminants released by the various refuse materials. Undoubtedly, much of this can be attributed to the types of coals and methods of mining and preparation. In addition, the total quantity of water-borne contaminants produced by waste piles will be a function of the hydrology of the area. However, the data reported in Tables VI-V to VI-IX amply demonstrate the general character and quantity of the dissolved mineral material in effluents from coal refuse.

The high concentrations of Fe, Al, Ca, Mg, and SO_4 ions in most of the refuse water samples are undoubtedly produced by dissolution of the major minerals (clays, pyrites, and carbonates). The information for the less abundant trace elements is limited to just a few elements. However, considering the overall extent of mineral dissolution in most of the effluents, it must be concluded that many other of the trace elements associated with the minerals are present in solution, also.

Vimmerstedt and Struthers (1968) conducted a long-term study of the chemical products in the leachates from weathered Ohio coal spoils. The spoils investigated were from 19 different sites, and they were classified according to their acid-forming tendencies in the following way.

Toxic pH <4 on more than 75% of the refuse surface.
Marginal pH <4 on 50 to 75% of the refuse surface.
Acid pH 4.0 to 6.9 on more than 50% of the surface area.
Calcareous pH >7 on more than 50% of the refuse surface.

The spoils (1-ft-diam by 4-ft-deep columns) were allowed to weather under natural climatic conditions, and each year for a total of 8 years the leachate percolating through the spoil columns was analyzed for total dissolved salts and several ionic species. The results of this study are reproduced as Figs. VI-1 to VI-4.

Although the rates of formation of dissolved products are generally slowing with time, the main conclusion to be drawn from this work is that significant quantities of mineral matter will continue to dissolve from refuse dumps for many years after initial disposal. The data in the figures show, as have the other studies discussed so far, that the concentrations of total dissolved salts

TABLE VI-V

ANALYSES OF EFFLUENTS FROM PENNSYLVANIA GOB PILES[a]

Sample	Location[b]	Acidity[c]	pH	Conduct[d]	SO_4	Fe	Al	Mn	Ca	Mg	Na	K	Zn	Cu	Ni
1	Drainage	34300	3.1	13600	40500	6168	999	63							
2	Drainage	24400	2.2	10000	29750	3737	668	69							
3	Drainage	23100	2.1	10400	27500	3758	948	545							
4	Drainage	15500	2.7	12400	17750	3197	1014	31							
5	Drainage	6100	2.6	5600	5750	1265	353	86							
6	Drainage	1330	3.7	3500	1125	130	68	15							
7	Drainage	1300	3.5	3700	1485	175	40	9							
8	Drainage	690	3.0	4400	3000	30	87	50	340	250	100	5	2.8	0.14	1.7
9	Drainage	325	3.6	925	420	6	28	4							
10	Drainage	250	4.0	3000	1600	1	50	90	180	140	60	15	2.4	0.18	1.1

[a]Acidity and elemental concentrations in ppm.
[b]Drainage includes seepage from the refuse pile, pile drainage and runoff and streams at the base of gob piles.
[c]Titratable hydrogen ion.
[d]Micromhos.
Source: Martin 1974.

TABLE VI-VI

ANALYSES OF EFFLUENTS FROM WEST VIRGINIA COAL-REFUSE BANKS[a]

Sample	Location[b]	Acidity[c]	pH	Conduct[d]	SO_4	Fe	Al	Mn	Ca	Mg	Na	K	Zn	Ni
1	Drainage	6940	3.0	9300	9560	2940	220	70	380	680				
2	Drainage	4090	2.9	16500	10054	2240	50	67	145	664				
3	Drainage	300	3.1	5200	3300	120	20	25	310	230	600	25	1.5	1
4	Drainage	150	4.9	5000	3800	260	4	9	415	146	780	22	0.2	
5	Pond	85	3.4	3200	2400	170	4	10	450	105	250	8	0.1	
6	Drainage	11	5.2	640	310	45	1	3	30	28	14	10	0.1	

[a]Acidity and elemental concentrations in ppm.
[b]See drainage definition in Table VI-V, a pond is a drainage impoundment.
[c]Titratable hydrogen ion.
[d]Micromhos.
Source: Martin 1974.

TABLE VI-VII

ANALYSES OF DRAINAGE FROM KENTUCKY SPOIL BANKS[a]

Sample	Location[b]	Acidity[c]	pH	Conduct	SO_4	Fe	Al	Mn	Ca	Mg	Na	K	Zn	Ni
1	Swamp	2380	2.4	4200	3629	630	244	26	200	90	150	1	2.9	0.45
2	Drainage	210	3.8	1200	1066	2	70	8	74	85	22	42	1.1	0.25
3	Drainage	7	6.9	880	690	6	2	4	50	26	115	3	0.1	

[a]Acidity and elemental concentration in ppm.
[b]See drainage definition in Table VI-V.
[c]Titratable hydrogen ion.
[d]Micromhos.
Source: Martin 1974.

TABLE VI-VIII

ANALYSES OF EFFLUENTS FROM INDIANA COAL REFUSE[a]

Sample	Location[b]	Acidity[c]	pH	Conduct[d]	SO_4	Fe	Al	Mn	Ca	Mg	Na	K	Zn	Cu	Ni	Pb
1	Subsurface	16400	2.2	15000	15200	5500		36								
2	Subsurface	13600	2.3	1200	1500	4500		56								
3	Subsurface	10300	2.5	9800	10400	4180		40	342	185						
4	Drainage	6500	2.4	6400.	9513	2600	340.	120	350	285	200	3	7.2	0.16	1.6	0.30
5	Lake	800.	2.8	2500.	1711	100	52	25	200	100	30					
6	Lake	760	2.6	2400	1700	160	50	24	160.	100	18	3	1.7		0.4	0.14
7	Lake	150	3.2	1480	850	25	6	11	150	75	40	6				

[a]Acidity and elemental concentrations in ppm.
[b]See drainage definition in Table VI-V, subsurface is underground flow near a spoil heap.
[c]Titratable hydrogen ion.
[d]Micromhos.
Source: Martin 1974.

TABLE VI-IX

ANALYSES OF EFFLUENTS FROM ILLINOIS COAL-REFUSE PILES[a]

Sample	Location[b]	Acidity[c]	pH	Conduct[d]	SO_4	Fe	Total Solids
1	Drainage	14400	2.4		3540	13500	35320
2	Drainage	8700	2.8		3500	4600	13860
3	Drainage	4600.	2.9		3200	1400	14420
4	Drainage	6100	3.3		2800	50	16830
5	Drainage	5900	3.1		1950	1200	11060
6	Drainage	640	3.6		1200	55	8570

[a]Acidity and elemental concentrations in ppm.
[b]See drainage definition in Table VI-V.
[c]Titratable hydrogen ion (ppm).
[d]Micromhos.
Source: Martin 1974.

