GEOCHEMICAL PROPERTIES OF COAL WASTES AND THE TOXICOLOGICAL EFFECTS ON AQUATIC LIFE

W.R. Roy, T.M. Skelly, I.G. Krapac, R.A. Griffin,
D.R. Dickerson, R.M. Schuller, J.J. Suloway, N.F. Shimp

Illinois Department of Energy and Natural Resources
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William R. Roy, Ivan G. Krapac, Robert A. Griffin,
Donald R. Dickerson, Rudolph M. Schuller, and Neil F. Shimp
STATE GEOLOGICAL SURVEY

Thomas M. Skelly and John J. Suloway
STATE NATURAL HISTORY SURVEY

NATURAL RESOURCES BUILDING
CHAMPAIGN, IL 61820

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ERRATA

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Page 2, paragraph 1, lines 13 and 14 - For "These acutely toxic, sublethal concentrations " read "These acutely nontoxic, sublethal concentrations".

Page 79, paragraph 2, line 2 - For "(an acutely toxic, sublethal concentration)" read "an acutely nontoxic, sublethal concentration)".

Page 85, paragraph 3, line 5 - For "acutely toxic, sublethal concentrations" read "acutely nontoxic, sublethal concentrations".

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Mention of trade names does not constitute an endorsement, either specific or implied, by any of the respective agencies.

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ABSTRACT

Leachates from solid wastes generated by coal mining, cleaning, and gasification are potentially harmful to the environment. The toxicological effects of leachates on aquatic organisms have not been adequately assessed. In this investigation, samples of seven coal-related wastes were characterized chemically and mineralogically. Laboratory extracts of each sample, obtained by a variety of extraction methods, were used in both acute and chronic bioassays.

A coal slurry sample (coarse fraction) and two samples of coal cleaning refuse were chemically and mineralogically similar; they generated acidic water-waste systems, both in the laboratory and in the field. Acidic laboratory extracts and field samples of acid mine drainage, collected from the same area as the solid samples, tended to be in equilibrium with some type of calcium sulfate ($CaSO_4$) phase and with maghemite. The chemical composition of the extracts was sensitive to the method used to generate the extracts, but generally had the same prevalent chemical character as the field samples. Acidic wastes contain appreciable quantities of soluble Al, Mn, Ni, SO_4, and Zn, as indicated by both laboratory extraction and field data. Long-term equilibrations suggest that Al, Fe, and SO_4 continued to be released by the acidic wastes after 22 weeks, although no associated change in pH was apparent.

Two mine spoil samples, essentially shale, tended to generate water-waste systems that were neutral in pH; consequently, they released lower quantities of potential pollutants than the acidic wastes. The gasification residue was compositionally similar to coal-fired power plant slag and fly ash; it generated moderately alkaline extracts with low concentrations of soluble, potentially toxic constituents.

All solid wastes contained a variety of organic compounds; many are on the EPA Priority Pollutant List; however, these compounds were essentially insoluble in aqueous media.

Each extract was tested for acute toxicity with four species of freshwater aquatic organisms; the green sunfish (*Lepomis cyanellus*), the fathead minnow (*Pimephales promelas*), a crustacean (*Daphnia magna*), and a snail (*Physa anatina*). The extracts of the two mine spoil samples and of the gasification residue were not toxic to any of the organisms; whereas the extracts from the acidic refuse and slurry samples were acutely toxic to all the organisms. For all cases, pH was significantly correlated to mortality; Al, Fe, Mn, Ni, and Zn were significantly correlated to mortality only in specific instances. Data from 96-hour LC-50 determinations showed that dilutions up to 1:1000 were necessary to eliminate mortality. The most toxic extracts were those with the lowest pH, which necessitated the largest amounts of dilution to eliminate mortality.

Chronic bioassays, using the same organisms, were investigated with leachate samples from a relatively unweathered refuse and an older, more weathered refuse. Leachate from the weathered refuse was not acutely toxic; organisms exposed to dilutions of this leachate showed no detrimental chronic effects. The unweathered refuse generated an acutely toxic leachate. Low concentrations of the acutely toxic leachate lowered hatchability for the *Lepomis cyanellus* and *Pimephales promelas* eggs, reduced weight gain for *Physa*, and with chronic exposure, increased the death rate for *Lepomis cyanellus*, *Daphnia*, and *Physa*. Dilutions of a toxic, high-iron leachate resulted in the precipitation of ferric hydroxide that was implicated as the major factor accounting for the physical and physiological toxic effects exhibited by all test organisms during the chronic experiments when exposed to these acutely toxic, sublethal concentrations. The toxicity of this leachate demonstrates the detrimental effects that this type of waste could have on the aquatic ecosystem, if it entered a receiving water in a natural setting.

INTRODUCTION

During the late 1970s, shortages of natural gas, fuel oil, and gasoline dramatically demonstrated the need for electric utilities to increase their use of coal. Predictions vary, but the National Coal Association forecasted an increase in coal usage from 787 million metric tons in 1976 to approximately 1.5 billion metric tons by 1985. Increasing the use of coal increases the production of coal wastes. Past and current mining techniques have produced various types of coal solid wastes that are potentially harmful to the environment. Coal conversion via gasification and liquefaction also produce solid wastes that pose environmental problems. The Energy and Research Development Administration (1977) concluded that coal solid wastes could create substantial leaching and revegetation problems. Abandoned mine spoil banks and coal preparation wastes pose similar problems (Beyer and Hutnik, 1969; Mason, 1978). The Southern Illinois University Wildlife Research Study Group of Klimstra and others has defined 6,500 acres of abandoned preparation wastes or "gob" and 4,300 acres of slurry in Illinois alone. The impact on the aquatic environment of leachates from surface-mine spoil banks and of solid wastes generated during coal cleaning and synthetic fuel production has not been adequately assessed.

This investigation comprises interrelated physical, chemical, and biological analyses for a broad-based evaluation. The analytical synthesis of the data from this investigation will aid control technology and reclamation development. It will also provide a basis for determining the potential degree-of-toxicity of these wastes as required by PL 95-87, the Surface Mine Control and Reclamation Act (SMCRA of 1977).

Much information has recently become available for developing fish and wildlife management of reclaimed surface mines (Cairns, 1978). However, to maximize the benefits and minimize the adverse effects of mining and reclamation technologies, it is essential to test the toxicity of leachates produced from abandoned spoil banks. Unreclaimed spoil banks abandoned before the passage of the Surface Mining Control and Reclamation Act of 1977 (PL 95-87) present a potential pollution hazard to our water resources (Hood et al., 1979).

Another reclamation problem associated with the increased use of coal is the proper disposal of solid wastes from coal conversion and coal cleaning processes. The solid wastes from coal liquefaction and coal gasification will probably be redeposited on site where the coal was mined or in landfills (Talty, 1978). The volume of solid wastes produced from coal conversion is enormous. One estimate (Sather et al., 1975) is that a commercial gasification plant (250 million ft^3 of gas/day) will generate 2.3 million tons of ash and dry refuse per year. Additional estimates (Seay, 1972; Asbury and Hoglund, 1974) predict that a single gasification plant will generate 625 acre feet of residue per year. This huge volume of materials, like the thousands of acres of spoil banks and coal cleaning refuse piles, are subject to leaching; the effect of these leachates on the aquatic environment has not been adequately assessed.

The potential environmental hazard of coal solid wastes lies in the relatively large concentrations of accessory elements and the possible formation of acid from pyritic minerals. It is well known that iron sulfates and acids are produced from the oxidation of pyritc minerals in coal solid wastes exposed to air (Singer and Stumm, 1969; Smith et al., 1968; and Jones and Ruggeri, 1969). Sun et al. (1978) and Stone and Kahle (1977) conducted leaching studies on wastes from fluidized-bed gasifiers, but most work was done with wastes other than those from coal conversion processes producing synthetic fuels. Wewerka et al. (1978) have done extensive leaching studies on bulk residue from the Illinois Basin. Griffin et al. (1978) found that 31 to 60 chemical constituents measured in Lurgi gasification and H-coal liquefaction wastes presented a potential hazard; 16 of these constituents exceeded federal water-quality standards in equilibrated solutions with pHs ranging from 3 to 8. In addition, other studies (Rubin et al., 1976; Herbes and Beauchamp, 1977; Hildebrand et al., 1977; Schultz et al., 1978; and Southworth et al., 1978) have suggested that selected inorganic and organic compounds, such as resorcinol and 6-methyl quinoline associated with synthetic fuel effluents, are toxic. Other workers have found similar results with fly ashes from coal combustion (Vaugham et al., 1975; Cherry et al., 1976; and Birge, 1978).

The 1977 Executive Summary for the Eastern Energy and Land Use Group identified spoil-bank leaching as having a major impact on the environment (Mason, 1978). Some environmental hazards related to surface mining have been well documented (Curry and Fowler, 1978); best known are acid production and sedimentation and their effects on aquatic organisms (Jones, 1964; Parsons, 1968; Roback and Richardson, 1969;

Archibald and Gentile, 1971; Dills and Rogers, 1974; Herricks and Cairns, 1974; Preston, 1978; Orciari and Hummon, 1975; Matler et al., 1978; Winger, 1978; and many others). Bell (1971) subjected typical aquatic stream insects to various acidic conditions and demonstrated the detrimental effects of low pH. Cairns et al. (1971) demonstrated that benthic communities were reduced when a small portion of a mountain stream was subjected to acute acidic stress. Reppert (1964) demonstrated with fish cultures how toxicity tests could delineate the severity of acid mine drainage. However, few studies have investigated the chemical properties of spoil-bank leachates (Beyer and Hutnik, 1969; and Barnhisel and Rotromel, 1974); no bioassays of spoil-bank leachates have been conducted; and little is known of the chronic effects from any of the various coal-waste leachates.

Toxicity tests or bioassays represent one of the best approaches for predicting the effects of land disturbance, mining related wastes, or coal processing and utilization wastes on aquatic life (Preston, 1978). After it is determined with bioassays whether a leachate or laboratory extract is toxic, the physicochemical character of the leachate can be analyzed to identify the potential toxic components of the leachate and to aid the development of control technology and reclamation methodologies.

METHODS AND MATERIALS

Sample Collection and Preparation

Seven waste samples produced by coal utilization were collected: two samples of overburden or mining spoils, three samples of coal cleaning wastes, one sample from a dry slurry lagoon, and one solid waste by-product from a coal gasification plant.

The two samples of mining spoils were taken from a mine operated by the Amax Coal Company (Delta Mine) in Williamson County in southern Illinois. One sample, DMNS, is a composite of the Lawson Shale Member, a dark gray Pennsylvanian unit stratigraphically located above the Herrin (No. 6) Coal Member; this shale is the largest unit of the overburden at the mine. DMNS was collected from a vertical section at the strip mine. At the same location, a second spoil sample, DMOS, was taken from a roadcut made through an 18- to 22-year old spoil mound, composed largely of the Lawson Shale.

Samples of coal cleaning wastes were taken from a strip mine operated by the Peabody Coal Company (Will Scarlett Mine) in Saline County in southern Illinois. One of these (WSNG) was a sample of fresh cleaning waste collected from an active preparation plant processing coal from the Davis-Dekoven seams at the time of sampling. A second refuse sample (WSOG) was collected at this mine from a waste pile estimated to be about 20 years old. A sample of the material (WSSL) slurried to a settling pond was also collected from the same preparation plant that generated WSNG and WSOG. A third refuse waste (OBG) was collected from a waste pile in Franklin County, Illinois. This pile was approximately 50 years old and was the result of mining by shaft methods, activities associated with the Herrin Coal (Old Ben Mine No. 9). The source preparation plant is no longer present.

From a Kilngas (KG) deep-bed gasifier, 19 liters of solid waste was supplied by Allis-Chalmers from their pilot plant in Milwaukee, Wisconsin. Specifications for the fuel used when the waste was generated could not be obtained from this proprietary operation. The Kilngas process is described elsewhere (Illinois Institute of Natural Resources, 1979).

Collecting representative samples from coal refuse and spoil piles would not only have been impractical, but beyond the scope of the study. Moreover, procedures have not been established for the collection of representative samples from waste piles; therefore, an effort was made to collect a 25-kg sample from each waste pile, visually avoiding anomalous materials. To divide the collected bulk waste samples into representative subsamples was more important than to attempt to collect an initial sample representative of the entire waste pile.

All the mining wastes were first air-dried and ground to pass through a 9.53-mm sieve. This sized material was then subdivided using a sample splitter to produce a series of representative subsamples for each waste. Twelve subsamples from each waste were used for the solubility studies. An additional subsample for each waste was then further ground to pass through a 0.25-mm standard sieve and split to obtain representative samples for chemical and mineralogical analysis of the solid wastes. The Kilngas solid residue used for the solubility studies was in pellet form, as received from the pilot plant. The pellets ranged in size from about 0.1 mm to 1.5 mm. Before the solid was analyzed, it was ground to pass through a 0.25-mm sieve and split.

Mineralogical Procedures

The seven waste samples were analyzed by X-ray diffraction for mineralogical characterization and by Mössbauer spectroscopy for the determination of iron species. Prior to X-ray diffraction analysis, subsamples of the solid wastes used were ashed in a low-temperature asher (LTA). Low-temperature ashing isolates the desired mineral residue from the organic matter in the sample, and it often facilitates the resolving capabilities of X-ray diffractometry. The samples were ashed on a LFE corporation Model LTA-504 radio-frequency asher. Then the ashed samples were qualitatively analyzed by X-ray diffraction with a Phillips Norelco X-ray diffractometer using copper Kα radiation and a graphite monochromometer. The method is discussed further in Russell and Rimmer (1979).

Mössbauer spectra were obtained with an Austin Science Associates spectrometer using a linear acceleration motor to move the source (^{51}Co in Pd). A Nicolet 1070 N Signal Averager with 1024 channels was used to collect the spectra. Two spectra were simultaneously collected and combined to yield a spectrum that was recorded in 512 channels. The spectra were obtained at room temperature; spectra obtained at liquid-nitrogen temperatures were not significantly improved. Liquid-helium temperatures were not available, and there was no identification of superparamagnetic species. A more detailed discussion of the Mössbauer spectroscopy techniques used in the analysis of these samples is given in Saporoschenko et al. (1980) and Hinckley et al. (1980).

Methods for Inorganic Analyses

The samples were chemically analyzed for Si, Al, Mg, Ca, K, Fe, Ti, and P using X-ray fluorescence spectrometry (XRF). Arsenic, Ba, Br, Ce, Co, Cr, Cs, Eu, Ga, Hf, La, Lu, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, U, W, Yb, and Zn were determined by instrumental neutron activation analysis (NAA). Mercury determinations were made by neutron activation with radiochemical separation. Boron, Cu, Ge, Li, Mo, Pb, Sn, and V were done by optical emission spectrochemical analyses (OES). A detailed discussion of sample preparation, detection limits, and procedures for these techniques can be found in Harvey et al. (1983). The sulfur determinations were carried out by ISO method 609-1975E.

Most chemical analyses of the supernatant solutions were determined by inductively coupled argon plasma spectrometry (ICAP) with a Jarrell-Ash Model 975 Plasma AtomComp. The constituents determined by ICAP were Al, As, B, Ba, Be, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Sn, V, and Zn. The procedures and techniques of this specific instrument are discussed by the Jarrell-Ash Division (1978). Sulfate was done turbidimetrically (American Public Health Association, 1975). Alkalinity was determined by titration with dilute sulfuric acid and oxidation-reduction potential (Eh), pH, and electrical conductance were measured by electrodes (U.S. EPA, 1979).

Analytical Methods for Organic Analyses

The solid samples were air-dried and ground to pass a 0.25-mm screen prior to organic analysis. The solid waste samples and laboratory extract samples were analyzed by the methods set forth in the IERL-RTP Procedures Manual: Level 1 Environmental Assessment (U.S. EPA, 1978). An overview of the methodology is shown in figure 1.

The solid samples were extracted with 1 L of methylene chloride (CH_2Cl_2) in a large (70-mm x 300-mm body) soxhlet extraction apparatus. The extracts were found to contain elemental sulfur. Free sulfur was removed from the extract by passing the solution over activated copper (Blumer, 1957).