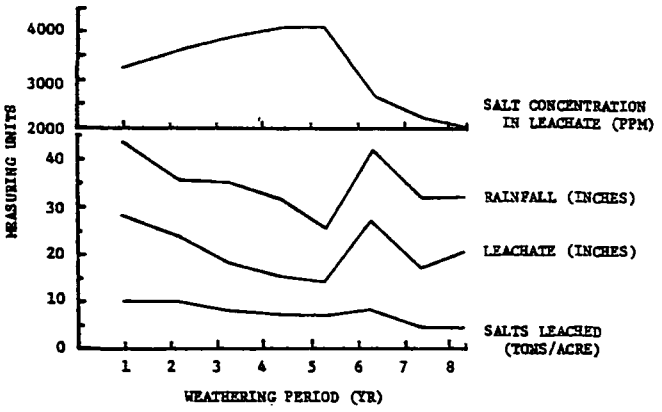

Fig. VI-1.
Rainfall and spoil leaching behavior during an 8-year period (for marginal spoil). Source: Vimmerstedt and Struthers 1968.

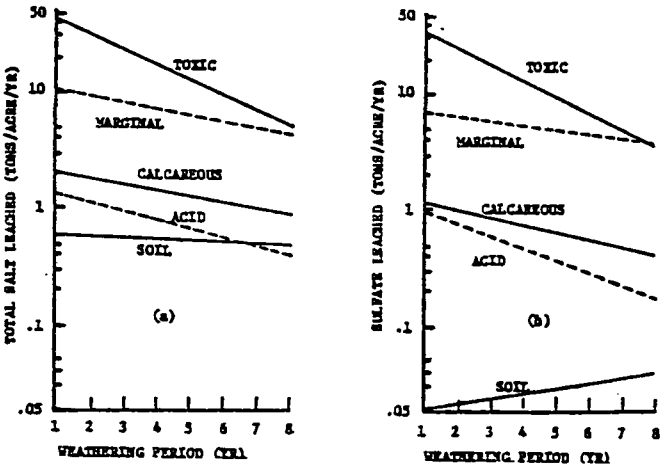

Fig. VI-2.
Leaching of total salts (a) and sulfate (b) from various spoil types as a function of time—normalized to constant rainfall (35 inches). Source: Vimmerstedt and Struthers 1968.

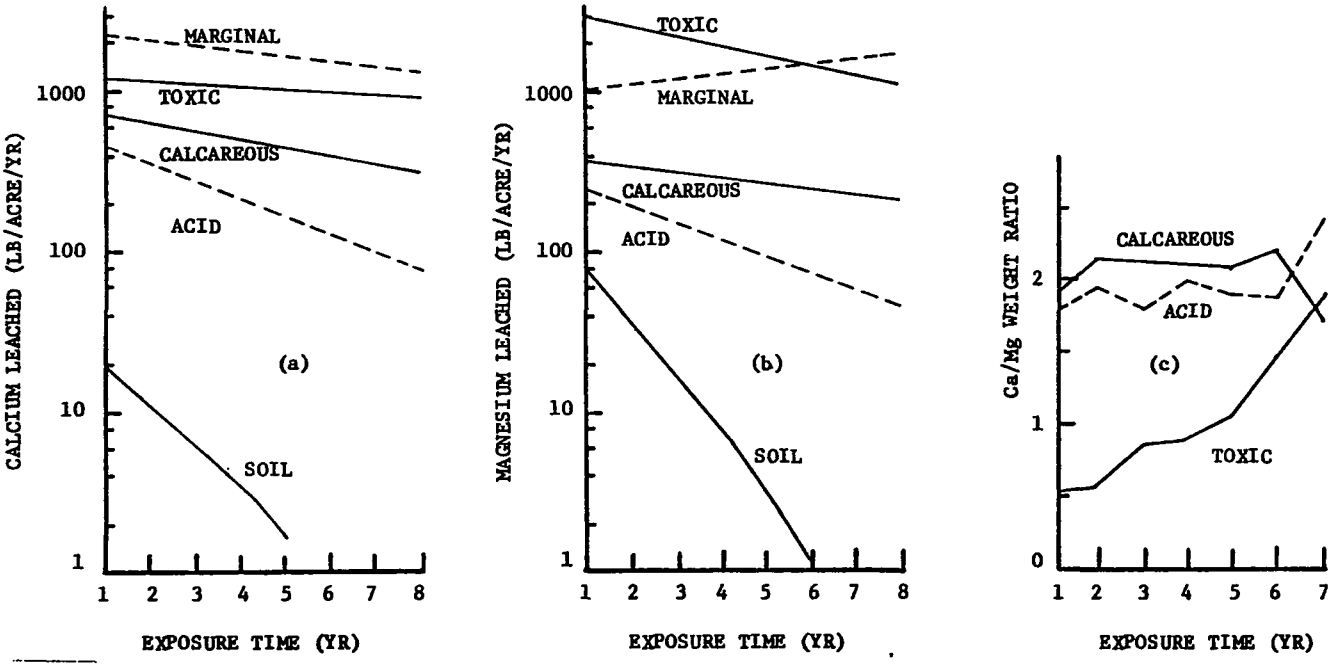

Fig. VI-3.
Amounts of calcium (a) and magnesium (b) leached from various spoil types and their ratios (c) as a function of weathering time under normalized rainfall conditions. Source: Vimmerstedt and Struthers 1968.

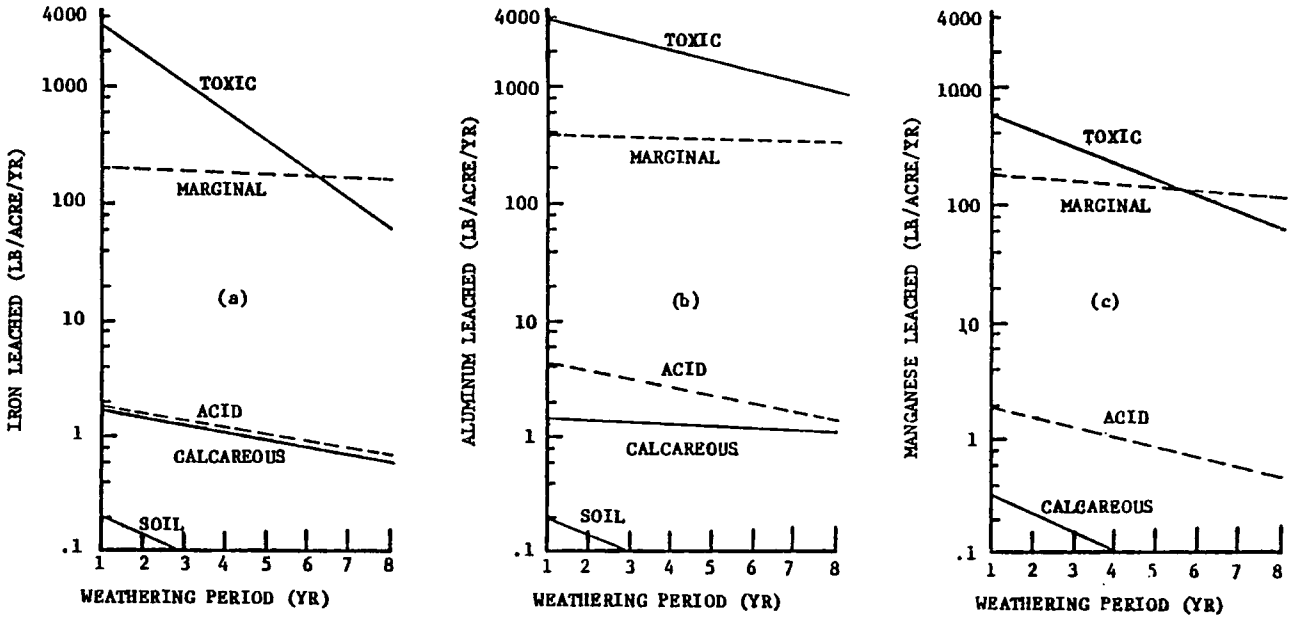

Fig. VI-4.
Amount of iron (a), aluminum (b) and manganese (c) leached from various spoil types versus exposure time under normalized conditions. Source: Vimmerstedt and Struthers 1968.

are highest in the effluents from the most acidic spoil materials, but significant amounts of materials were dissolved from nonacidic spoils.

The results of Vimmerstedt and his colleagues are substantiated by Curtis (1972), who conducted a 4-year study of the water quality in several watersheds in coal-mining areas of eastern Kentucky. His work shows that significant dissolution of the mineral matter from coals can continue for many years after exposure to natural climatic conditions. Curtis observed that appreciable contamination of drainage water occurs even for nonacidic spoil materials, although the total quantities of dissolved and suspended matter appear to be much lower than is usually the case for acid spoils. A "before-and-after" comparison of stream water quality in four different watershed locations where nonacid spoils have been produced is given in Table VI-X. Ca and Mg, probably produced from limestone and dolomites, are the most significant contaminants, although the concentrations of several other ions increased by more than an order of magnitude after mining in the area was commenced. The relatively low concentrations of Al in the coal-field drainage waters likely indicates a resistance of clay minerals to dissolution by neutral water.

Finally, the results from an interesting study of the water-pollution potential of mine spoils from the coals of the southern Rocky Mountain region were reported by a Colorado State University group in 1974 (McWhorter et al.). Western coals generally contain low amounts of pyritic materials, so the wastes from these coals are usually nonacidic. Accordingly, this study provides an interesting contrast to the major body of work on refuse-pile contaminants, which has been done principally with acidic waste materials.

Mine spoils from two locations were studied. The quality of typical runoff and leachates from these spoils is illustrated by the data in Table VI-XI.

These results correspond quite closely to those obtained by Curtis (see above) in his study of nonacidic spoils from eastern Kentucky coals. The total salt content is low, pH is high, and the concentrations of metallic elements are modest compared to those found in acid-spoil drainage.

TABLE VI-X

EFFECT OF SURFACE MINING ON WATER QUALITY OF SOME EASTERN KENTUCKY STREAMS

Stream	Sample[a]	pH	Cond.[b]	SO_4	Fe	Al	Mn	Ca	Mg	Zn	Cu
1	Before	7.3	55	12	0.38	0.07	0.08	4.8	3.6	0.90	0
	After	7.8	407	178	4.00	0.44	1.85	45.0	35.5	1.80	0
2	Before	7.1	151	18	0.31	0.07	0.00	4.5	2.4	0.10	0
	After	8.1	522	176	1.55	0.25	1.80	50.4	36.0	2.20	0
3	Before	7.0	73	12	0.27	0.05	0.12	6.2	4.4	0.80	0
	After	7.5	334	132	3.80	0.15	1.20	30.0	24.3	1.20	0
4	Before	7.0	95	10.	1.38	0.06	0.30	6.6	3.8	0.90	0
	After	7.5	264	61	3.50	0.19	0.70	18.3	17.6	1.26	0.

[a]Before or after surface mining.
[b]Cond(uctivity) in micromhos, concentrations in ppm.
Source: Curtis 1972.

TABLE VI-XI

WATER QUALITY OF RUNOFF OR LEACHATES FROM WESTERN COIL SPOILS[a]

Sample	pH	Cond.	SO_4	Fe	Mn	Ca	Mg	Na	K	Zn	Cu	Cl
1	7.4	2510	>460	<0.05	0.34	370	160	21	48	0.09	<0.01	5
2	7.4	3160	>800	<0.05	<0.01	340	240	92	13	0.04	<0.01	4
3	7.5	4700	>450	<0.05	<0.01	250	150	1180	17	0.02	<0.01	9
4			610	0.07	<0.01	388	41	1290.	80	0.09	0.03	22

[a]Conductivity is in micromhos, concentrations in ppm.
Source: McWhorter et al. 1974.

Here, too, Mg and Ca are the dominant observed water contaminants, although as in most other instances, only a limited number of elemental constituents was considered.

An interesting sidelight to this study is the observation by these researchers that the quantity of annual precipitation is so limited at some Southwestern sites that the chances of significant drainage of water through those waste materials is remote.

Other notable work in this area includes studies by Barnhisel and his colleagues (1974; 1969) on the weathering of clay minerals and of the extractability of Kentucky spoil materials. Beyer and Hutnik (1969) have investigated the exchange behaviors of certain ions in Pennsylvania spoil banks. Maneval (1975) has reported on the composition of waters associated with several mining sites, and the effects of AMD on the quality of a Missouri reservoir were studied by Brezina et al. (1970). The hydrology and chemistry of coal-mine drainage in Indiana is the subject of a report by Agnew and Corbett (1969).

In addition to the works cited above, other studies have been conducted on the quality or composition of the drainage, runoff, or leachates from coal mineral wastes or spoils. However, those discussed or referenced here were considered to be the most informative and the most useful for demonstrating the present state of knowledge in this area.

Throughout this section, the nature and magnitude of the trace element releases in the effluents from coal refuse and mineral wastes were discussed. It is, of course, difficult at this time to assess the overall seriousness of this type of discharge because suitable data are generally lacking on the behavior and effects of the various trace elements in the environment. EPA, however, recently published a set of proposed effluent limitations that apply to discharges from coal-refuse materials. These guidelines are listed in Table VI-XII. Although only a few elements and effluent characteristics are covered by the proposed regulation, these data, nonetheless, serve as a useful point of reference. Significantly, it is seen that nearly all of the waste effluents discussed earlier exceed the proposed EPA effluent limitations—some by orders of magnitude.

There are a number of observations and conclusions which can be drawn from the foregoing concerning the nature of the dissolved contaminants in the drainage from coal-processing wastes.

There seems to be little doubt that the runoff or drainage from coal waste disposal areas will be contaminated to some degree with dissolved or suspended mineral matter. Generally the highest concentrations of contaminants are found in the more highly acidic effluents, although the runoff even from nonacidic wastes contains enough added material to be notable and based on this criterion to be of possible concern. The acid drainage from coal-processing refuse and mining activities typically contains high concentrations of Fe, Al, Ca, Mg, and SO_4 ions. These are derived, apparently, from the major minerals in the wastes.

Little is known about the effects of weathering and leaching on the less abundant or minor elements in coal-processing wastes. Many of these elements have been identified in the effluents or leachates from wastes, but a comprehensive assessment of the behavior of the full spectrum of trace elements which are present in the wastes has not yet been made. It is more than likely that the minor elements associated with the soluble mineral phases will also be solubilized during waste-bank leaching. Quite obviously, many questions remain to be answered concerning the fate of trace elements in weathering coal wastes and waste drainage, particularly if and how these elements enter into the surrounding environment. Of added concern is the possibility that some

TABLE VI-XII

EPA PROPOSED EFFLUENT LIMITATIONS FOR COAL REFUSE

Effluent Characteristic	Maximum for any 1 day (mg/ℓ)	Average of daily values for 30 consecutive days shall not exceed (mg/ℓ)
Iron, total	7.0	3.5
Iron, dissolved	0.60	0.30
Aluminum, total	4.0	2.0
Manganese, total	4.0	2.0
Nickel, total	0.40	0.20
Zinc, total	0.40	0.20
TSS	70	35
pH	Within the range 6.0 to 9.0	

Source: Federal Register, 40, No. 202, October 17, 1975.

of the more toxic elements will be concentrated by chemical or biological processes to produce even greater hazards.