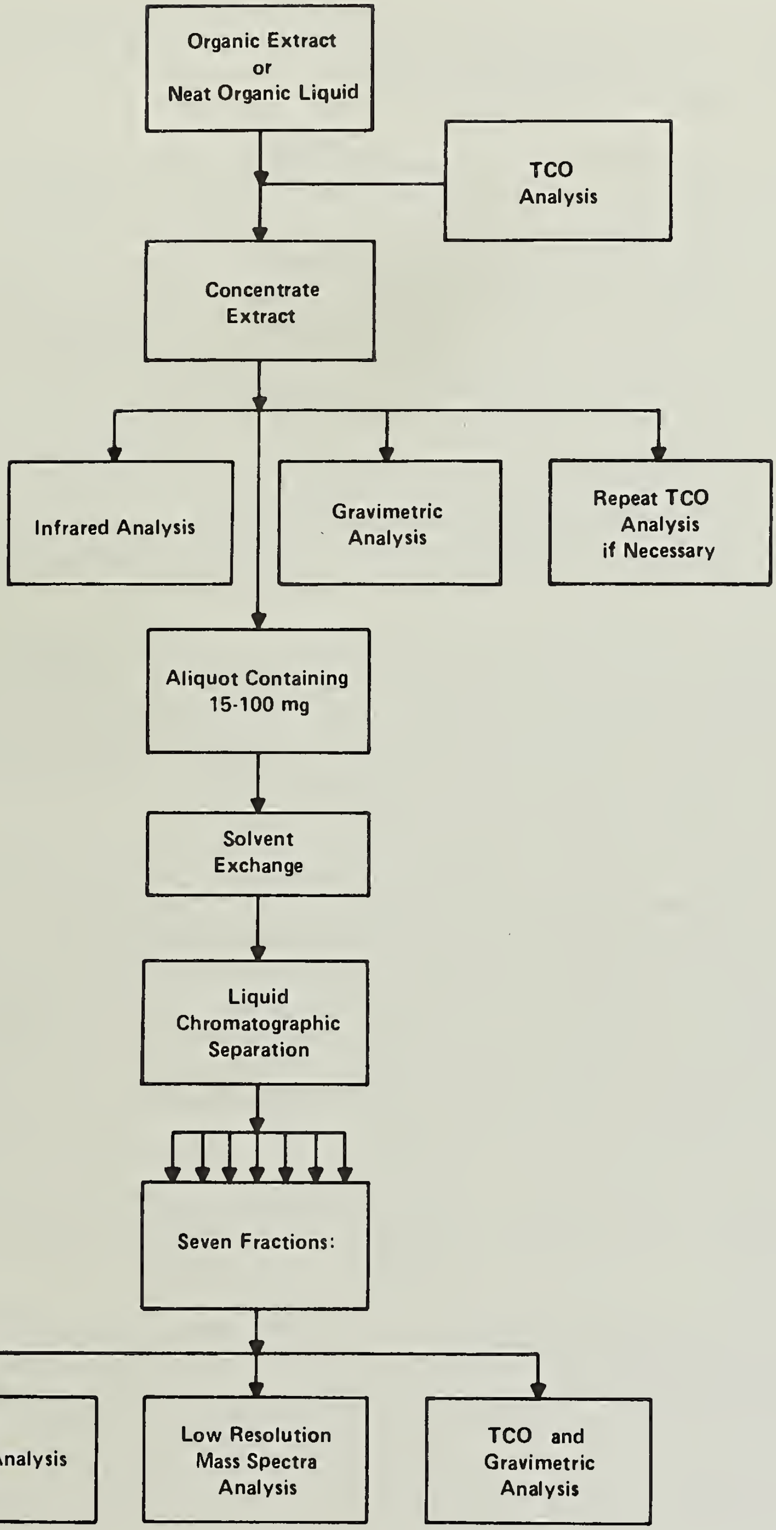


Figure 1
Organic analysis methodology.

Five liters of aqueous solutions (5 L) were extracted two separate times, at pH 2 and pH 12, using a 50-mL volume of CH_2Cl_2 per liter of solution for each extraction step. The extracts were combined to give a total volume of 1000 mL.

A total chromatographable organics (TCO) determination was run on each of the extraction solutions at concentrations of 1000 mL, 100 mL, and 10 mL; Kuderna-Danish evaporators were used for the concentrations. The TCO analysis is designed and calibrated to quantify the weight of organics that have boiling points between 100^o and 300^oC. The TCO were determined using a Perkin-Elmer Sigma I gas chromatographic system. A 1.8-m by 3-mm O.D. stainless steel column packed with 3 percent SP2100 on 100/120 Supelcoport was used for separation. The eluted organics were analyzed with a flame ionization detector.

The solvent was then evaporated completely by carefully heating at 40^oC under a stream of dry nitrogen. The organic residues were dried to constant weight in a dessicator. The final weight is designated the gravimetric analysis (GRAV).

An infrared (IR) spectrum was obtained for each organic residue using a Perkin-Elmer 283B Infrared Spectrophotometer. Where there was sufficient material available, the IR spectrum was obtained using a neat smear of the sample between two NaCl plates. Where only smaller (approximately 5 mg) amounts were available, the sample was dissolved in carbon tetrachloride (CCl_4) for IR analysis.

All sample extracts of adequate quantity (>15 mg) were subjected to liquid chromatographic (LC) separation. The LC column was 200 mm x 10.5 mm ID, glass, with Teflon stopcock and a waterjacket. Davison Silica Gel, 60 to 200 mesh, Grade 950 (Fisher Scientific Company) was used as adsorbent. The adsorbent was sequentially extracted with methanol, methylene chloride, and pentane, then activated at 110^oC for 2 hours just prior to use. Table 1 shows the sequence for the chromatographic elution. The column elution rate was maintained at 1 mL/min. A TCO analysis was run on each fraction from the LC separation.

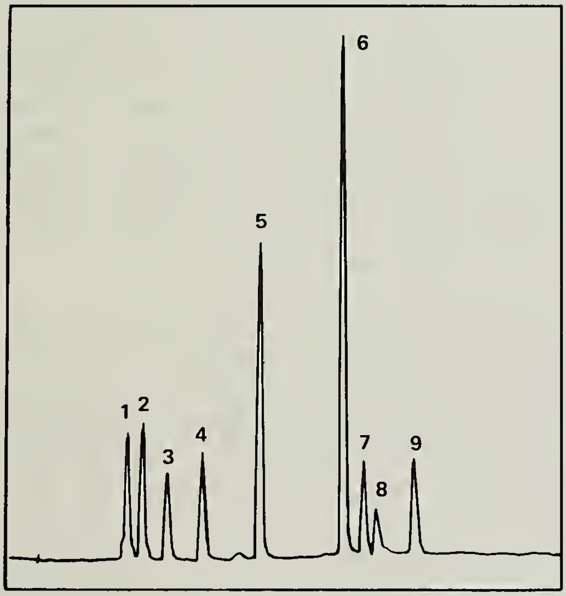
The solvent was evaporated by gentle heat and a stream of dry nitrogen. GRAV analysis and an IR spectrum was obtained for each fraction.

Low-resolution mass spectrometry (LRMS) was obtained for only selected samples of organic material extracted from the KG sample. Information derived from the LRMS of the KG sample was incorporated into the characterization of the organics extracted from the other solid wastes.

High-pressure liquid chromatography (HPLC) analyses were run using UV detection at a wavelength of 254 nm. An altex Ultrasphere^R ODS, 5 µm,

Table 1. Liquid-chromatography elution sequence.

	Fraction	Solvent composition	Volume (mL)
LC-1	Paraffins, olefins	Pentane	25
LC-2	Small aromatics (benzenes, naphthalenes)	20% Methylene chloride in pentane	10
LC-3	Large aromatics	50% Methylene chloride in pentane	10
LC-4	Large aromatics, some low polar O and S compounds	Methylene chloride	10
LC-5	Polar species (e.g. phenols, alcohols phthalates, amines,) with increasing polarity	5% Methanol in methylene chloride	10
LC-6		20% Methanol in methylene chloride	10
LC-7	Weak acids	50% Methanol in methylene chloride	10



ISGS 1983

Figure 2
HPLC of a known mixture of phenols and polyaromatic hydrocarbons referenced to toluene. Peak identification: 1. phenol; 2. p-cresol; 3. 2, 3-dimethylphenol; 4. 2, 4, 5-trimethyphenol; 5. toluene; 6. phenanthrene; 7. pyrene; 8. chrysene; 9. benzo (α) pyrene.

4.6 x 250 mm HPLC column (Beckman Instruments, Inc., Berkeley, CA) equipped with a guard column was used. The total extractable organics and the LC fractions were dissolved in methanol for HPLC analysis. Toluene was added as an internal standard. The elution solvent was 80:20, v:v, methanol:water with a 1 mL/min flow rate. A mixture containing four methyl-substituted phenols, toluene, and four polyaromatic hydrocarbons was prepared and used as a reference standard (fig. 2).

MINERALOGICAL CHARACTERIZATION

W. R. Roy and R. M. Schuller

It is reasonable to predict that the predominant mineral assemblages in mining spoils and preparation wastes will be much like those in the sedimentary strata associated with the coal seam and the mineral matter within the coal. Coal preparation wastes consist primarily of shale clasts, fragments, and nodules; pyritic coal; pyrite lenses and nodules; and underclay fragments.

The three refuse samples (WSNG, WSOG, and OBG) and the slurry sample (WSSL) were mineralogically similar (table 2). They were primarily composed of quartz, pyrite, illite, kaolinite, feldspars, and anhydrite. These results were comparable to those reported elsewhere: Wewerka et al. (1978) also identified quartz, pyrite, illite, and kaolinite in three refuse samples, and generalized that most refuse samples from Illinois Basin coals are composed largely of clay minerals with lesser amounts of quartz and iron sulfides. They also found marcasite, calcite, and gypsum as minor components in some samples. Bush et al. (1974, 1975) noted the presence of chlorite and muscovite in addition to the major minerals previously mentioned.

While the major mineralogical assemblages are similar between studies, the discrepancies relative to minor minerals may stem from masking effects. The abundance of quartz and pyrite in the samples of this study made further characterization by X-ray diffraction difficult, due to the masking by these dominant minerals. There was some indication that coquimbite ($Fe_2(SO_4)_3 \cdot 9H_2O$) was present in refuse samples WSNG and WSOG, and that hematite was present in refuse OBG. Neither mineral was identified by Bush et al. (1974, 1975) or Wewerka et al. (1978) in their refuse samples. Griffin et al. (1980) reported a similar masking that was overcome to a certain extent by the application of Mössbauer spectroscopy, a more definitive technique for differentiating iron species.

The Mössbauer spectrum of refuse OBG suggested a mixture of ferrous and ferric iron clays (table 2). The presence of pyrite was anticipated but not clearly established. The amount of pyrite may have been below the resolving capabilities of this technique.

Table 2. Mineralogical composition of the seven solid waste samples by X-ray diffraction.

	WSNG	WSOG	OBG	WSSL	DMNS	DMOS	KG
Nonferrous Minerals							
anhydrite	tr	x	x	x	x	x	
ankerite					tr		
calcite					x	x	
chlorite					x	tr	
dolomite						x	
feldspars	x	x	x	tr	x	x	x
gypsum						tr	
illite	x	x	x	x	x	x	
kaolinite	x	x	x	x	x	x	
mixed layer clay	x	x	x		x	x	
Mg-calcite					?		
mullite							x
muscovite					x	x	
quartz	x	x	x	x	x	x	x
siderite					x		
Ferrous Minerals							
coquimbite	x[2]	x[2]					
Fe^{+2} clay	x[1]	x[1]	x[1]	x[1]	x[1]	x[1]	
Fe^{+3} clay	x[1]	x[1]	x[1]	x[1]	x[1]	x[1]	
hematite			x[2]				x[2]
natrojarosite			x				
pyrite	x[1]	x[1]	x[2]	x[1]	tr	tr	

[1] determined or varified by Mössbauer spectra.

[2] not found in Mössbauer spectra.

The Mössbauer spectrum for the slurry sample was resolved into three absorptions, similar to the spectra of refuse WSNG and WSOG. The most prominent peak was attributed to pyrite, while the other two were identified as ferrous and ferric clays.

The mineralogy of the two spoil samples largely reflects the composition of the Lawson Shale, a micaceous and calcareous gray shale. DMNS is entirely Lawson Shale; visual inspection of hand samples of DMOS revealed pre-mining soils, weathered and unweathered flakes of shale, and carbonate fragments. The mineralogical compositon as indicated by X-ray was essentially quartz, illite, kaolinite, muscovite, and calcite.

The iron species found in the two spoil samples by Mössbauer spectroscopy were characteristic of clays. For both samples, there were two ferric and two ferrous species. The ferric absorptions have parameter values typical of trans OH^- and cis OH^- sites in illite and similar dioctahedral clays. The Mössbauer parameters for the cis OH^- species were within the range usually assigned to pyrite, which is often the case. X-ray diffraction indicated only traces of pyrite, so the assignment of a clay species was preferred. The presence or absence of iron sulfate species identified by X-ray diffraction in the two spoil samples could not be confirmed by Mössbauer spectroscopy. The absorption values for the iron sulfates fell within ranges that were also characteristic of clays, so that positive identification was not possible.

The Kilngas solid waste sample possessed a mineral assemblage that indicated high temperature and oxidizing conditions. X-ray diffraction data indicated the presence of quartz, mullite, and iron oxides that are commonly found in coal fly ash (Roy et al., 1981), another high-temperature residue of coal. Although feldspars appear to be rare in coal fly ash, they were present in the Kilngas waste sample. Griffin et al. (1980) found Lurgi ash samples were mineralogically similar to coal ashes, but they also contained feldspars. The Mössbauer spectrum was characteristic of a water-quenched bottom ash (slag); the absorptions were broad and unresolved. Most of the iron was identified as ferrous iron with one ferric species. The broad absorptions were typical of iron in silica glass. Although hematite was suggested by X-ray diffraction, it was not confirmed by the Mössbauer data.

INORGANIC CHEMICAL CHARACTERIZATION

W. R. Roy

Major and Minor Constituents

The initial step in assessing the potential pollution hazards of coal solid wastes is commonly a complete chemical characterization of the samples. Such analytical data will determine the maximum amount of a given constituent that may be released to the environment.

Mineralogical data (table 2) indicated six of the seven wastes were composed of primarily aluminosilicates; thus, the major elements in the refuse samples (table 3), the spoil samples (table 4), and the Kilngas sample were silicon and aluminum. Reported as percent silica (SiO_2) and alumina (Al_2O_3), the SiO_2 content of the refuse samples WSNG, WSOG, and OBG ranged from 30.21 percent to 40.43 percent, and Al_2O_3 ranged from 7.88 percent to 9.66 percent. Comparisons between these three refuse

Table 3. Major and minor constituents in refuse samples (concentrations in weight percent).

	Wewerka et al. (1978)			Griffin et al. (1980)		This work			Range in composition
	Plant A	Plant B	Plant C	Waste no. 1	Waste no. 2	WSNG	WSOG	OBG	Illinois Basin coal refuse
SiO_2	30.63	29.03	34.64	31.12	55.92	30.21	40.43	30.77	29.03-55.92
TiO_2	0.77	0.58	0.77	0.80	2.38	0.05	0.05	0.05	0.05- 0.80
Al_2O_3	13.23	9.62	13.91	10.68	18.33	8.36	7.88	9.66	7.88-18.33
Fe_2O_3	11.44	15.73	13.15	12.35	3.55	14.20	11.30	14.78	3.55-15.73
CaO	5.68	0.15	2.01	3.94	2.97	0.57	0.31	0.86	0.15- 5.68
MgO	0.68	0.43	0.53	0.31	0.64	0.17	0.02	0.16	0.02- 0.68
Na_2O	0.15	0.11	0.40	0.33	0.49	0.14	0.25	0.95	0.11- 0.95
K_2O	2.09	2.04	2.53	1.81	3.11	1.98	1.95	2.05	1.81- 3.11
P_2O_5	0.54	-	1.05	0.19	0.32	0.13	0.04	0.11	0.04- 1.05
organic C	-	-	-	-	-	29.77	22.14	13.80	13.80-29.85
inorganic C	-	-	-	-	-	0.08	0.05	<0.01	<0.01- 0.08
SO_3	22.72	33.71	28.96	27.17	1.27	25.72	21.92	9.02	1.27-33.71

Table 4. Major and minor constituent composition of the two spoil samples, the slurry sample, and the Kilngas waste.