Finally, it has been shown that abandoned coal-waste materials will continue to produce water-borne contaminants for years after their disposal. Several investigators have pointed out that older refuse is an even more prolific producer of acid drainage than recently discarded material. The inescapable conclusion is that exposed coal mineral wastes are environmentally innocuous only where water is absent or severely limited.

VII. TRACE-ELEMENT EMISSIONS FROM BURNING COAL REFUSE

Under certain circumstances, the oxidation of residual coal or other mineral matter in coal-refuse piles can produce sufficient concentrations of heat to ignite the interior of the pile. In the late 1960s, there were approximately 300 to 500 such piles burning in the U.S. (Magnuson and Baker 1974; McNay 1971; Anon. 1965; Stahl 1964; Sussman and Mulhern 1964). These burning wastes are an acknowledged source of gaseous contaminants from the combustion of residual coal and minerals (carbon and sulfur oxides and hydrocarbons); however, whether or not emissions of volatile trace elements from burning wastes pose a substantial environmental threat has not yet been assessed.

The cause of gob pile fires is not known with certainty. Some, of course, are caused by carelessness or are deliberately set, but most appear to result from the spontaneous generation of heat by reactions occurring within the waste mass. Fires occur most frequently in wastes containing a lot of finely divided coal and pyrite materials, and in those which are poorly compacted so that good air circulation is maintained in the pile (Magnuson and Baker 1974; McNay 1971; Sussman and Mulhern 1964; Hebley 1956; Zimmerman 1952; Harrington and East 1948). Most authorities consider the heat from the oxidation of the residual coal to be the major cause of coal-refuse fires, but they recognize that the oxidation of pyritic materials is an important contributing factor (Magnuson and Baker 1974; Coalgate et al. 1973; Harrington and East 1948; Jones and Scott 1939; Scott and Jones 1937).

Only a limited effort has been made to identify the air-borne pollutants from burning refuse (Coalgate et al. 1974; McNay 1971; Sussman and Mulhern 1964; Harrington and East 1948). An estimate of the amounts of gaseous pollutants released by all of the burning coal refuse in the U.S. was made by Hoffman in 1968, and is given in Table VII-I. Of course, the total load of contaminants originating from burning coal wastes is small compared to national totals; nevertheless, coal-refuse pollutants are highly concentrated in the vicinity of the sources, where they can have considerable local impact.

It is widely known that coals contain a number of trace elements which are volatilized or converted to volatile forms during combustion and subsequently released in the gaseous products (Ruch et al. 1974; Magee et al. 1973). Only one study concerning trace elements in burning coal refuse was found in the literature. Finkelman and his colleagues (1974) at USGS have shown that a large number of trace elements, many of which are toxic, are transported from the hot zone and subsequently deposited in cooler areas by the vapors generated within the burning refuse. Clearly, trace-element emissions from burning refuse have the earmark for being a potentially serious environmental problem, particularly at the local level. However, this is an area which still needs to be comprehensively assessed.

It is not likely that aqueous leaching of burning waste piles presents any additional problems with trace elements (to those already recognized), unless the leach zone extends into areas of the refuse mass where concentrations of trace elements have been deposited by vapor transport from the burning area. So little is known about the chemistry and mineralogy of burning coal refuse, however, that further speculation about leaching behavior is unwarranted. Likewise, there is

TABLE VII-I

GASEOUS POLLUTANTS EMANATING FROM BURNING REFUSE BANKS[a]

Gas	Total Amount Emitted (10^6 tons)	Portion of Total Emitted From All U.S. Sources (%)
Sulfur Oxides	0.6	1.8
Particulates	0.4	1.4
Carbon Monoxide	1.2	1.2
Nitrogen Oxides	0.2	1.0
Hydrocarbons	0.2	0.6

[a] 1968 data.
Source: Hoffman 1970.

practically nothing on which to judge the particular vulnerability of burned-out wastes to weathering and leaching.

Most of the interest in burning coal wastes has concerned the prevention and control of refuse fires (Magnuson and Baker 1974; Coalgate et al. 1974; McNay 1971: Maneval 1969; Stahl 1964; Hebley 1956; Zimmerman 1952; Harrington and East 1948). Preventive measures include proper grading and compacting or sealing of the waste-pile perimeters to reduce the flow of air through the bank. With care, and attention to sound engineering practices, waste-pile fires can be almost entirely prevented. To control or extinguish refuse fires once they have begun is another matter. Success in this area has been rather limited. The most effective method for extinguishing coal-refuse fires has been to dig out the burning materials and allow them to cool at the surface. A few of the more successful methods of waste fire control include sealing the piles with soil or other materials to control air circulation or injecting slurries, usually of water and finely divided incombustible materials, to essentially smother the burning waste.

The best overall practice, though, is to prevent the fires in the first place. When ignited, gob pile fires can smolder or burn for years, in spite of the efforts to extinguish them.

VIII. TRACE ELEMENTS OF ENVIRONMENTAL CONCERN IN COAL-PROCESSING WASTES

One of the main reasons for conducting this search of the literature was to determine if the available information could provide a guide as to whether potentially toxic trace elements are released into the aqueous or atmospheric environments from discarded coal-processing wastes. This information is, of course, essential to assess the threat of environmental contamination from the trace elements and mineral matter in these wastes, and to map adequate preventative or control measures should they be necessary. Unfortunately, as detailed in the previous sections, there are large gaps in the body of knowledge on this subject. Therefore, a satisfactory judgement of the hazards posed by the inorganic constituents of coal mineral wastes really cannot be made at this time.

Very certainly there is a host of potentially toxic or harmful inorganic elements present in the wastes from coal preparation and mine development, and it is known that some of these can find their ways into the environment. Fe, Al, and Mn, which often leach out of these wastes in large

amounts, can be detrimental to soils and destructive to plant and aquatic life. For example, Lowry (1961) reports that as little as 400 ppm of Fe or Al ions in soils result in the complete mortality of pine seedlings, and it has been reported that fish may be killed by concentrations of these same ions of less than 0.5 ppm each (Massey and Barnhisel 1972). Solutions containing 2.5 ppm Ni, 5 ppm Cu, 25 ppm Zn, or 250 ppm Mn were found to be toxic to oat plants (Hunter and Vergnano 1953), and concentrations of Cu ranging from 1.5 to 11.6 ppm have been reported by Rehwoldt et al. (1971) to kill several species of fish in 24 h. All of these effects are caused by quantities of trace elements that are known to sometimes be present in the effluents from coal-waste materials or in the waste dumps themselves (see earlier sections). In fact, the notorious inability of many of the acidic waste materials to support any substantial plant life at all is thought to be the result of toxic amounts of Fe, Al, and Mn present in these materials (Coalgate et al. 1973; Massey and Barnhisel 1972; Beyer and Hutnik 1969).

In addition to these documented cause-and-effect relationships, of concern also are the highly toxic heavy metals present in coal wastes; little about the waste-bank behavior of this group of elements is known. Such elements as Pb, Se, Cd, As, and Hg have been singled out as being bad actors in coal-combustion systems (Piperno 1975; Magee et al. 1973). But, this is largely because these elements are volatile or tend to form volatile compounds and, therefore, can rather easily escape from the burning coal along with the stack gases. Undoubtedly, many of these same elements are also released from burning waste banks, but whether or not these volatile trace elements will so readily escape into the drainage from weathered refuse remains to be seen. In addition to these volatile heavy elements, many other elements, which have been implicated as being generally harmful or injurious, are also thought to be present in most coal refuse. These include Be, Ni, Co, Cu, and Y (Piperno 1975; Anon. 1971). Here again, little has been reported about the behavior or fate of this class of trace elements under the dynamic conditions in waste dumps.

Another aspect of trace-element behavior which merits attention concerns the possibility that toxic elements can be chemically concentrated or accumulated either in the waste banks or in the surrounding environment. There are many instances of this kind of behavior reported in the geochemical literature (Randama and Sahama 1950). For example, Vine as previously noted has observed extremely high concentrations of Zn, Cu, and Ni in shales of a type found in close association with coals. This phenomenon has been attributed to biogeochemical enrichment. Within the waste dump, both the clay minerals and carbon residues are known to have considerable ion exchange capacity (Coalgate et al. 1973; Grim 1968; Reese and Lovell 1966; Broderick and Bogard 1941; Broderick and Hertzog 1941), and such processes as coprecipitation and selective dissolution can concentrate or deplete certain elements or compounds from solution (Massey 1972). Also, many of the soils in the areas surrounding the waste disposal sites can accumulate toxic ions, presumably via an ion exchange mechanism (Beers et al. 1974; Beyer and Hutnik 1969; Rankama and Sahama 1950).

As can be readily seen from the foregoing discussion, considerably more research needs to be done to provide a less fragmented picture of the behavior of the more toxic coal-related trace elements under the conditions prevailing in coal-refuse dumps. Until such work is conducted, it will be difficult if not impossible to assess the full potential for environmental contamination from trace elements in coal refuse and mineral wastes. Likewise, a determination of which trace elements are of most concern from an environmental standpoint is equally difficult.

IX. PREVENTION AND TREATMENT OF CONTAMINATION FROM COAL-PROCESSING WASTES

Trace elements may be released into the environment from coal-processing wastes by two plausible routes: as volatile components from burning wastes or as dissolved or suspended

materials in the effluents or drainage from waste dumps. The control of trace-element emissions from burning wastes can be dismissed rather briefly by stating that the best method is to extinguish the fire; this subject was discussed sufficiently in a previous section and is, therefore, not belabored here. Actually, nothing a great deal more profound can be said about controlling trace elements in the drainage from coal-refuse materials either, because so very little is known about the extent or nature of such elements in waste effluents. However, especially in recent years, much attention has been given to various methods for preventing, reducing, or controlling acid drainage from coal mines and refuse dumps. (The amount of acidic contaminants allowed in the drainage from coal-mining activities is now regulated in most places by federal, state, or local laws.) These techniques are directed primarily at neutralizing the acidic refuse and mine effluents, and at reducing the large quantities of dissolved and suspended mineral matter in them. Although these control measures are often only peripherally directed at trace elements, the trace-element contents of acidic waters will be affected to varying degrees by the control methods used. Consequently, some of the methods used to prevent or treat AMD may also be useful for controlling or removing environmentally harmful trace elements. The following paragraphs address this subject.

Acid drainage from coal mineral matter is essentially indentical in character, whether it originates from refuse piles or abandoned mines. Therefore, methods for treating or preventing acids apply equally to either source of contamination, and generally no distinction is made regarding the origin of the drainage. However, in the literature all acidic effluents are referred to by the generic term "acid mine drainage," so, this terminology has been adopted here, also.

Basically acid mine drainage (AMD) control methods can be divided into two groups: Those directed primarily at preventing the formation of AMD and those concerned with treating AMD once it has formed. A list of the various techniques used to prevent or treat AMD from coal-refuse materials is given in Table IX-I. In addition, many other control or treatment methods have been proposed, but these are yet to be proven technically or economically feasible under field conditions.

TABLE IX-I

METHODS FOR PREVENTING OR CONTROLLING ACID DRAINAGE FROM COAL-REFUSE MATTER

Preventative Measures

Control of air influx
Control of water influx
Disposal in underground or strip mining sites

Treatment Methods

Neutralization
Flash Vaporization
Ion Exchange
Reverse Osmosis

Source: See text.

Prevention and Control of Acid Drainage

Sulfuric acid is formed when the pyritic material in coal refuse is oxidized by air in the presence of water (see Sec. VI). Therefore, the most effective means of preventing the generation of acids in acid-forming coal mineral wastes is to restrict or prevent the influx of air and flow of water through the waste pile (Foreman 1974; Coalgate et al. 1973; Robins and Troy 1971; Bell and Escher 1969). The circulation of air or water through waste materials can be markedly reduced by carefully sizing and compacting the waste to reduce permeability, or by sealing the edges of the pile with clay or some other suitable agent (National Academy of Sciences 1975; Loy 1974; Lorenz 1962). Mixing coal wastes with water glass, silica gel, or fly ash has been reported as an effective means for reducing permeability and sealing the waste pile (Capp and Gillmore 1974; Capp and Adams 1971; Walitt et al. 1970; Jones and Ruggeri 1969). These substances not only help to reduce waste pile porosity, but they also help to neutralize acids as they are formed.

Possibly the most widely used method for controlling water and air influx in coal-refuse materials involves grading the wastes and covering them with top soil (Brundage 1974; Kosowski 1972; Krause 1972; Hill 1969). In addition to reducing the seepage of water and air through the underlying wastes, the added soil will often support vegetation, which further contributes to the structural stability of the pile (Coalgate et al. 1973; Grube et al. 1971; Limstrom 1964).

Another method for preventing acid build up in coal wastes, which is a variation of the above technique, is to bury the refuse back into the mining sites (National Academy of Sciences 1975; Foreman 1974; Loy 1974; Poundstone 1974; Hill 1969; Moebs 1968, 1966). This is fairly easily accomplished for strip mines and indeed has now become a standard practice. However, to place coal wastes back into underground mines is not so easy to do because of high costs and safety and drainage control problems. In either case, when properly done, the formation of AMD from the buried wastes is substantially reduced or alleviated entirely.

A very effective approach to prevent acid drainage is to direct the flow of incoming surface and subsurface water away from refuse disposal areas (Loy 1974; Coalgate et al. 1973; Krause 1972; Ramsey 1970; Hanna et al. 1963; Lorenz 1962). This is accomplished by the use of aqueducts, diversion ditches, barriers, and impoundments, but the proper placement and grading of the waste piles is also an important factor in preventing the influx of water (Maneval 1975).