	DMNS	DMOS	WSSL	KG	Average coal fly ash composition*	Slag**
SiO_2	59.03	64.00	15.51	49.00	44	47.69
TiO_2	0.09	0.07	0.03	0.07	1.3	0.74
Al_2O_3	15.82	13.14	4.41	22.09	23	15.98
Fe_2O_3	6.66	5.89	5.02	16.84	11	19.62
CaO	3.26	3.78	0.27	4.27	8.2	6.11
MgO	0.11	0.08	0.12	0.15	2.7	0.84
Na_2O	0.73	0.57	0.14	0.41	1.8	0.80
K_2O	4.18	3.54	0.96	3.10	2.0	2.43
P_2O_5	0.14	0.10	0.03	0.03	0.8	0.18
SO_3	2.07	1.20	10.56	1.50	1.60	0.28
Organic C	2.19	2.63	57.24	4.48	5	—
Inorganic C	1.00	0.78	0.04	0.01	—	—

* Roy and Griffin, 1982. ** Griffin et al., 1980.

Table 5. Sulfur species and total sulfur content of the seven solid wastes (percent weight).

	WSNG	WSOG	OBG	WSSL	DMNS	DMOS	KG
Sulfate sulfur	0.30	1.79	3.22	0.56	0.06	0.04	0.05
Pyritic sulfur	9.56	5.56	0.25	2.84	0.76	0.44	0.12
Organic sulfur	0.44	1.42	0.17	0.83	0.01	0.00	0.43
Total sulfur	10.30	8.77	3.64	4.23	0.83	0.48	0.60

samples, two samples studied by Griffin et al. (1980), and the three samples studied by Wewerka et al. (1978) suggest that the SiO_2 content of refuse from Illinois Basin coals varies from about 29 to 56 percent (table 3).

The Fe_2O_3 content of seven of the refuse samples was about 13 percent; SO_3 varied from about 1 percent to nearly 34 percent. The iron and sulfur contents were partially related to the pyrite content, which was the principle reactant in the production of acidic effluent. Analytical data for sulfur species (table 5) indicated that nearly all (92.8%) of the sulfur in WSNG was pyritic; whereas only 0.30 percent was the sulfate form. In WSOG, which is about 20 years old, about 63.4 percent occurred as pyritic sulfur. Also, WSOG contained 1.49 percent more sulfate sulfur than the younger WSNG sample. The oldest refuse sample, OBG (about 50 years old) contained only 6.87 percent pyritic sulfur; most of the sulfur, 88.5 percent, occurred as sulfate compounds. The apparent shift from pyritic forms of sulfur to sulfate forms with increasing age of the wastes may be due to the gradual oxidation of the pyrite in the refuse piles, with the formation of sulfate compounds as a by-product. A simplified reaction for the formation of sulfuric acid from pyritic wastes (Wewerka et al., 1976) would account for this apparent trend:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$

The relative acidity of leachate produced by refuse may be buffered by the neutralizing effect of carbonates mixed within the wastes; however, the calcium content, reported as percent CaO (table 3) was low, ranging from about 0.15 percent to 6 percent. The CaO content of the three samples in this study appeared to be lower than those reported by Wewerka et al. (1978) and Griffin et al. (1980).

Although the methods used to mine and clean the coal will ultimately influence the composition of the resulting refuse, the trends for iron concentration observed here agree with the conclusion by Gluskoter et al. (1977) that coals from the Illinois Basin tend to have higher Fe concentrations than those from the Appalachian Basin (table 3).

Organic carbon was a major component in the three refuse wastes, WSNG, WSOG and OBG, ranging from about 14 to 30 percent by weight. The fact that organic carbon makes up much of the bulk composition of refuse is often overlooked in published studies.

The major and minor constituents in the two spoil samples DMNS and DMOS are shown in table 4. The composition of these two samples is typical for sedimentary rocks (Krumbein and Sloss, 1963), with the exception of the higher sulfur concentrations. As with the unweathered refuse sample (WSNG), most of the sulfur (92%) occurred in pyritc forms (table 5).

The spoil sample DMNS is a composite sample taken from mine outcrops of the Lawson Shale. We believe that the mineralogical and chemical data in this report may represent the first such published data on this shale. Studies of Paleozoic shales in Illinois by the Illinois State Geological Survey researchers include the work by Lamar (1948), Grim, Bradley, and White (1957), and Kosanke et al. (1960); but none of these studies contains analytical data for the Lawson Shale. The stratigraphic equivalent of the shale in Indiana has also not received attention from the Indiana Geological Survey (Shaver et al., 1970). However, it should be noted that there was little stratigraphic control with respect to sampling; thus the results may be suggestive but not decisive.

The major component of the slurry sample (WSSL) is organic carbon (table 4). Inspection of hand samples indicated that much of the material consisted of fine-grained coal particles, reflecting its mode of deposition as a slurry mixture pumped into a storage basin next to the source preparation plant. Unlike the other six wastes, WSSL had a low SiO_2 content (15.51%)·relative to most geological materials; but a sulfur trioxide (SO_3) concentration (10.56%) was within the range expected for SO_3 concentrations of coal preparation refuse from Illinois Basin coals (table 3). About two-thirds of the sulfur in WSSL occurred as pyritic compounds (table 5).

The mineralogy of the Kilngas waste was described as being similar to coal fly ash and slag in many respects. The major elemental composition was also comparable to other high-temperature combustion residues (table 4). Comparisons between the composition of the KG sample (table 4), an empirical formula for coal fly ash from Roy and Griffin (1982), and a slag sample (Griffin et al., 1980) suggested the KG sample had an intermediate composition: the concentrations of some major and minor constituents fell between the ranges in composition established by fly ash and the slag sample.

Trace Constituents

The concentrations of trace constituents in the three refuse samples WSNG, WSOG and OBG are listed in table 6, along with data for other refuse samples for comparisons. As with most natural materials, the trace constituent concentrations of refuse are variable. Arsenic varied from 12 to 94 mg/kg in refuse samples, vanadium from 4 to 86 mg/kg, and zinc from 39 to 500 mg/kg.

The central concept of coal cleaning is to concentrate the coal from the noncarbonaceous materials, e.g. silicates, sulfides, oxides, phosphates; therefore, trace constituents that generally occur with inorganic phases are concentrated in cleaning wastes relative to the concentrations of these same constituents in the material mined. For example, As, Co, Ni, Pb, and Sb commonly occur as sulfides (Gluskoter et al., 1977) and could be expected to be concentrated in refuse by present coal cleaning techniques. In fact, the arithmetic means of As, Co, Ni and Pb in the samples of Illinois Basin coal refuse were found to be more than twice the arithmetic means (Gluskoter et al., 1977) of the same constituents in Illinois Basin coals.

The trace constituents of the two spoil samples, DMNS and DMOS (table 7) are very similar, with the exception of F and Mn. Barium, F, Mn, Sr, and Zn were the predominant trace constituents in these two samples; concentrations exceeded 200 mg/kg. The trace-constituent concentrations of the slurry sample were broadly similar to those of the refuse samples WSNG, WSOG and OBG, although As, Ce and F were lower than in Illinois Basin coal refuse. The Kilngas sample was broadly comparable to the other six wastes, with the exception of the relatively high levels of Cr

Table 6. Trace constituent concentrations in refuse samples (mg/kg).

	Wewerka et al. (1978)			Griffin et al. (1980)		This work			Range in composition	
	Plant A	Plant B	Plant C	Waste no. 1	Waste no. 2	WSNG	WSOG	OBG	Illinois Basin coal refuse	W. VA coal refuse (Wewerka et al., 1976)
Ag	-	0.5	-	0.20	0.3	-	-	-	0.3-0.5	0.3-2.5
As	56	94	22	13	68	24	241	26	12-94	
B	62	64	79	9	200	-	-	-	9-200	
Ba	-	-	-	300	400	251	241	338	251-338	
Be	-	3	-	2	3	-	-	-	2-3	0.2-3
Br	-	2	-	1	3	4	3	6	1-6	
Cd	0.2	0.4	1	<1.4	2	1	<1	<1	0.2-2	0.3-1
Ce	92	73	89	92	100	90	73	76	73-100	
Cl	30	57	109	300	700	-	-	-	30-700	
Co	19	30	27	10	13	20	4	6	4-30	3-25
Cr	60	62	69	45	78	74	72	64	45-78	3-25
Cu	52	35	39	29	36	49	32	20	20-52	12-25
Cs	6	7	8	10	15	-	-	-	6-15	
Dy	6	4	5	-	-	-	-	-	4-6	
Eu	2	1	2	1	2	1	0.7	0.7	0.7-2	
F	630	374	1257	1105	900	320	215	220	215-1257	
Ga	19	-	17	11	19	11	9	14	9-19	3-25
Ge	5	<8	5	1	4	-	-	-	1-5	
Hf	3	3	4	3	8	6	7	4	3-8	
Hg	-	-	-	-	-	0.3	0.6	0.1	0.1-0.6	
La	45	37	45	43	50	35	32	33	32-45	
Li	51	52	15	-	-	55	38	52	15-55	
Lu	0.4	0.4	0.4	0.3	0.4	0.5	0.4	0.4	0.3-0.5	
Mn	301	144	132	310	310	185	45	-	45-310	65-1300
Mo	12	52	12	3	<1	-	-	-	<1-52	

Table 6. continued.

	Wewerka et al. (1978)			Griffin et al. (1980)		This work			Range in composition	
	Plant A	Plant B	Plant C	Waste no. 1	Waste no. 2	WSNG	WSOG	OBG	Illinois Basin coal refuse	W. VA coal refuse (Wewerka et al., 1976)
Ni	44	71	59	48	55	40	13	13	13-71	
Pb	45	34	50	55	55	259	495	78	34-495	20-150
Rb	-	96	258	100	200	35	32	33	32-258	
Sb	1	1	1	0.2	3	4	3	2	0.2-4	
Sc	12	12	11	9	15	9	7	9	7-15	3-25
Se	9	6	8	13	3	10	10	3	3-13	
Sm	7	6	7	7	8	8	5	4	4-8	
Sn	<9	<8	<9	3	7	-	-	-	3-7	
Sr	-	-	-	100	79	104	90	78	78-104	
Ta	1	1	1	1	1	1	1	1	1	
Tb	-	-	-	-	-	1	1	0.5	0.5-1	
Te	-	-	-	1	2	-	-	-	1-2	
Th	12	10	12	13	20	12	7	10	7-20	
Tl	-	-	-	8	8	-	-	-	8	
U	7	3	8	3	3	-	-	-	3-8	
V	78	86	73	35	40	7	4	5	4-86	25-250
W	-	-	-	3	3	1	1	1	1-3	
Y	35	18	28	-	-	-	-	-	18-35	3-25
Yb	3	3	2	2	4	3	2	2	2-4	
Zn	83	149	125	300	500	205	39	164	39-500	30-85
Zr	150	87	126	100	200	162	213	96	87-213	

(-) no data reported

Table 7. Trace constituent concentrations in the slurry, mine spoil, and Kilngas samples (mg/kg).

Sample	WSSL	DMOS	DMNS	KG
As	9	15	9	3
Ba	223	533	573	560
Br	7	<2	<2	<2
Cd	<0.5	<1.9	<1.9	<1.9
Ce	38	119	98	119
Co	9	20	16	24
Cr	30	89	71	1437
Cs	2	5	5	17
Cu	16	25	25	205
Eu	1	1	2	2
F	150	460	363	75
Ga	7	17	22	25
Hf	3	10	9	6
Hg	0.12	0.11	0.17	0.07
La	17	43	57	47
Li	24	51	53	64
Lu	0.2	0.6	0.6	0.7
Mn	150	530	1075	424
Ni	16	33	29	210
Pb	40	31	33	25
Rb	17	43	57	47
Sb	3	2	2	1
Sc	5	15	13	19
Se	4	14	11	5
Sm	4	9	10	9
Sr	57	192	225	206
Ta	0.3	1	1	1
Tb	0.5	1	1	1
Th	5	17	14	18
V	4	7	7	20
W	0.6	<1	<1	1
Yb	1	4	3	4
Zn	58	106	92	113
Zr	95	252	278	130

and Ni. Chromium levels of this magnitude (1531 mg/kg) are generally not associated with solid wastes from coal utilization (Wewerka et al., 1976; Griffin et al., 1980; Roy et al., 1981). The observed Cr concentration may have been an artifact of the gasification process.

AQUEOUS SOLUBILITY OF THE SOLID WASTES

W. R. Roy, I. G. Krapac, and R. M. Schuller

Solubility studies by laboratory extraction or leaching procedures are currently considered the best available approach for assessing the potential environmental impact of leachates from solid wastes. At present, there are more than 50 different extraction methods cited in the literature, although many are essentially variations of the "shake-test." Some procedures were designed to simulate a particular disposal scenario and may not apply to more than one type of waste or technique for its disposal.

It would be expeditious if one extraction procedure could be developed to represent all possible disposal systems and waste materials. At present there is no universally accepted procedure. Moreover, such a universal procedure may be an unrealistic expectation.

One objective of this investigation was to generate aqueous extracts from selected coal utilization wastes using five extraction procedures that are most widely used by the scientific community or have been previously studied by the authors. The five extraction procedures that were used with each of the seven wastes included (1) the American Society for Testing and Materials Method-A (ASTM-A), (2) the ASTM-B method, (3) the U.S. EPA Extraction Procedure (EP), (4) a carbonic acid extraction procedure (CAP), and (5) a long-term equilibration procedure (LTE). Also, a large-volume generation (LVG) procedure was developed for the chronic bioassays.

ASTM-A and ASTM-B

The methods developed by the American Society for Testing and Materials (1979) are the Method-A (water shake extraction) and Method-B (acid shake extraction). These procedures involve (1) the shaking of a known weight of waste with either water of a specified composition or an acidic buffer solution, and (2) the separation of the aqueous phase for analysis. Both were designed to quickly obtain a solution for evaluating extractable materials from wastes.

The ASTM procedures recommend using the waste materials in the physical form in which they were disposed. For the seven wastes currently being studied, this recommendation was found to be impractical. The extreme variability of particle size (clay to boulder) would have made effective subsampling impossible. Thus, the samples were air dried and ground to pass a 9.53-mm (3/8-inch) standard sieve.

The ASTM-A procedure used is a short-term shake test and involved shaking a slurry composed of 700 ± 1 g of waste with a volume of distilled-deionized water equal to four times the weight of the sample. The slurries were formed in one-gallon, wide-mouth glass bottles and sealed with Teflon-lined plastic lids. Great effort was taken to avoid contact between the slurries and any surface that might cause sample contamination. Use of the Teflon liners prevented leaching of plastisizers from the plastic lids, which could have interfered with organic analysis of the samples. The slurries were shaken for 48 hours at 100 strokes per minute using a large capacity reciprocal shaker; then they were allowed to settle for one hour. Immediately after the bottles were opened, pH, oxidation-reduction potential (Eh), specific conductance, and alkalinity measurements were made. Next, the slurries were filtered through Whatman^R Qualitative I filter paper, followed by filtering through Millipore 0.45-µm pore size, cellulose acetate membrane filters. Subsamples were taken for cation, anion, and organic characterization.

The ASTM-B procedure was conducted identically to the ASTM-A procedure; however, a sodium acetate-acetic acid buffer solution (pH 3.5 ± 0.1) was the extraction media.