Treatment of Acid Drainage

By far the most widely used method for treating AMD once it has formed and drained out of the coal refuse or mine area is by neutralizing with alkaline materials (O'Brien et al. 1974; McDonald et al. 1974; Bhatt 1974; Wilmoth et al. 1972; Kemmer and Beardsley 1971). Agents which have been used for this purpose include limestone, lime, caustic soda, or a combination of these. In the neutralization process, the acid drainage is brought into contact with the neutralizing agents, and as the pH of the water rises, iron and aluminum hydroxides precipitate. Although at first glance this seems like a straightforward process, there are many complicating factors which limit the choices of neutralizing agents and operating conditions.

Lime or caustic soda are soluble in water throughout a broad pH range and will rapidly reduce acidity and effect the precipitation of iron and aluminum salts (Bhatt 1974; Holland 1970, 1969: Girard and Kaplan 1966). But, these agents are relatively expensive, careful control of reaction conditions is required, and they are dangerous materials to store and handle. Proper disposal of the large volumes of sludge produced by the use of lime or caustic is also a problem (Lovell 1970; Kostenbader and Haines 1970).

Limestone, on the other hand, is a much cheaper neutralizing agent for AMD compared to lime or caustic soda, and it is easier to use and safer to handle (Ford 1972; Mihok et al. 1968; Calhoun

1968; Reidl 1947). Also the volumes of sludge produced by limestone treatment are smaller than for caustic or lime. There are also several disadvantages of using limestone. Limestone has a low solubility in neutral solutions, so a pH of about 7 is all that can be practically achieved with this agent. This is not a particular problem if the iron present in solution is principally in the form of Fe^{+++}, which rapidly precipitates as the hydroxide at a pH of 6.5 (Wilmoth and Scott 1970). However, if a substantial amount of Fe^{++} is present, additional processing steps are required to completely remove iron from solution. Fe^{++} hydroxide does not precipitate until the solution pH is increased to about 9, a value unattainable in a practical sense with limestone. Consequently, the usual practice is to oxidize the Fe^{++} to Fe^{+++} before or during limestone neutralization. This oxidation step is often accomplished by direct aeration (Selmeczi 1972; Holland 1970; Stauffer and Lovell 1969), but many other methods have also been used in conjunction with the limestone process (Gaines et al. 1972; Jasinski and Gaines 1972; Streeter et al. 1971; Beller et al. 1970; Mihok 1969; Steinberg et al 1968). In addition to these problems, the low solubility of limestone in water requires that the acidic effluents remain in contact with the limestone for relatively long times to complete neutralization. This severely limits the volume effectiveness of limestone treatment facilities. Another general disadvantage of using either hydrated lime or limestone for neutralizing AMD is that water hardness is increased (Ca and Mg ions) during treatment. In spite of these drawbacks the economy, ease of operation, and safety of handling still make limestone a popular and widely used agent for neutralizing acid drainage from coal mine wastes.

There are now about 300 plants in operation in the U.S. for treating AMD with the various alkaline neutralizing agents. Most of these plants utilize hydrated lime; but many of the problems with limestone are being overcome, and it is expected that a higher proportion of limestone treatment facilities will begin to appear in coming years. Regardless of the neutralizing agent used, it must be pointed out that these processes are designed primarily to treat solution acidity. Only those ions, such as Fe, Al, and Cl, whose solubilities are sensitive to pH in the acid to neutral range, will be removed by the alkaline neutralization process (McDonald et al. 1974). The solubilities of other ions (Ca, Mg, and Pb, for example) are not highly dependent on solution pH, and thus will probably not be affected, but may be even increased in AMD by alkaline neutralization. Typically, waters treated by alkaline agents tend to retain relatively high contents of dissolved salts as indicated by the specific conductance values given in Table IX-II.

Under certain circumstances, the utilization of ion-exchange technology offers a more highly refined method of treating AMD than does direct neutralization with alkaline agents. Ion exchange is a method where specific ions are removed from solution by exchanging them with other ions of like charge at the surface of an adsorbent. This accumulates the removed ions on the adsorbent, but releases the ions originally held by the adsorbent into solution. The newly adsorbed ions are removed from the adsorbent by flushing it with a regenerating solution. The adsorbents used are either natural ion-exchange materials, like clays or zeolites, or, increasingly, various types of synthetic resins.

Ion-exchange treatment of acidic effluents reduces both the total acidity and a substantial part of the dissolved ions. For example, Kunin et al. (1974) have reported the effectiveness of a 1×10^6 gal/day ion-exchange, AMD treatment facility located in Pennsylvania. This facility utilizes weakly basic, bicarbonate anion exchange columns. As the acidic coal mine drainage water is passed through the ion-exchange column, the metal sulfates in solution are converted to soluble metal bicarbonates. Aeration releases CO_2 and raises the pH of the solution, precipitating Fe, Mn, and Al as hydrous oxides. Part of the Ca and Mg also precipitates, but to produce the highest quality water, further treatment with lime will precipitate more of the latter ions as the less soluble carbonates. The ion-exchange resins are regenerated by backflushing with NH_4OH followed by CO_2. Typical results from the treatment of AMD with this ion-exchange facility are recorded in Table IX-III.

TABLE IX-II

EFFECTIVENESS OF ALKALINE NEUTRALIZATION FOR IMPROVING QUALITY OF MINE DRAINAGE[a]

Parameter[b]	Feed Water Range	Lime Treatment	Limestone Treatment	Limestone - Lime Treatment
pH	2.4-3.1	7.1	6.0	7.1
Total acidity	1700-9200	7.6	107	33
Alkalinity	0-93	10.3	93	35
Specific Conductance	2800-7900	5200	4600	2900
Sulphate	2200-6600	3500	4200	3000
Iron, total	145-1130	1.94	3.40	1.75
Aluminum	---	1.80	2.65	1.00
Magnesium	---	135	282	82
Calcium	---	900	965	170

[a]From McDonald et al. (1974).
[b]Concentrations in ppm, conductance in micromhos.

TABLE IX-III

TYPICAL WATER ANALYSES FROM ION-EXCHANGE TREATMENT OF ACID MINE DRAINAGE[a]

Variable[b]	Feed Water	Product Water
pH	3.7	9.5
Free Acidity	384	---
Iron	101	0.2
Calcium	295	85
Magnesium	100	99
Total Hardness	395	184
Sulfate	648	192
Total Dissolved Salts	1084	284

[a]From Kunin et al. (1974).
[b]Concentrations in ppm.

Several other ion-exchange processes have been suggested or tested to treat the acidic effluents from coal mineral wastes (Holmes and Schmidt 1972; Rose 1970; Downing et al. 1968; Pollio and Kunin 1967). These have included both anionic and cationic exchange columns.

The sludges produced by the ion-exchange methods appear to be easier to dewater and dispose of than those produced by alkaline neutralization. The ion-exchange technique for treating AMD is apparently limited, however, to drainage with medium to low total solids levels (<1000 ppm). Above this point both economic and technical difficulties become excessive. Several 0.5 to 1 x 10^6 gal/day ion-exchange treatment plants are now in operation in the U.S.

Reverse osmosis is a technique in which special types of semipermeable membranes are utilized to selectively remove disssolved ions from the acidic waste waters (Blackshaw et al. 1974; Wilmoth et al. 1972; Kremen et al. 1970; Mason 1970). The membranes used are permeable to water but relatively impermeable to dissolved ions. High pressures are used to force the contaminated solutions through the membrane. The ions removed from the drainage solutions, which are concentrated in a brine on the fore-side of the membrane, must be collected for disposal or further processing. Typical before-and-after results from a reverse-osmosis AMD processing facility are given in Table IX-IV.