U.S. EPA Extraction Procedure

The EP was also intended to serve as a quick test for identifying wastes that are potential pollution hazards (U.S. EPA, 1980). The EP required grinding the solid sample to pass through a 9.53-mm (3/8-inch) standard sieve. Wide-mouth, one-gallon glass bottles with Teflon-lined lids, identical to those for the ASTM procedures, were used for the EP. Also, the samples were shaken at the same rate using the same shaker. A total of 200 g of solid waste and 3200 mL of distilled water were placed in the gallon bottles and shaken for 24 hours ± 0.5 hour. During the 24-hour period, the slurries were periodically removed from the shaker and pH adjusted to 5.0 ± 0.1 pH units with 0.5 N acetic acid. The pH was adjusted at 15-, 30-, and 60-minute intervals, with advancement to the next longest interval when the change in pH did not exceed 0.5 pH units. Adjustment continued for a total of 6 hours.

After the 24-hour period, the pH of the slurry was between 4.9 to 5.2. The total volume of acid added for pH adjustment could not exceed 4 mL per gram of solid waste. Adjustment was stopped when this volume was exceeded. At the end of the extraction period, the liquid and solid phases were separated. The volume of the liquid phase was then adjusted with distilled water so that its volume was 20 times that occupied by a quantity of water at 4°C, equal in weight to the initial solid sample. Sample filtration and preparation procedures were identical to those used for the ASTM methods.

Carbonic Acid Procedure

The last short-term shake procedure was a carbonic acid procedure (CAP). This method involved shaking 700 g of sample with 2800 mL of deionized water that had been purged with CO_2 gas. The CO_2-saturated water had a pH of 4.1. The extract was shaken for 48 hours, in a procedure similar to the ASTM methods.

The rationale for using CO_2-saturated water as an extractant was to simulate the solubilization of the waste in contact with soil solutions. Soils often contain higher partial pressures of CO_2 than the atmosphere above the soil, due to the aerobic metabolism of microorganisms and the decay of soil organic matter. Also, carbonic acid was used as an acidic extract since carbonic acid itself was not toxic to the organisms used in the bioassays. It would have beeen difficult to assess the biological toxicity of the extracts due to solutes if the aqueous medium was also toxic as was the sodium acetate used in ASTM-B.

Long-Term Equilibration Procedure

The long-term equilibration procedure (LTE) used in this study was developed by Griffin et al. (1980) for samples of coal solid wastes. A variation of this procedure was also used by Suloway et al. (1983) for coal fly ash samples. This procedure involved mixing 1700 g of sample with 17 L of deionized water in a 19-L reaction vessel made of Pyrex glass.

These mixtures were stirred for 30 minutes, twice a week, for 20 to 21 weeks in order to (as a first approximation) simulate slurry ponding environments. However, this extraction procedure is more specifically oriented toward generating a solution at chemical equilibrium with the solid wastes. This was done to produce a solution that may approximate the aqueous chemistry of pond effluent or leachate in settings where conditions of metastable chemical equilibrium develop. Samples of the extracts were periodically taken and analyzed over the 21 weeks to monitor the changes in chemical composition of the solutions.

Large-Volume Generation Procedure

A large-volume generation procedure (LVG) was designed to produce the large amount of acidic leachate that was initially anticipated for the chronic bioassays. Two 5678-L (1500 gal) Agro^R tanks were each filled with about 4.5 tons of coal refuse (fig. 3). Refuse from the OBG and WSNG sites was used in the LVG procedure. The selection of these two sites as source wastes was influenced by several factors including age, acute toxicity of extracts, and accessibility of large amounts of the material.

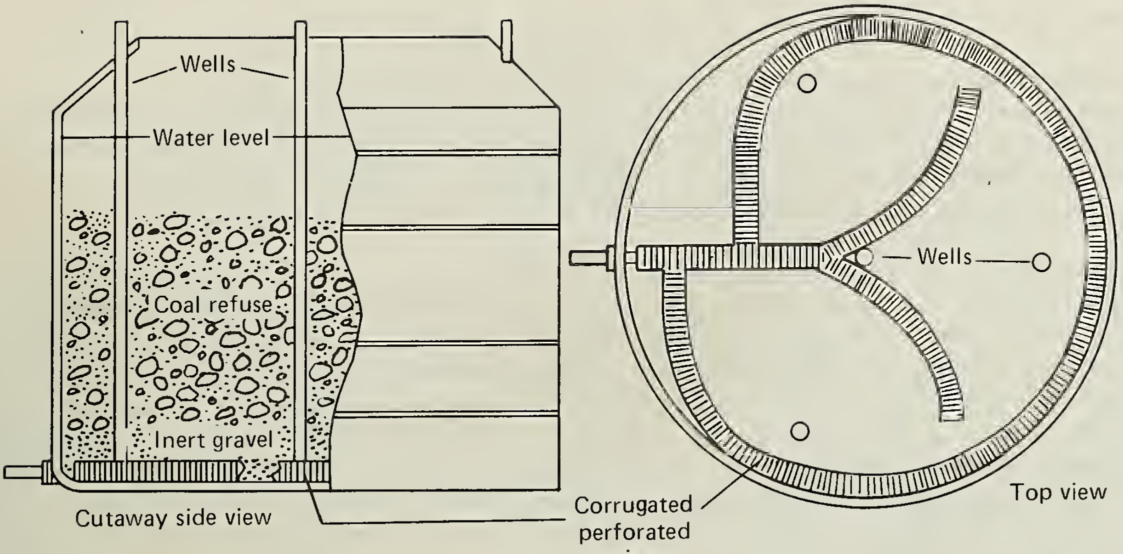


Figure 3
Cutaway side and top view of an Agro^R tank set up to generate a large volume of coal waste leachate.

A drainage system constructed of plastic corrugated and perforated pipe was installed in each tank (fig. 3), and four monitoring wells were evenly placed in each tank. The bottom of the tanks were each lined with chert gravel (the Meramac Gravel, a Mississippian-age gravel of relatively inert chemical composition) to ensure that the drainage system would remain permeable. Then each tank was filled with 6.53 kL (725 gal) of deionized water, completely saturating the solid waste (fig. 3). At the bottom of each tank a pump was connected to an outlet that was fed by the drainage system. The leachate was pumped at a rate of 454 L/hr (120 gal/hr) for 6 to 7 hours twice a week. The solution was recycled through the waste for 31 to 36 weeks, forming acidic leachates.[1]

The leachate was pumped through polyethylene tubing to a discharge point at the top of each tank, below the surface of the leachate. Samples of the leachate were periodically collected from the bottom drain, the surface of the solution, and the four monitoring wells to assess the compositional variability within the tanks.

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[1] By definition, solutions formed by shake procedures such as the ASTM-A and EP are extracts and not leachates, although the terms extracts and leachates are often used synonymously in the literature. Since the liquid phase was passed through the wastes in the LVGs, the acidic effluent was considered a true leachate.

Results

Representative subsamples from the seven wastes were used in the generation of extracts by the four short-term shake procedures (ASTM-A, ASTM-B, CAP, EP) and the LTE procedure. The results of the short-term extractions, long-term equilibrations, and the two large volume applications are given in Appendix A.

Although it is beyond the scope of this project, the triplicate data (not shown) for each waste for each of the short-term shake procedures did give some indication of the reproducibility of the methods. The limited amount of data does not permit statistical analysis and also, the reproducibility of the analytical methods used for each aqueous constituent would have to be evaluated and taken into account. In most cases, however, either the ranges of the triplicates fell within one standard deviation of the mean, or the means could be regarded as accurate to about 10 percent, depending on the constituent and analytical concentration.

There have been several studies aimed at evaluating the nature of extraction methods (Löwenbach, 1978). Gulledge and Webster (1979) analyzed the precision and reproducibility of the ASTM-A, the ASTM-B, and the U.S. EPA's TEP or toxicant extraction procedure. Epler et al. (1980) conducted an evaluation of the EP using a wide variety of waste materials. Studies by Cox et al. (1977) and Chu et al. (1976) indicated that small-scale laboratory shake tests could not accurately simulate the field leaching characteristics of coal storage piles. Davis et al. (1981) further supported this conclusion for both short-term shake tests and column leaching methods. They further suggested that the data collected from laboratory procedures would have to be normalized with relation to the size of the storage pile and the duration and intensity of rainfall events before the in-situ leachate quality could be predicted from the laboratory results. On the other hand, Wewerka et al. (1978) concluded that the initial results from column leaching studies using coal refuse from the Illinois Basin were very representative of in-situ leachates. This comparison was made with data from another study (Martin, 1974), however, not with leachates from the same piles from which the extracted material was collected. Further study of laboratory extraction procedures and their relationship to in-situ leachates is needed.

It is difficult to generalize solubility trends from evaluating the short-term procedures in this study. Differences in the amount solute per gram of sample by each waste may stem principally from differences in pH and dissolution kinetics. It is not unreasonable to expect that solution concentrations will increase with decreasing pH where many aqueous metal ions are stable in solution and where the solid sample may dissolve. Thus, the acidic extractions such as EP (pH 5.0), CAP (pH 4.1), and ASTM-B (pH 3.1) would be expected to progressively extract more (depending on final pH) than the non-acidic ASTM-A procedure. The

Table 8. Soluble constituents: range in pH and percent extracted from four types of solid wastes, using four short-term procedures.

	Coal cleaning refuse (WSNG, WSOG, OBG)	Mine spoil (DMNS, DMOS)	Slurry (WSSL)	KilnGas (KG)
pH	1.62- 4.27	5.07- 7.57	2.43- 3.88	5.00- 8.10
Extracted (%)				
Al	0.08- 3.7	-[1]	0.6 - 1.20	-[1]
Ca	22.4 -80.0	1.6 -21.2	31.6 -38.4	1.2 - 4.4
Fe	0.04-28.0	-[1]	10.8 -19.2	-[1]
Mg	22.0 -52.4	23.2 -70.0	42.0 -52.4	7.2 -84.0
Mn	10.7 -23.5	0.8 -28.2	36.0 -52.4	1.76- 6.64
Ni	9.2 -24.9	0.4 - 7.2	36.3 -52.2	4.72-12.0
SO_4	2.6 -31.3	6.92- 8.75	8.14-18.7	5.58- 9.45
Zn	2.7 -28.0	0.4 - 6.0	44.0 -53.2	0.32- 8.0

[1] all or most of the analytical concentrations were below detection limits.

ranges in pH and the percent extracted for selected elements for each of the four types of wastes by the four short-term procedures are presented in table 8. Magnesium appears to be the only constituent that was essentially soluble in all seven wastes by all four short-term procedures. The slurry sample released substantial amounts (greater than 35% of the matric concentration) of Mn, Ni, and Zn independent of the extraction procedure. These anomalously high solubilites warrant further study.

Unlike the short-term extracts, the long-term equilibrates (LTEs) permitted the study of changes in chemical composition with time. These LTEs were carried out for 20 to 21 weeks, at which time the experiments were terminated and the resulting extracts used in the toxicity characterizations. During the extraction interval, subsamples were periodically taken to monitor the chemical status of the solutions. The composition of the LTEs when the experiments were terminated is given in table 9.

The pHs of the slurry and refuse samples were acidic presumably as a result of soluble Al salts, exchangeable Al, and the oxidation of sulfide minerals; whereas Kilngas samples generated an alkaline solution. The pH of many fly-ash water systems is alkaline and has been attributed to the hydrolysis of matrix oxides (Talbot, Anderson, and Adren, 1978; Shannon and Fine, 1974; Elseewi, Page, and Grimm, 1980).

Table 9. Chemical analysis of the long-term equilibrates (LTEs) after 147 days of equilibration (concentrations in mg/L).

	WSNG	WSOG	OBG	WSSL	DMNS	DMOS	KG
pH	2.66	1.92	3.27	2.24	7.56	7.77	9.02
Eh (mv)[1]	+686	+695	+797	+855	+545	+536	+446
EC (dSm^{-1})	3.4	10.9	2.2	4.6	0.8	0.57	0.6
Al	41.9	69.8	64.5	27.4	<0.07	<0.07	<0.07
As	0.57	Si[2]	<0.14	0.58	<0.07	<0.07	<0.07
Ba	<0.001	0.006	0.004	<0.01	0.02	0.04	0.004
Be	0.03	0.01	0.006	0.02	<0.01	<0.01	<0.01
Ca	262	123	458	60.4	144	67.0	40.8
Cd	0.48	1.26	0.02	0.64	<0.01	<0.01	<0.01
Cl	6.5	2.90	15.8	<1.0	2.1	4.1	3.6
Cr	0.09	0.10	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	0.03	0.51	0.01	0.58	<0.01	<0.01	<0.01
F	-	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Fe	623	2552	0.21	971	<0.05	<0.05	<0.05
K	7.21	52.7	0.44	0.60	6.30	2.59	4.48
Mg	49.8	3.26	25.3	32.5	25.5	21.5	40.8
Mn	4.73	<0.05	2.35	6.42	0.15	<0.01	<0.01
Mo	<0.02	<0.02	<0.02	<0.02	<0.02	0.05	0.12
Na	<0.55	<0.55	3.60	<0.94	3.94	5.53	4.00
Ni	1.95	0.34	0.22	0.91	<0.05	<0.05	<0.05
Pb	<0.01	1.67	<0.01	0.01	<0.01	<0.01	<0.01
Sb	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Se	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	0.06
Si	143	103.1	51.2	55.2	3.45	7.25	7.06
Sn	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
SO_4	3042	8721	1383	3001	427	245	314
V	<0.02	<0.08	<0.06	<0.08	<0.06	<0.06	<0.06
Zn	5.43	Si[2]	4.59	2.99	0.33	0.11	0.42

[1] relative to a normal hydrogen electrode.

[2] concentration could not be determined due to spectral interferences (see Appendix B).

Roy and Griffin (1984) incorporated this conclusion into a qualitative model of fly ash-water interactions that accounted for changes in solution chemistry as a function of time. Analogous investigations with coal conversion wastes are lacking.

The pHs of the LTE extracts of the seven wastes (fig. 4) were essentilaly constant after two weeks of equilibration. However, pH may not be a conclusive parameter to evaluate the development of chemical equilibrium or a meta-stable equilibrium in aqueous systems. The concentrations of iron in the four acidic extracts (OBG, WSNG, WSOG, and WSSL) varied to a greater extent than the corresponding pHs (fig. 5). Solution Fe was still increasing in the LTE extract of WSSL after 20 weeks. Sulfate concentrations (fig. 6) appeared to reach steady state conditions after about a week in the alkaline solutions, but continued

Table 10. Total organic-carbon content (mg/L) of generated leachates.

	Method				
Sample	ASTM-A[1]	ASTM-B[2]	CAP[1]	EP[1]	LTE[1]
WSOG	4.42	2717	20.59	136.0	4.73
WSNG	4.43	2837	7.19	1.05	1.08
OBG	2.42	2685	2.18	1.16	0.78
WSSL	34.25	2838	6.63	202.0	1.41
DMOS	13.1	2802	5.34	--[3]	3.17
DMNS	0.87	2821	1.12	--[3]	1.76
KG	-0.45[3]	2767	0.17	43.0	1.17
Blank	3.95	2841	1.81	2.24	

[1] values corrected for blank.
[2] values not corrected for blank.
[3] value for sample less than blank.

to increase in the acidic systems until reaching steady state conditions after about 11 weeks. Aluminum concentrations became essentially invariant in the WSOG and OBG extracts after about 10 weeks (fig. 7); but aluminum continued to go into solution in the LTE extracts of WSNG and WSSL throughout the extraction interval. The amount of solution silicon in the WSNG and WSSL extracts (fig. 8) paralleled aluminum in that the silicon concentrations had not reached invariant levels but were steadily increasing. In contrast, the amount of soluble silicon in the alkaline samples decreased with time even though the pHs of these solutions remained alkaline. A plot of electrical conductance as a function of time (fig. 9) indicated that the acidic systems (OBG, WSOG, WSSL, and WSNG) had not reached equilibrium after 21 weeks; whereas the alkaline systems appeared to have reached steady state conditions with respect to the ionic composition of the solutions.

ORGANIC CHARACTERIZATION OF THE SOLID WASTES AND LABORATORY EXTRACTS

D. R. Dickerson and R. A. Griffin

The total organic carbon (TOC) content of the laboratory extracts generated by the ASTM-A, ASTM-B, carbonic acid procedure (CAP), U.S. EPA Extraction Procedure (EP), and long-term equilibration (LTE) was determined for each of the seven solid wastes (table 10). The extracts generated by the ASTM-A and LTE methods presented no particular problem for routine TOC analysis.

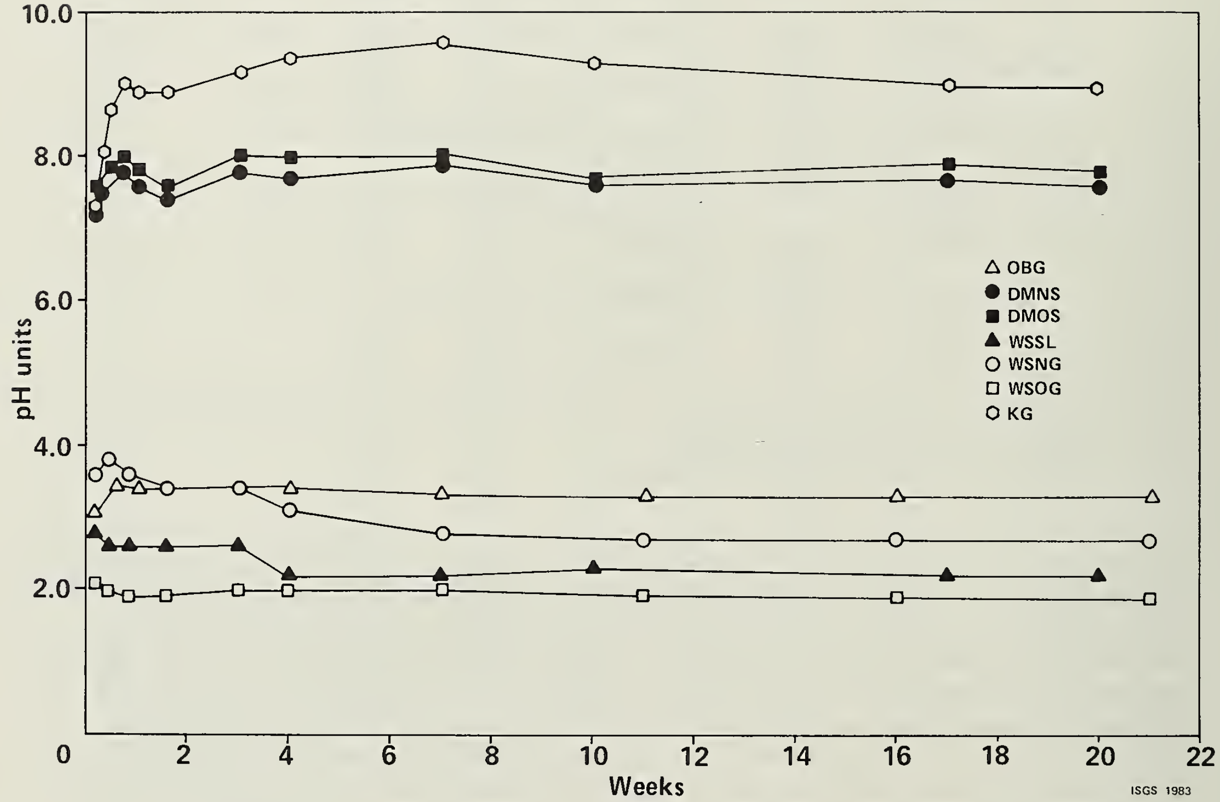


Figure 4
Changes in pH for all seven long-term equilibrations.

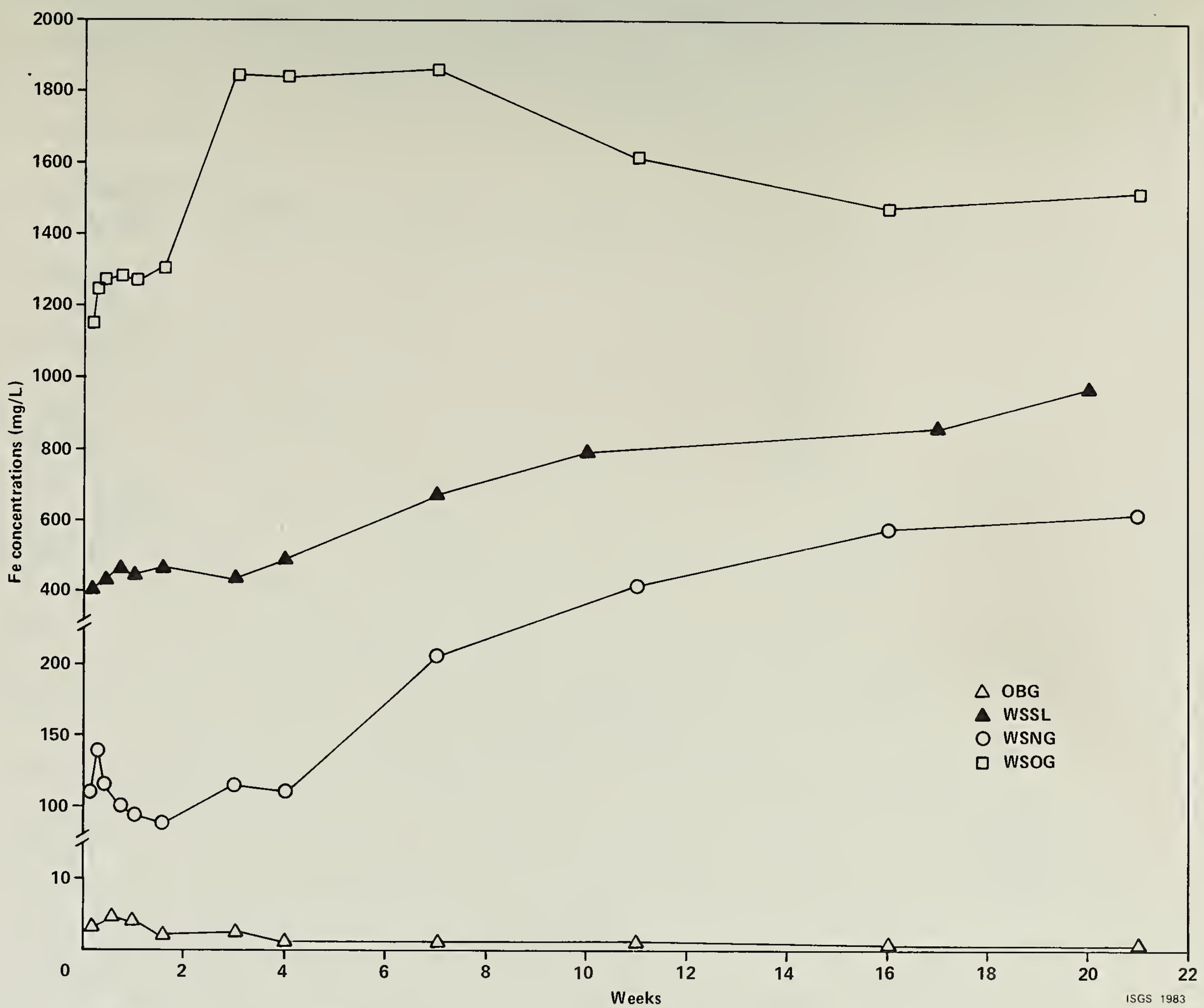


Figure 5
Changes in total Fe concentrations for the four acidic long-term equilibrations.

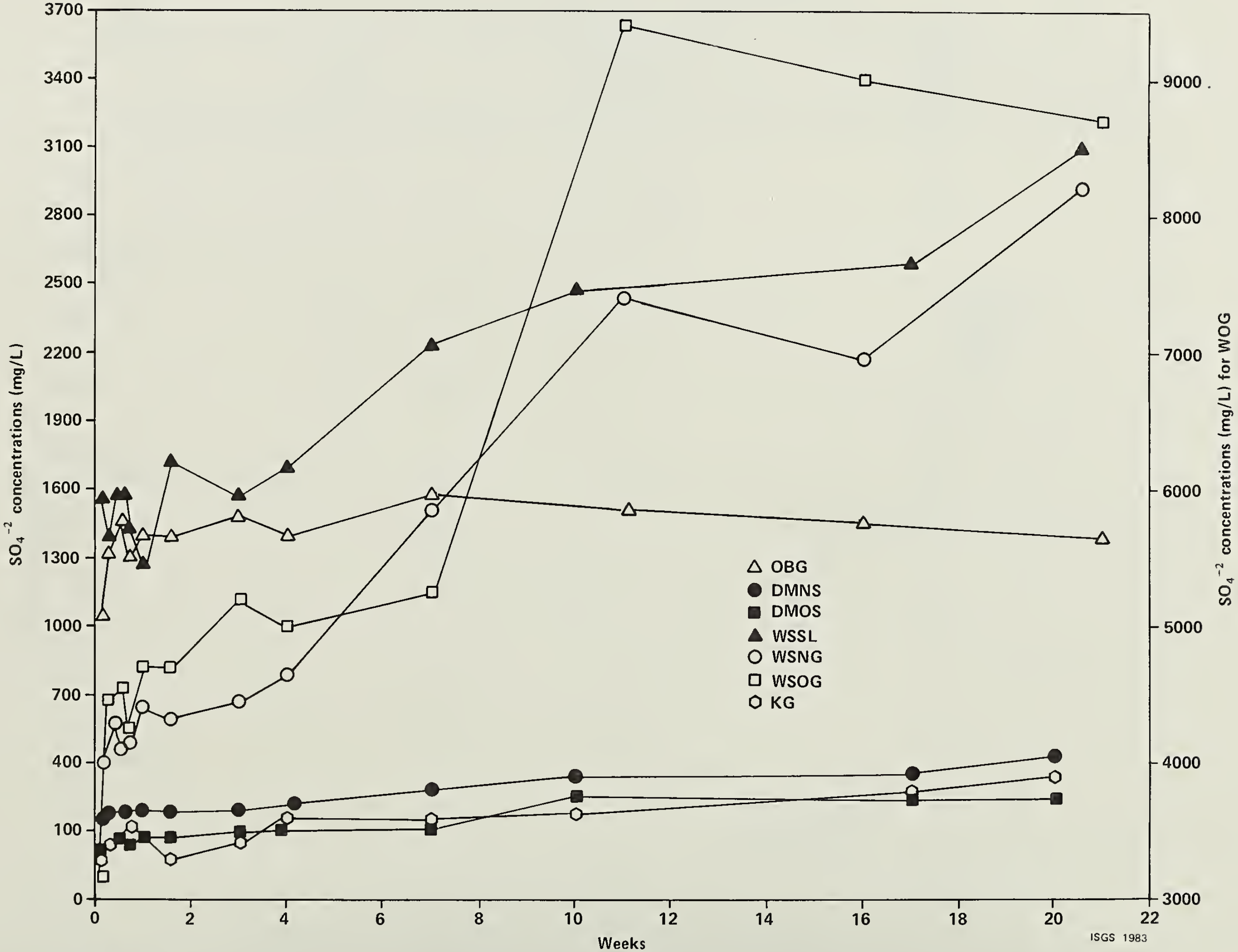
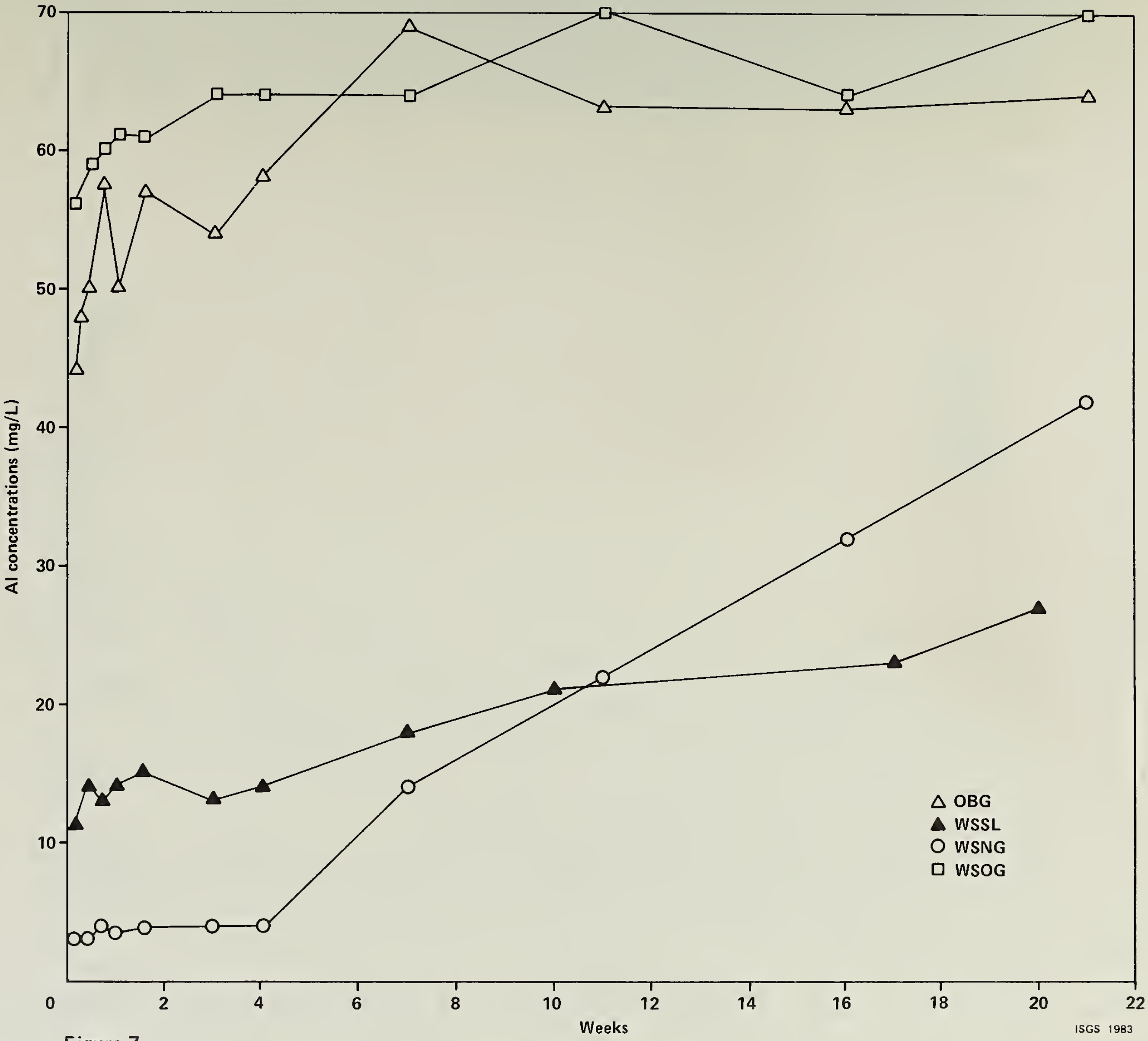
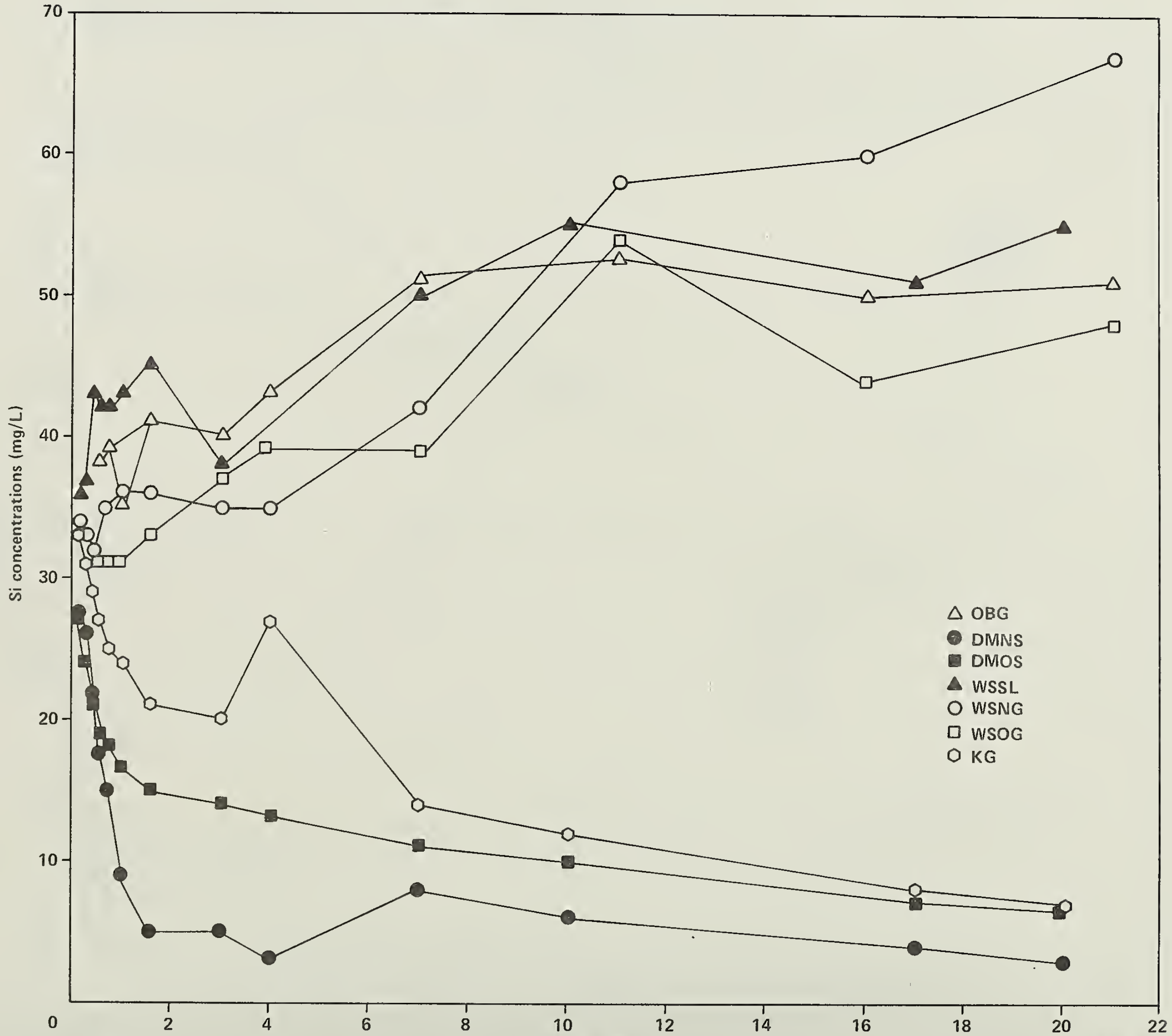