Although reverse osmosis does an excellent job of removing dissolved salts from solution, additional treatment of some kind is necessary to adjust the pH of the solutions. Also, some trouble has been experienced with fouling of the membranes by iron precipitates at low pH, causing a reduction in efficiency. In spite of these difficulties, reverse osmosis is considered feasible for treating AMD, and several pilot-scale plants have been built and tested.

Flash distillation is a simple and highly effective method to clean up AMD which is highly contaminated (>1000 ppm) with dissolved salts (Bhatt 1974; Maneval and Lemezis 1972). With this method, the contaminated feed water is heated to the vaporization point in a series of enclosed chambers. The product water is condensed in another part of the cell in a highly purified state. Residual salts are collected for disposal.

A pilot plant utilizing flash distillation has been constructed to treat AMD. Initial estimates are that this method is expensive, but it is still one of the more promising techniques for upgrading the quality of the most highly contaminated waste waters.

In addition to the methods described above, there are many other techniques that may be feasible for cleanup or prevention of AMD. These include: sulfide precipitation (Streeter 1970); antibacterial agents (Shearer et al. 1970); microbial polymers (Dugan 1970); foam separating agents (Hanson 1972); biological treatment (Rice and Rabolini 1972); deep-well injection (Stefanko 1969; Linden and Stefanko 1966); sewage treatment (Pearson and Nesbitt 1974; Morgan 1942); and metal-hydroxide precipitation (Evans 1966). Most of these methods, however, have not been carried beyond the laboratory stage. Consequently, their general economic or technical feasibility for large-scale work is unproven.

TABLE IX-IV

SUMMARY OF QUALITY OF ACID MINE DRAINAGE AFTER TREATMENT BY REVERSE OSMOSIS UNIT[a]

Variable[b]	Feed Water	Product Water
pH	4.7	3.8
Conductivity	3800	48
Total acidity	930	132
Total dissolved salts	4850	23
Total iron	393	1.5
Aluminum	29	0.22
Calcium	427	1.5
Magnesium	137	0.5
Sulfate	3400	16

[a]From Blackshaw et al. (1974).
[b]Concentrations in ppm, conductivity in micromhos.

At this point, then, several observations can be made regarding the possible effectiveness of the various methods used to prevent or treat AMD for removing or controlling the trace-element contents of the waste waters.

It is fairly well established that the highest contents of dissolved and suspended materials in the effluents from coal wastes are carried in the most highly acidic solution. Therefore, the techniques for initially preventing the formation and buildup of AMD by excluding oxygen and water from coal-processing wastes should also be effective for keeping the levels of dissolved or suspended trace elements to a minimum in the waste runoff.

The situation becomes more complex after acid has been generated in the waste material and the runoff has become contaminated with large quantities of acid and dissolved salts. Undoubtedly, many of these solutions carry large amounts of trace elements in addition to the major elemental components, but the effectiveness of AMD treatment methods at removing these trace elements can, at this point, only be surmised.

The methods for neutralizing AMD with alkaline agents are particularly nebulous with regard to the fate of trace elements during processing. It has been seen that, although certain elements are precipitated as a result of the treatment, others are unaffected and remain in solution. The almost universal use of these neutralization techniques for treating AMD makes it imperative that a careful assessment of the chemistry and behavior of the trace elements in coal-refuse drainage be made within the context of the treatment parameters. This will be especially necessary if some of the more toxic trace elements are eventually identified in AMD in appreciable quantities.

Ion exchange, reverse osmosis, and flash distillation have all been shown to be effective for removing a substantial part of the dissolved mineral matter for AMD. Accordingly, these techniques should be fairly effective at removing many of the minor- or low-abundance elements as well. Again though, it will be necessary to evaluate each method of treatment on a case-by-case basis to establish the effectiveness for removing the specific elements of concern.

The main conclusion to be drawn from this section is that the methods now being utilized to prevent or treat contaminated runoff or drainage from coal mineral wastes are directed mainly at the control of acidity and only in some instances at removing disssolved constituents. Should the removal of particular trace elements prove necessary or desirable, a reassessment of the specific treatment methods will be needed to determine their suitability for this purpose. Undoubtedly, in many cases, additional steps or modifications of existing methods will be necessary to accomplish the desired objective. Apparently, there has already been some concern about these latter aspects, as laboratory studies concerning the removal of specific ions from treated waste waters are now being reported (Swain and Roselle 1974; Huck et al. 1974).

X. RECOVERY OF TRACE ELEMENTS AND MINERALS FROM COAL-WASTE MATERIALS

Workers have experimented for many years with various processes for utilizing the material in coal-waste piles with the idea of reducing the enormous areas occupied by such piles, and subsequently, their contamination of air and water. An additional incentive has been the desire to retrieve some of the minerals or other economically valuable products contained in the coal wastes. A partial review of the literature on this subject has been written by Coalgate (1975); and, Kenahan et al. (1973) conducted a survey for the Bureau of Mines on possible uses of wastes. Generally, coal-waste utilization falls into one of three categories: coal salvage, building or construction materials, and metals or minerals recovery.

The use of coal refuse as a direct fuel source was discussed recently by Leonard and Lawrence (1973). Effective utilization of this resource requires a knowledge of a past history of the bank's

deposition, since suitable deposits of coaly waste must be located within the refuse dump. There is a large potential for using the residual coal in refuse for power plant applications. Of particular interest are the low- to medium-energy coals, which were discarded along with the wastes at times when consumers demanded higher energy coals. With beneficiation, 70% of the waste piles studied could qualify for presently available power generation processes. The recovery of salable coal from these banks seldom exceeds 20% of the total waste material (MacCartney and Whaite 1969), but one large steel company has seriously engaged in a program to obtain steam coal from the refuse produced by its metallurgical coal plant (Charmbury 1970).

The use of coal wastes for building and construction materials has shown promise of economic success (McNay 1970). Products which have been considered are road aggregates, non skid materials, and building materials (Spicer and Luckie 1970). Several processes have been studied to make lightweight aggregate building materials (e.g., cinder blocks) from coal wastes (Myers et al. 1964; 1962). The fusion heat required was supplied by the residual carbon in the refuse. Pelletization of the refuse before fusion produces a stronger, more uniform product. However, one of the two plants studied required many modifications of the original design because flat slate particles did not easily form pellets; also, the process used may be impractical for some refuse. In later studies, Utley et al. (1965) related washability data to aggregate production and concluded that the ideal refuse, which resulted in a finished product with greatest compressive strength and best expansion characteristics, was that which sank at 2.60 specific gravity and contained 12-25% pyrites. Two much carbon decreased expansion, and excess alumina required high fusion temperatures. Clearly, much work will be needed to adapt a variable source, like coal waste, to the manufacture of finished products like those mentioned above.

Interest in recovering metals from coal wastes has flourished since the forties, when wartime conditions threatened to cut off supplies. Current interest is also stimulated by the realities of external dependence, as more than one-half of the total U.S. requirements of 20 strategic metals and minerals are imported, and much of these from "Third World" suppliers (Falkie 1975). Trace metals and minerals in coal and, hence, in coal waste, could supply much of the U.S. demands if they were to be recovered from these materials. The problems encountered in utilizing these sources—low-quality ore and a widely scattered resource—are not small, however. The following paragraphs will briefly describe some of the technical solutions which have been reported on securing materials from coal wastes.