Figure 6
Changes in SO_4^{2-} concentrations for all seven long-term equilibrations.



ISGS 1983

Figure 7
Changes in Al concentrations for the acidic long-term equilibrations.



ISGS 1983

Figure 8
Changes in silica concentrations for all seven long-term equilibrations.

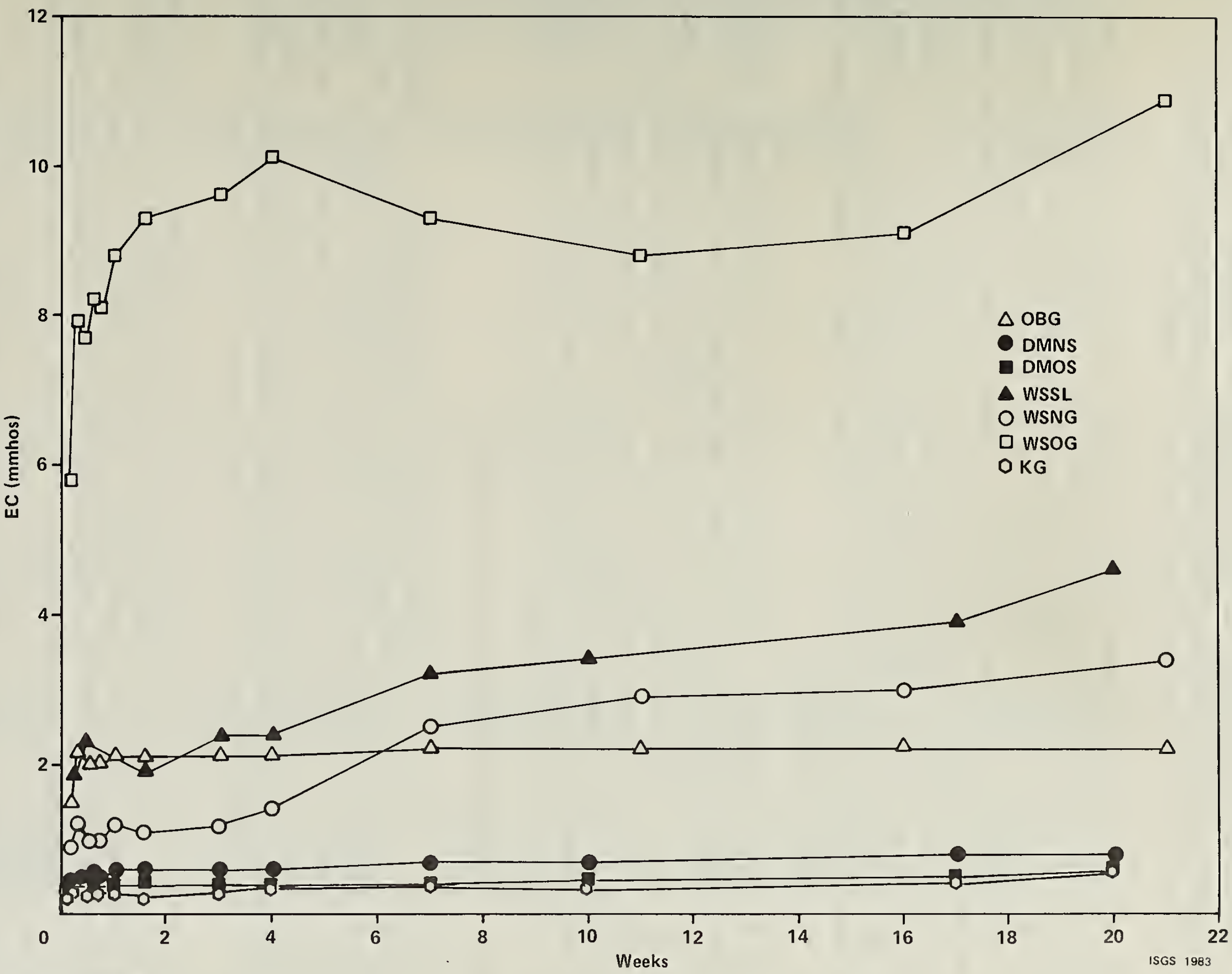


Figure 9
Changes in electrical conductance (EC) for all seven long-term equilibrations.

The CAP extracts were generated using water saturated with carbon dioxide, as previously discussed. To determine the TOC values for this set of solutions, it was necessary to first determine total carbon, then remove the inorganic carbon by an acid sparge, and follow with a second total carbon analysis. Thus, the second total carbon value is also the total organic-carbon value. The inorganic carbon is the difference between the first and second total carbon values.

The EP necessitated the addition of organic matter via the buffering solution. Theoretically, it should have been possible to determine the TOC value of the leached organic matter by correcting for the amount of acetic acid added. This would appear to be valid for the KG extract, where a reasonable TOC was obtained. However, the TOC values determined for the DMOS and DMNS extracts were only about one-half the theoretically expected value calculated for the added acetic acid. The TOC values obtained for the WSOG and WSSL extracts (no acetic acid added) would be expected to be similar in value to those obtained for the ASTM-A extracts. However, for poorly understood reasons, they are about an order of magnitude greater.

The ASTM-B extracts were also prepared using an acetate buffer system; thus the results should be interpreted as suggested for the EP extracts. The results, however, were somewhat erratic and showed the blank to have a slightly higher TOC value than any of the sample extracts. This may have been due in part to experimental error in attempting to find a small difference between two large numbers. It was more likely due to microbial utilization of some of the acetate buffer, which is an excellent substrate for microbial growth.

Methylene Chloride Extraction of Leachates

The results of the total chromatographable organics (TCO) and gravimetric analyses of the methylene chloride (CH_2Cl_2) extracts of the solutions generated from the solid wastes are given in table 11. The results indicate that the TCO levels in the liquid phases were below the detection limits of the recommended EPA method and calibration range. The GRAV analysis yielded only very small amounts of extracted organics (table 11), consistent with the low TOC content of the extracts.

The infrared (IR) spectra obtained for the CH_2Cl_2 extracts were all very similar, although five dissimilar extraction methods and seven different solid waste materials were used (fig. 10, for example). The main absorption bands were in the regions of 3400 cm^{-1} (H-bonded OH groups), 2900 cm^{-1} (aliphatic C-H stretching), 1735 cm^{-1} (C=O stretching of COOH, -COOR, or ketonic C-O), 1610 cm^{-1} (aromatic C=C and/or H-bonded C=O), 1510 cm^{-1} (aromatic C=C), 1460 cm^{-1} (C-H deformation of CH_2 or CH_3 groups), 1365 cm^{-1} (O-H deformation, CH_3 bending, or C-O stretching), 1250 cm^{-1} (C-O of ether linkage), 1100 cm^{-1} (very broad and unresolved due to a mix of C-O, C-O-H linkages of alcohols, esters, and ethers),

Table 11. Total chromatographable organics and gravimetric analysis of methylene chloride (CH_2Cl_2) extraction of coal waste extracts.

Sample	Extraction method	Extract (L)	CH_2Cl_2 (L)	TCO (mg/L)	Gravimetric (g/L)
	ASTM-A				
Blank		3	0.6	<0.022	0.0001
WSOG		5	1	<0.022	0.0007
WSSL		5	1	<0.022	0.0003
WSNG		5	1	<0.022	0.0004
DMNS		5	1	<0.022	0.0007
DMOS		5	1	<0.022	0.0008
KG		5	1	<0.022	0.0004
OBG		5	1	<0.022	0.0004
	ASTM-B				
Blank		2.5	0.5	<0.022	0.0003
WSOG		5	1	<0.022	0.0003
WSSL		5	1	<0.022	0.0003
WSNG		5	1	<0.022	0.0003
DMNS		5	1	<0.022	0.0005
DMOS		5	1	<0.022	0.0007
KG		5	1	<0.022	0.0004
OBG		5	1	<0.022	0.0005
	CAP				
Blank		2.5	0.5	<0.022	0.0006
WSOG		5	1	<0.022	0.0008
WSSL		5	1	<0.022	0.0005
WSNG		5	1	<0.022	0.0006
DMNS		5	1	<0.022	0.0005
DMOS		5	1	<0.022	0.0007
KG		5	1	<0.022	0.0004
OBG		5	1	<0.022	0.0005
	EP				
Blank		2.5	0.5	<0.022	0.0000
WSOG		5	1	<0.022	0.0003
WSSL		5	1	<0.022	0.0003
WSNG		5	1	<0.022	0.0003
DMNS		5	1	<0.022	0.0004
DMOS		5	1	<0.022	0.0006
KG		5	1	<0.022	0.0005
OBG		5	1	<0.022	0.0003
	LTE				
WSOG		2.5	0.5	<0.022	0.0006
WSSL		2.5	0.5	<0.022	0.0005
WSNG		2.5	0.5	<0.022	0.0005
DMNS		2.5	0.5	<0.022	0.0006
DMOS		2.5	0.5	<0.022	0.0004
KG		2.5	0.5	<0.022	0.0006
OBG		2.5	0.5	<0.022	0.0003

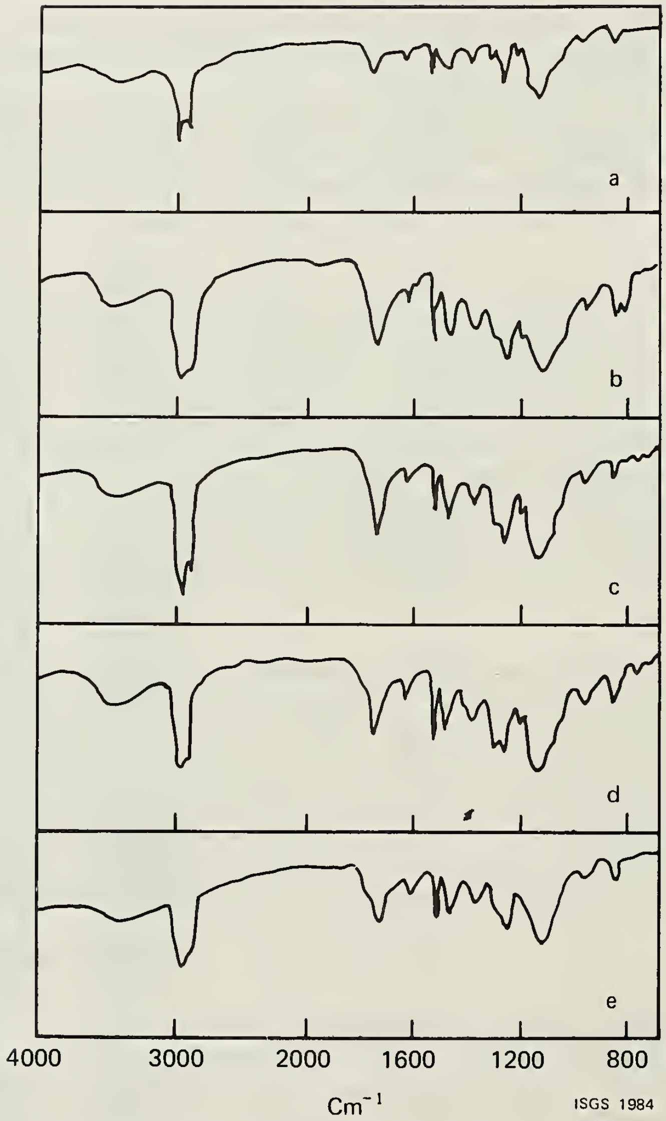


Figure 10
Infrared spectra of the organics extracted by CH_2Cl_2 from extracts of WSSL generated by these methods: (a) LTE, (b) ASTM-A, (c) EP, (d) CAP, (e) ASTM-B.

and 800 cm^{-1} (aromatic substitution). The general shape of the conglomerate of peaks in the 3600 cm^{-1} to 2700 cm^{-1} regions indicated the presence of carboxylic acid groups, which should also be reflected in the 1735 cm^{-1} peak. Peaks in the 1800 cm^{-1} to 1600 cm^{-1} range may also be enhanced by overtone and summation peaks.

From the functional groups indicated by the IR spectra, the organics contained in the extracts were of a highly polar nature, as expected in an aqueous extract. Since these organics are derived from coal solid wastes, it is likely that some may be included on the EPA priority

Table 12. Total chromatographable organics and gravimetric analysis of the methylene chloride (CH_2Cl_2) extraction of coal solid wastes. Values expressed for TCO are based on duplicate runs and computed from a standard curve. Error is estimated as ± 10%.

Solid	Sample (g)	CH_2Cl_2 (L)	TCO (mg/kg)	Gravimetric (g/kg)
WSNG	150g	1	287	20.5
WSOG	150g	1	239	22.3
OBG	75g[3]	1	153	7.23
WSSL	50g[3]	1	372	18.9
DMNS	150g	1	27	0.73
DMOS	150g	1	33	0.22
KG	130	1	NA[1]	0.91
Solvent		1	ND[2]	0.0001

[1] not analyzed.

[2] less than detectable limit.

[3] mixed with equal weight of organic free silica before extraction.

pollutant list. They do not, however, appear to be in concentrations considered to be hazardous, although long-term accumulation may increase concentrations to hazardous levels.

Characterization of Organics Extracted from the Coal Solid Wastes

The soxhlet extraction of coal solid wastes WSOG, WSNG, WSSL, and OBG presented considerable difficulty. These four solid wastes each contained more than 20 percent organic carbon (table 3), which apparently brought about the problem. Only a small part of the organic matter was soluble in CH_2Cl_2. The combination of another part of the organic material and the CH_2Cl_2 was a "tacky" semisolid. This latter combination tended to plug the extraction thimble and to render the bed of solid waste impervious to the bulk of the CH_2Cl_2. Hence, during each cycle the majority of the solvent flowed over rather than through the thimble of solid waste. Three wastes (KG, DMOS, and DMNS), which contained less than 5 percent organic carbon (table 12) presented none of the above extraction problems.

Table 13. Elemental sulfur content of the methylene chloride (CH_2Cl_2) extracts of the coal solid wastes.

Sample	Sulfur (wt %)	
WSOG	34.3	(elemental analysis)
WSNG	4.2	(elemental analysis)
OBG	≤ 50	(calculated by difference)
WSSL		Not determined
DMOS	≤ 20	(calculated by difference)
DMNS	≤ 17	(calculated by difference)
KG	≤ 91	(calculated by difference)

In an attempt to circumvent this problem, a smaller quantity, 50 to 75 g, of coal solid waste (OBG and WSSL) was diluted with an equal weight of organic-free silica sand before extraction. This method worked very well for the OBG solid waste (about 14% organic C), but less well for the WSSL waste (57% organic C). This fact indicates a need for a greater dilution (with an inert material) of wastes with a high organic carbon content.

The CH_2Cl_2 extracts of the solid wastes were found to contain varying amounts of elemental sulfur (table 13). The presence of elemental sulfur was confirmed by a melting point-mixed melting point technique. The free sulfur was removed by passing the extract in solution through a separate column of activated copper (Blumer, 1957) or by packing the lower 5 cm of the liquid chromatography (LC) column with activated copper. The quantity of elemental sulfur in the CH_2Cl_2 extracts of wastes DMOS, DMNS, OBG, and KG (table 13) were estimated from the percent extract recovered from the LC column. The sulfur content of the CH_2Cl_2 extracts of WSOG and WSNG (table 13) was determined by the ASTM method.

After extraction and, where necessary, filtration, analyses were continued as specified by the U.S. EPA (1978). The total chromatographable organic (TCO) was determined as prescribed in the Level I Manual; except that after many trials, it was determined that a 3 percent loading of SP 2100 (Supelco, Inc., Bellefante, PA) gave better resolution with the chromatograph than did either a 10 percent loading of SP 2100, or of OV-101 as recommended in the Level I procedures.

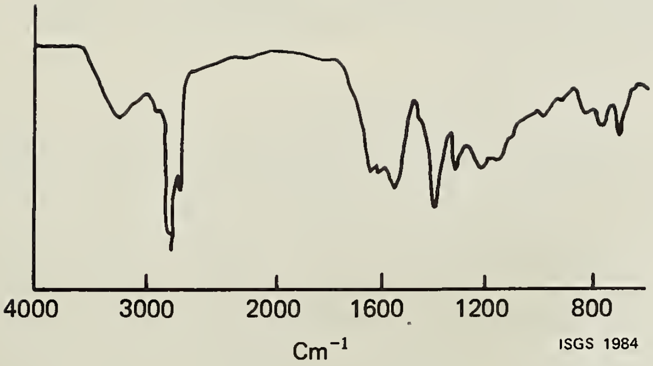


Figure 11
Infrared spectrum of the methylene chloride (CH_2Cl_2) extraction of the OBG solid waste.

The results of the TCO analyses are given as milligram TCO per kilogram of solid waste in table 12. Also shown in table 12 are the grams of organic matter extracted per kilogram of solid waste. Except for the DMNS and DMOS (which are low in total organic carbon), the total chromatographable organics are 2 percent or less of the total extracted organic (gravimetric in table 12).

The infrared spectra of the CH_2Cl_2 extracts of the coal solid wastes did not generally show well resolved peaks due to the myriad of organic compounds with varying functional groups that can be extracted from a coal waste. The infrared spectrum of the CH_2Cl_2 extract of the OBG solid waste is depicted in figure 11. This spectrum is much better resolved than the spectra of the other wastes. Discernible in this spectrum are peaks at 3350 cm^{-1} (H-bonded OH and/or NH_2), 3040-3020 cm^{-1} (naphthalene-type aromatic C-H) 2950, 2925 and 2860 cm^{-1} (aliphatic C-H stretching), 1800-1700 cm^{-1} (C=O stretching of COOH, -COOR, or ketonic C=O), 1600 and 1500 cm^{-1} (aromatic C=C), 1460 cm^{-1} (C-H deformation of CH_2 or CH_3 groups), 1356 cm^{-1} (CH_3 bending, or C-O stretching), 1300 cm^{-1} to 1000 cm^{-1} (unresolved C-O, C-O-H linkages of alcohols, esters and ethers), 870, 810 and 740 cm^{-1} (aromatic substitution). The CH_2Cl_2 extracts of the other solid wastes are generally similar, but peaks were less well resolved.

Liquid Chromatography of the Methylene Chloride (CH_2Cl_2) Extracts of the Coal Solid Wastes

A portion of the CH_2Cl_2 extractable matter from each solid waste was separated further into seven fractions, using liquid column chromatography (LC). Each fraction was analyzed for TCO content and total gravimetric organic content.

Table 14. Gravimetric (GRAV) analysis of liquid chromatography fractions from methylene chloride (CH_2Cl_2) extracts of the solid wastes.

Fraction (mg)	WSNG	WSOG	OBG	WSSL	DMNS	DMOS	KG
Total LC	92.7	100.2	102.9	100.0	112.0	90.4	41.2
LC 1	22.5	48.7	1.7	9.1	9.6	17.0	24.7
LC 2	4.4	13.6	1.0	5.5	1.8	2.4	3.6
LC 3	15.4	14.4	14.7	16.0	22.9	15.3	5.3
LC 4	16.4	7.8	8.6	7.9	15.8	5.1	2.2
LC 5	16.4	10.0	9.4	10.2	1.8	4.3	
LC 6	25.4	16.8	34.4	24.1	26.5	17.5	5.9
LC 7	1.8	1.2	11.4	4.9	14.0	10.4	1.0
Recovered	102.3	112.5	80.2	77.7	92.3	72.0	42.7
Recovered (%)	110.4	112.3	77.2	77.7	82.4	79.6	103.6

The LC analyses were run on samples WSNG and WSOG before discovering that the extract was contaminated with large quantities of "free" sulfur. Some unforeseen effects of this sulfur may partially account for the greater than 100 percent recovery of the CH_2Cl_2 extractable matter from the LC columns for these two samples. For these two samples, the TCO quantity was below the detectable limits of the method and calibration range used.

The free sulfur was removed from the WSSL, DMNS, DMOS, and OBG by passing the dissolved fraction over freshly prepared, reduced copper powder as part of the LC column packing. The recovery of material from the LC column for these samples was less than the amount loaded onto the column. The greater part of the amount lost was assumed to be due to the amount of free sulfur removed by the activated copper in the packing.

The TCO was determined on all fractions from the LC runs. In only the first three LC fractions of each set was there any determined value for TCO that was above the lower detection limits of the calibration curve. Since these values, although positive, are so close to the lower detection limit, their validity must be questioned at this time. Also, the amount of TCO is relatively insignificant compared to the gravimetric values (table 14). In general, fractions 1, 3, and 6 contained the greater portions of the total LC fractions: LC fraction 1 contained the paraffins, fraction 3 the large aromatics, and fraction 6 the polar compounds. These organic classes are in keeping with the type of solid waste being extracted.

For all practical purposes, the organics found in the wastes originated from coal, and were quite similar. Thus, the LC analyses of only two wastes, OBG and KG, will be discussed. Also, it can be assumed that most compounds found in one waste will be found in the other wastes, although concentrations may vary. This was confirmed by the infrared (IR) spectra of the CH_2Cl_2 extracts, typified by the spectrum of the CH_2Cl_2 extract of the OBG solid waste (fig. 11). A gross interpretation of the spectrum indicated the presence of aliphatic (saturated and unsaturated), aromatic, and polyaromatic compounds with hydroxyl, amino, and carbonyl (ester, ketone, aldehyde, and carboxyl) functional groups.

The IR spectra of the LC fractions of the CH_2Cl_2 extract of the OBG solid waste are presented in figure 12. They show a direct increase in complexity as the eluting solvent was made more polar. It would appear that the majority of the polar compounds contain oxygen functional groups. Peaks for nitrogen functional groups were no doubt present (shifting to slightly longer wavelength of the broad peak at 3450 cm^{-1} to 3320 cm^{-1}) but tended to be masked by other peaks.

The spectrum of LC-1 had a weak peak at 3050 cm^{-1}, indicating unsaturation rather than aromatic compounds. Also the peak at 1268 cm^{-1} and at 745 cm^{-1} may indicate t-butyl- and/or iso-propyl-groups. The latter may also be due to an aliphatic chain $-(CH)_n-$, where n equals at least 4. The spectrum of the LC-6 fraction was almost identical to the spectrum of the total CH_2Cl_2 extract (fig. 12). Approximately 40 percent of the total extract was found in LC-6.

The CH_2Cl_2 extract of KG was subjected to analysis by high performance liquid chromatography (HPLC) and GC/MS. No nitrogen compounds were identified by gas chromatography/mass spectrometry (GC/MS) in the CH_2Cl_2 extract of the Kilngas residue. The HPLC analysis of the total extractable organics from KG was obtained with toluene as an internal marker. There were two prominent peaks, one preceding and another following toluene. The former is due to polar compounds such as phenols, and the latter to di- and polyaromatic hydrocarbons. The HPLC analysis of LC-2 showed essentially all the compounds eluting later than toluene in the range expected for naphthalene and alkyl substituted naphthalenes. The HPLC analysis of LC-3 showed two small peaks eluting ahead of toluene, indicating few or no polar compounds in this fraction; the larger concentration of peaks were in the elution range of napthalenes and phenanthrenes. Fractions LC-4 and LC-5 were combined before HPLC analysis; the chromatogram showed the majority of compounds eluting later than toluene. Since there was a relatively strong hydroxyl peak in the IR spectrum, one would expect these later peaks to be due to larger molecular weight phenols ($\geqslant$200) and to aryl esters, as well as

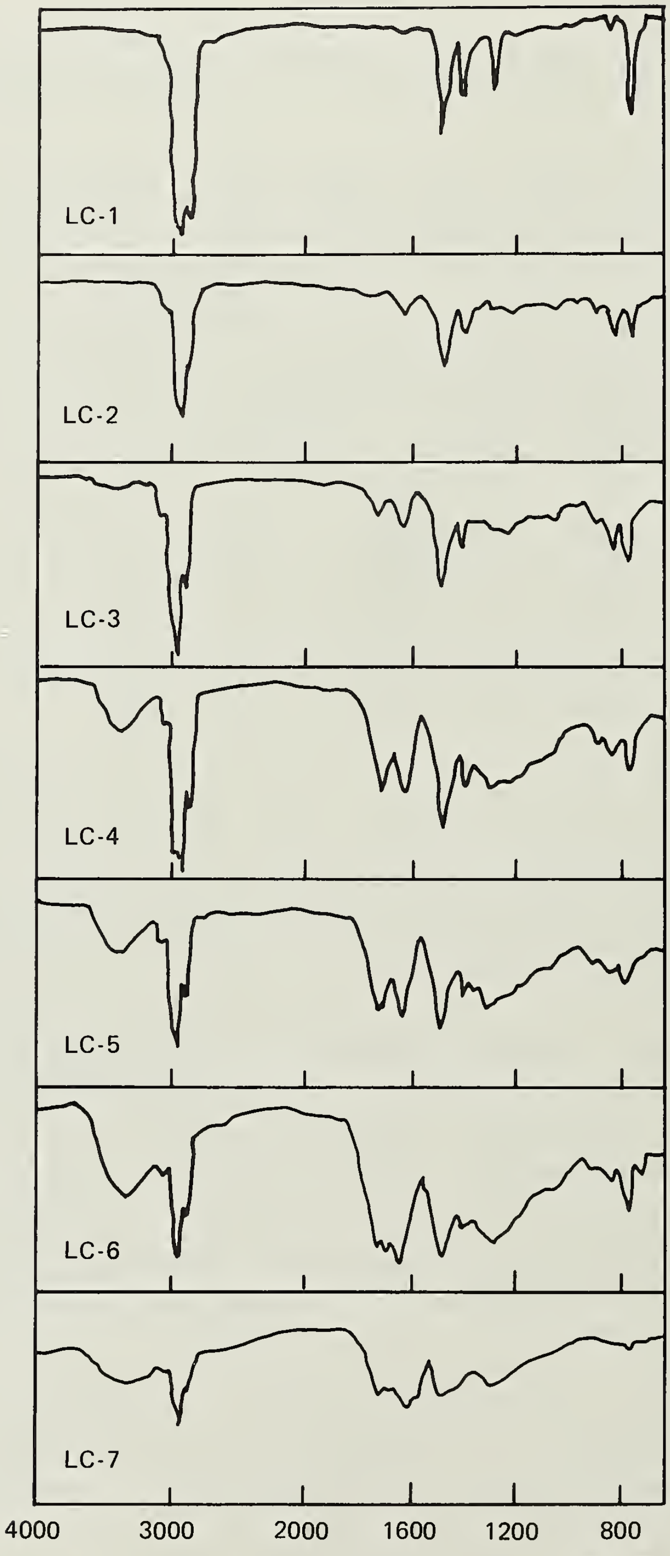


Figure 12
Infrared spectra of the liquid chromatography fractions of the methylene chloride (CH_2Cl_2) extract of OBG.

polyaromatics. The HPLC analysis of LC-6 showed a large envelope of early eluting peaks, as expected for highly polar compounds.

Table 15 lists all compounds tentatively identified by GC/MS in the LC fractions of the CH_2Cl_2 extract of KG. The chromatogram of LC-1 (KG) showed a large envelope of both unresolved and well resolved peaks eluting in the C_{15} to C_{21} range; the major compounds identified were mostly n-paraffins (table 15). In the GC/MS chromatogram of LC-2, 36 peaks were analyzed; 19 were identified as alkyl substituted benzenes and biphenyls, or acenaphthene. In the GC/MS analysis of fraction ration LC-3, 14 major peaks were identified as fused ring aromatics with alkyl substitutions in most cases. The combined fractions LC-4 and LC-5 were not analyzed by GC/MS. Eleven of the compounds in fraction LC-6 were identified by GC/MS: five of the peaks were due to phthalate esters; two thiophenols were also identified.

The aqueous extracts from the spoil banks and solid waste may contain some phenolic and other compounds (polyaromatic hydrocarbons) that are on the EPA priority pollutant list. None were identified directly in the organics extracted from the aqueous extract; however, they were identified in the organics extracted from the solid coal wastes by an organic solvent. By inference, those that are water soluble should be found in the aqueous leachate. Since not more than 0.8 mg/L total organic material was extracted, and since the TOC was also the same order of magnitude, it seems doubtful that any single priority pollutant would be present in the extracts in a quantity that would be hazardous.

EQUILIBRIUM SOLUBILITY MODELING OF LABORATORY EXTRACTS AND FIELD LEACHATES FROM COAL SOLID WASTES

W. R. Roy and R. A. Griffin

The application of chemical equilibrium models can lead to useful insights into the chemistry of aqueous systems such as coal waste leachates or acid mine drainage. However, the results of such modeling must be interpreted cautiously. The lack of uniform experimental procedures can result in discrepancies in reported values for solubility constants for some mineral phases, making the determination of equilibrium controls difficult. Moreover, pure mineral compounds in distilled water are often used to determine thermodynamic parameters that might not be representative of these compounds when they are associated with complex multicomponent materials such as coal solid wastes. However, solubility models do provide a first approximation for understanding these complex solutions.

As a step towards understanding coal-waste aqueous systems, the chemical analyses of laboratory extracts and field leachate samples were treated by the thermodynamic model WATEQ2. This program uses equilibrium constants to estimate the theoretical activities of aqueous species and

Table 15. Compounds identified by gas chromatography/mass spectrometry (GC/MS) in the liquid chromatography fractions (LC) of the methylene chloride (CH_2Cl_2) extract of the Kilngas residue.