Sulfuric acid is the major chemical produced in the U.S. A constant supply is vital to the nation's economic health. Mitchell (1944) attempted to recover pyrite from coal waste to be used for sulfuric acid production. The method used was mechanical separation with jig tables. Although borderline quality raw materials could be obtained from coal waste by this method, the economic picture at the time was not optimistic, particularly in view of the capital outlay required for concentrating the pyrite.

Stimulated by a shortage of sulfur and sulfuric acid, and an increased interest in environmental contaminants in the late 1960s, more workers turned their attention to pyrite recovery from coal waste. Sun and Savage (1968) developed a comparatively successfully flotation process, in which separation took place in stages. The process involved dual flotation, using collectors and frothers, first to separate the coal from mineral matter, then pyrite from the remaining clay minerals in the waste.

A magnetic pyrite separation process, aimed generally at pollution control via sulfur reduction of coals for electric utility use, was developed by Ergun and Bean (1968). This process was also thought useful for the recovery of iron or sulfur. An attempt was made to increase the magnetic susceptibility of pyrite above its normal value by using heat to rapidly convert a part of the iron into a ferromagnetic state. The most promising result was obtained using dielectric heating of the coal. A study of Brazilian raw coals indicated a potential for the use of magnetism to effect the separation of the mineral constituents of coal, other than pyrites (Trindade 1973).

Many processes have been used for alumina extraction from coal wastes. Kelley et al. (1946) present a detailed study of the thermodynamics of the conversion of various aluminum-containing compounds to alumina. These included a high-alumina clay (20% available alumina as kaolinite) and alunite. Also, coal waste has been burned in the presence of alkaline-earth compounds to solubilize the silicates in the ash, from which alumina could be extracted (Freling and Dorren 1937). Muller and Oversohl (1951) patented a method in which coal tailings were treated with chlorine at temperatures between 600 and 1000°C in rotary kilns or shaft furnaces to recover iron and aluminum. Another method was employed by Sukhanova and Ponomarev (1969), who used sulfuric acid to extract alumina from coal wastes by countercurrent leaching. Korshunov and Shmuk (1957) obtained alumina by extracting coal flotation tailings with nitric acid, but they obtained some iron impurities in the final product. By treating coal ash with sodium oxide, Ni (1973) succeeded in separating alumina from the other products and achieved a 93-97% recovery of the alumina present.

Less has been done on the technology of the recovery of specific trace elements from coal. Mitchell (1944) reported that copper, zinc, lead, silica, alumina, phosphorous, manganese, and additional elements were associated with the mineral, pyrite, and that these elements could be separated from the pyrites in coals, should their quantity and concentration make separation economically feasible. Sun et al. (1971) indicated that perhaps the most generally useable portions of the coal waste are silica (30-60% of most coals) and alumina (10-40%), from which gallium or germanium might be by-products.

Manganese and molybdenum have also received attention. Molybdenum has been extracted with hydrochloric acid from tailings of the sulfuric-acid treatment of coal ash, yielding 85% of the metal present (Mirzakarimov 1970). Ozone, hypochlorite ion, and chlorine gas have been used to remove manganese as MnO_2 from acid mine drainage (Swain and Rozelle 1974). The hypochlorite ion worked best, but all had the disadvantage that iron in the acid drainage had to be removed from the water first, since it was preferentially oxidized.

In other studies, the mineral portions of coal, containing various metals, were enriched using horizontal cyclone burners in a process described by Gol'dina (1968). A foam separation technique, using sodium dodecyl sulfate as a surfactant, was applied to acid mine drainage. This process removed only 6% of the metals per pass through the foam column. Because the acid drainage did not foam easily, and the foaming agent was not readily recovered, the method was not concluded to be economically advantageous. Finally, ion-exchange methods have been used to recover germanium from coal ash (Adamenko et al. 1972). Germanium was removed from the exchange column by elution with hydrochloric acid.

The carbon left in the coal refuse might also be of use. Experiments have been conducted using bone coal and high-carbon refuse as materials for water purification (Broderick and Hertzog 1941). In most cases, the product contained too much ash to meet federal water purification standards. Combined with other techniques, this problem might be overcome.

As the above suggest, there are many possible ways to utilize coal refuse and recover useful materials from it. However, most of the processes investigated require modifications for adaptation to the various types of wastes, and often the other components in the wastes interfere with the recovery operation. Many of the processes are not adaptable to large-scale, commercial operations. Nonetheless, there is little doubt that coal mineral wastes represent a resource of fuel, metals, and minerals of enormous magnitude. Research is needed to develop suitable utilization and recovery methods and to establish the feasibility of these processes within the context of today's rapidly evolving economics.

XI. SUMMARY AND CONCLUSIONS

The major conclusions from this review of the literature are:

- Few studies of the trace elements in coal-processing 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 the contributions of trace elements to this form of environmental contamination, let alone the effects of these, are not 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-processing 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 could themselves produce undesirable effects.
- 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 this review.

Introduction

The mineral wastes from coal processing and mine development constitute a major environmental problem. Over 3 billion tons of these materials have accumulated in the U.S., and the current annual rate of waste production (100 million 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 or cave-ins. 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 utilize the available information in the literature to assess the potential of this latter possibility.

Literature Search Format

An extensive search of the open literature on trace elements in coal processing 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-Processing Wastes

Only a few studies of the minerals and trace elements in coal-processing 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

A large volume of data on this subject is available, and most of the information can be applied to coal-processing 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 is still not well defined. Laboratory investigations of elemental behavior utilizing 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 quantitites of trace elements are discarded in the washing refuse.

Water Contamination from Trace Elements in Coal-Processing Wastes

The aqueous drainage from coal refuse is usually contaminated by acids and dissolved or suspended mineral matter. The highest 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 were burning in 1968. The cause 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-Processing Wastes

There are numerous potentially toxic trace elements in coal wastes, and many of these find their way into the environment. Ions, such as Fe, Al, and Mn, 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-processing wastes cannot be made.

Prevention and Treatment of Contamination from Coal-Processing 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. Preventative measures include grading, compaction, 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 utilization 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.

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16. ABSTRACT The report gives results of collecting and evaluating available information on the chemistry and behavior of trace elements in coal preparation wastes, and assessing the potential for environmental contamination from the trace elements in these wastes. Only limited attention has been given previously to the chemistry of trace elements in coal waste materials; however, most of the knowledge concerning trace elements and minerals in raw coals can be applied directly to coal wastes. Nearly every naturally occurring element is likely to be present in coal and coal refuse. The fate of these elements during coal preparation is poorly defined; but, large concentrations of trace elements are discarded in the washing refuse. Although the behavior of trace elements during refuse weathering, leaching, and burning is not well understood, sifficient data exists to show that toxic or harmful quantities of elements (e.g., Fe, Al, Mn, Co, Ni, and Zn) are often released to the environment. A comprehensive assessment of the full potential for environmental contamination from the trace elements in these wastes cannot be made without further extensive research.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Weathering	Pollution Control	13B
Coal Preparation	Leaching	Stationary Sources	08I
Wastes	Combustion		21B
Trace Elements			
Chemical Reactions			07D
Washing			13H, 07A

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