Fraction LC-1

C_8-Cyclohexane
C_{16}-Branched Alkane
n-Hexadecane
C_{10}-Cyclohexane
n-Heptadecane
Pristane (branched $C_{19}H_{40}$)
n-Octadecane
n-Nondecane
n-Eicosane
n-Heneicosane
n-Docosane
n-Tricosane
n-Tetracosane
n-Pentacosane
n-Hexacosane

Fraction LC-2

2 C_1-Naphthalenes
5 C_2-Naphthalenes
C_4-tetrahydronaphthalene
5 C_3-Naphthalenes
8 C_4-Naphthalenes
C_7-Benzene
2 Acenaphthenes or C_2-Biphenyls
2 C_3-Acenaphthenes or C_3-Biphenyls
Acenaphthene or C_4-Biphenyl

Fraction LC-3

2 C_2-Naphthalenes
3 C_3-Naphthalenes
3 C_4-Naphthalenes
Phenathrene
C_2-Phenanthrene
C_3-Phenanthrene
Acenaphthene or C_4-Biphenyl
C_1-Phenanthrene
C_4-Phenanthrene

Fraction LC-6

2,6-Di-t-butyl benzoquinone
C_5-Thiophenol
C_6-Thiophenol
Diethyl phthalate
Methoxyanthracene
Substituted cychohexane
2,4-*bis*-(1-Methyl butyl) phenol
Phthalate (di-isobutyl?)
Phthalate (di-butyl?)
Phthalate (diethyl hexyl?)
Phthalate

calculates the saturation indicies for 309 minerals. The theory of WATEQ2 and its computer implementation are discussed elsewhere (Truesdell and Jones, 1974; Plummer et al., 1976; Ball et al., 1979).

As previously discussed, subsamples of the LTE extracts were taken with time and analyzed. The analytical data from these samples were submitted to the WATEQ2 program. The results of the WATEQ2 program were subsequently used as an aid in constructing solubility diagrams. In addition to the LTEs, the chemical composition of the ASTM-A extracts was also modeled using the final composition at the end of the 48-hour extraction interval.

To provide a limited basis for comparison, field samples of waste streams at the Old Ben No. 9 mine site and the Will Scarlett mine site were also collected and modeled using WATEQ2. Two samples were collected from the OBG site: one was a sample of acid mine drainage, flowing from the base of a refuse pile into a manmade basin. The second sample was taken from the ponded effluent. The chemical analysis of these samples (table 16) indicated that they were acidic and contained high concentrations of Fe, Al, and SO_4^{2-}. The solid waste sample used to generate the laboratory extracts was taken at the same location from the refuse pile that generated the two effluent samples.

Three field samples were taken at the Will Scarlett mine. One sample was of effluent from a ridge of coal cleaning refuse where the WSOG sample was collected. A second sample was collected from a slurry lagoon downstream from an active discharge pipe. The high water-to-waste ratio may account for the low iron and SO_4^{2-} concentrations (table 16) observed at the site, relative to the other samples. A sample of stagnant effluent from an inactive slurry basin (table 16) contained 68 times more iron in solution than the current basin and a lower pH. The inactive lagoon was estimated to be about 40 years old; the differences in chemical composition between the two sites may be a function of the water-to-waste ratios, parent waste variation, and duration of pyrite dissolution and acid formation. Neither site corresponds to the slurry sample taken for the laboratory extracts (WSSL) because that particular basin was dry at the time of sampling. All three slurry deposits were in proximity to one another.

While the samples suggest the composition and variability of waste streams in the field, they were not collected in an attempt to characterize acid mine drainage in the two mining areas--an objective well beyond the scope of this investigation. These samples were collected to evaluate the solubility relations predicted by WATEQ2 for laboratory extracts, relative to some actual field waste systems.

The acidic solutions, both laboratory and field samples, tended to be in equilibrium with a calcium sulfate ($CaSO_4$) phase (fig. 13). This may be true for most solutions influenced by acidic coal solid wastes. Griffin et al. (1980) found that three Lurgi ashes, a medium-temperature char, and a liquefaction residue were generally in equilibrium with gypsum ($CaSO_4 \cdot 2H_2O$); whereas a fly ash sample (an acid Fersic by the classification system of Roy and Griffin, 1982) and a high-sulfur, cleaning refuse sample were in equilibrium with gypsum in long-term equilibrated extracts. Roy and Griffin (1984) also noted that both acidic and alkaline coal fly ash extracts from Illinois Basin coals equilibrated with anhydrite in long-term studies. The LTE of WSNG was

Table 16. Chemical composition of acid mine drainage from the Old Ben No. 9 mine (OBG), and the Will Scarlett mine (concentrations in mg/L).

	OBG pond	OBG acid mine drainage	WSOG acid mine drainage	WSSL discharge	WSSL inactive
pH	2.83	3.25	2.40	3.35	2.63
Eh (mV)[1]	+686	+493	+735	+747	+643
EC (dSm^{-1})	3.88	13.98	5.79	2.55	9.01
Al	190	1120	272	43.9	664
As	<0.07	<0.07	<0.07	<0.07	<0.07
B	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	0.009	<0.002	<0.002	<0.002	0.02
Be	0.02	<0.001	<0.001	<0.001	0.01
Ca	288	445	218	695	471
Cd	0.17	<0.03	<0.03	0.07	0.04
Cr	0.03	<0.02	<0.02	<0.02	<0.02
Cu	<0.02	<0.02	0.45	0.34	<0.02
Fe (total)	669	5625	1440	24.1	1645
K	2.63	<1.54	3.74	5.80	<1.54
Mg	94.5	502	54.0	96.8	694
Mn	12.9	65.3	14.0	12.3	184
Mo	<0.01	<0.01	<0.01	<0.01	<0.01
Na	65.0	260	<1.79	20.2	<1.79
Ni	0.55	<0.01	<0.01	<0.01	5.05
Pb	<0.08	<0.08	<0.08	<0.08	<0.08
Sb	<0.03	<0.03	<0.03	<0.03	<0.03
Se	<0.08	<0.08	<0.08	<0.08	<0.08
Si	12.4	33.8	8.33	7.49	38.6
Sn	0.04	<0.04	<0.04	<0.04	<0.04
V	0.06	<0.06	<0.06	<0.06	<0.06
Zn	11.5	56.0	7.25	4.61	37.7
SO_4^{2-}	3841	20,397	6194	1805	12,183

[1] relative to a standard hydrogen electrode.

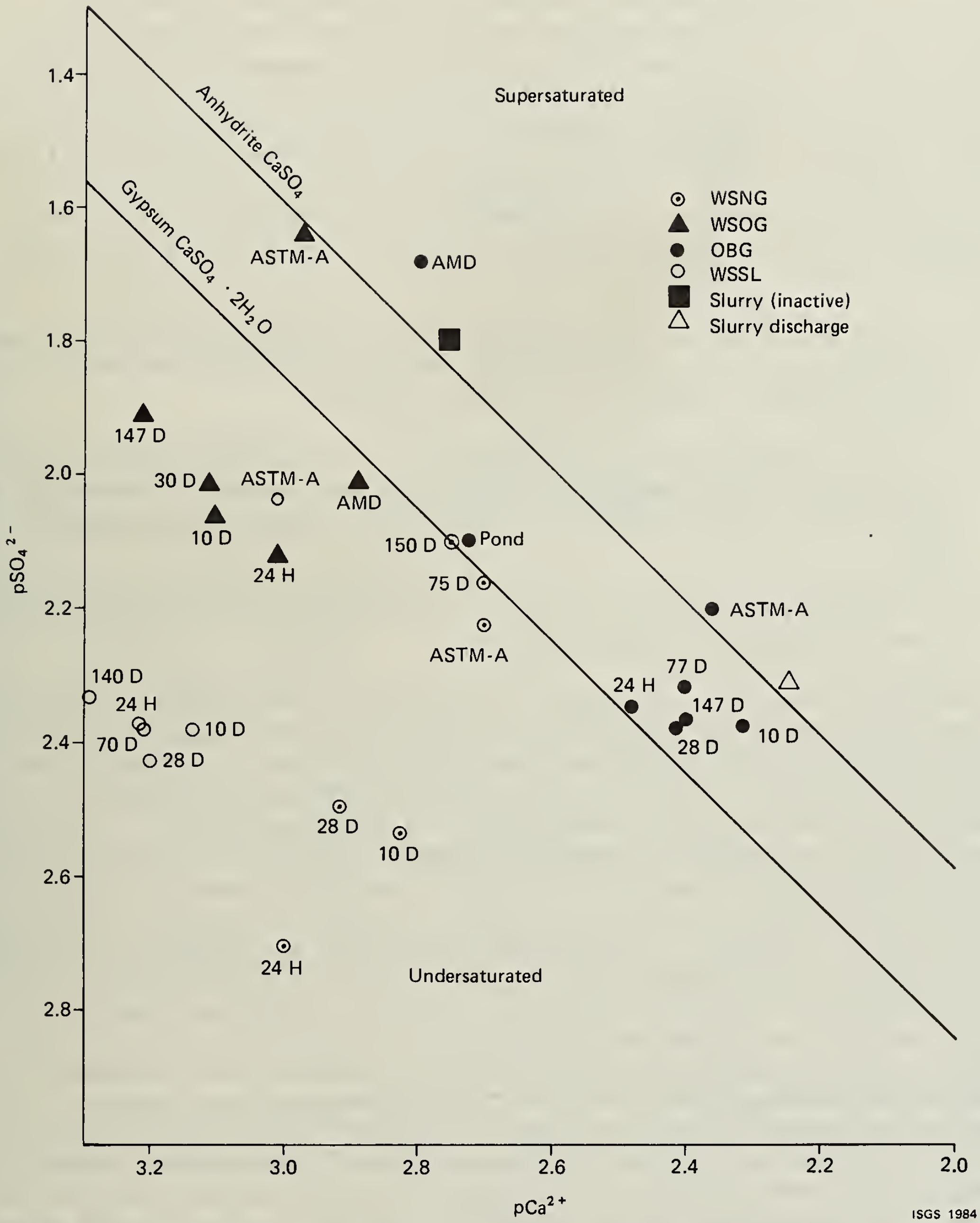


Figure 13
Calcium sulfate equilibria of the acidic laboratory extracts (ASTM-A and the long-term equilibration) and field leachate samples.

initially undersaturated with respect to gypsum, then came into equilibrium with this solid phase after 75 days. The ASTM-A extract of WSNG also was in near equilibrium with gypsum, suggesting that even though the two laboratory extraction methods are dissimilar with respect to slurry concentrations and extraction intervals, the solubility of gypsum exerted a dominant influence over calcium and sulfate activities in both systems. The LTE of the WSOG sample appeared to be undersaturated with respect to both gypsum and anhydrite during the entire extraction interval. This situation could be interpreted in three different ways:

(1) The solution had not reached thermodynamic equilibrium, thus, the liquid phase would have equilibrated with a $CaSO_4$ phase if the equilibration interval had been extended.

(2) The solution was in equilibrium, but a calcium sulfate phase more soluble than gypsum or anhydrite was present. Anhydrite was detected in all of the seven waste samples with the exception of KG.

(3) The WATEQ2 model could not yield accurate data due to the high ionic strength of the solution.

The last interpretation is made in reference to the method by which this thermodynamic model calculated the activities of Ca^{2+} and SO_4^{2-}. The activity coefficient of a given constituent may be calculated using equations resulting from the Debye-Hückel Limiting Law (table 17). For dilute solutions (an ionic strength of <0.005), equation 1 is used. For solutions having an ionic strength greater than 0.01, the more reliable Extended Debye-Hückel equation 2 is used, which attempts to take into account the hydrated sizes of the ions in addition to the electrostatic interactions. However, this equation begins to break down in solutions containing ionic strengths greater than 0.1. The Davies equation (table 17, equations 5 and 6) can be used to estimate individual activity coefficients in solutions having an ionic strength up to 0.5 M. The WATEQ2 program uses both the Debye-Hückel equations and a Davies-Extended Debye-Hückel equation (7); but the single ion activity coefficients of Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, CO_3^{2-}, and HCO_3^- are always calculated by the Extended Debye-Hückel relationship, since WATEQ2 was written primarily for natural surface waters. Several acidic, high-salt extracts and leachates had ionic strengths in excess of 0.1; thus solubility interpretations involving Ca^{2+} and SO_4^{2-} must be made with extreme caution.

The ASTM-A extract of WSOG appeared to be in equilibrium with anhydrite (fig. 13), which was found to be present by X-ray diffraction. Unlike the laboratory extracts, the field sample of acidic effluent at the WSOG site was in equilibrium with gypsum.

The LTE extracts of WSSL were undersaturated with respect to $CaSO_4$ phases during the equilibration interval. The ionic strength of the

Table 17. The Debye-Hückel Limiting Law and variants.

Debye-Hückel Limiting Law (1923) $\log \gamma i = -Azi^2\sqrt{I}$ (1)

Extended Debye-Hückel (1923-1934) $\log \gamma i = \frac{-Azi^2\sqrt{I}}{1 + Ba\sqrt{I}}$ (2)

Güntelberg (1926) $\log \gamma i = \frac{-Azi^2\sqrt{I}}{1 + \sqrt{I}} + bI$ (3)

Guggenheim and Schindler (1934) $\log \gamma i = \frac{-Azi^2\sqrt{I}}{1 + \sqrt{I}}$ (4)

Davies (1938) $\log \gamma i = -Azi^2 \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2\ I$ (5)

Davies (1962) $\log \gamma i = -Azi^2 \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30\ I$ (6)

Robinson and Stokes (1959) $\log \gamma i = \frac{-Azi^2\sqrt{I}}{1 + Ba\sqrt{I}} + bI$ (7)

γi = activity coefficient of ion i

I = ionic strength

Zi = charge of ion i

A = $1.82 \times 10^6 (\varepsilon T)^{-3/2}$ (where ε = dielectric constant)

a = radius of hydrated ion

B = $\frac{50.2916 \times 10^8 d^{\frac{1}{2}}}{(\varepsilon T)^{3/2}\ \text{moles}^{\frac{1}{2}}} (10^3 gH_2O)^{\frac{1}{2}}$ (d = density of water)

b = empirical constant

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liquid phase never exceeded 0.05; therefore, the model was not suspect. The electrical conductance of this system was still gradually increasing when the experiment was terminated, suggesting non-equilibrium conditions. The LTE extracts of OBG clustered between the gypsum-anhydrite boundaries and compared favorably to the pond sample taken at the OBG site. The sample of the acidic effluent (AMD) flowing from the OBG refuse pile appeared to be supersaturated with respect to both $CaSO_4$ phases; but again the high ionic strength (0.3866) rendered the activities calculated for Ca^{2+} and SO_4^{2-} suspect due to the limitations of the Extended Debye-Hückel equation. The short-term ASTM-A extract of the solid waste collected from the OBG site appeared to be in equilibrium with anhydrite, which was detected in the solid sample by X-ray diffraction. The laboratory extracts of the slurry sample were also undersaturated with respect to gypsum; however, they were in equilibrium with anhydrite, as were both the field slurry samples. The stagnant effluent (WSSL-inactive) sample had an ionic strength of 0.2313, making the calculated activities open to question.

The LTE and ASTM-A extracts of the non-acidic materials, DMNS, DMOS, and KG, were all undersaturated with respect to $CaSO_4$ (fig. 14). The LTE of DMNS was also initially undersaturated with respect to calcite (fig. 15), like the ASTM-A extract, but later appeared to approach equilibrium. The LTE of DMOS was initially near equilibrium with calcite. Later it appeared to have equilibrated with aragonite, a metastable phase of calcite, some time after 75 days. The aragonite, which could have formed as a precipitate at the expense of the dissolution of calcite, eventually became the dominant $CaCO_3$ phase controlling the aqueous solubility of Ca^{2+}. Note that the ASTM-A extract was in equilibrium with calcite, possibly as a result of the comparatively short solubilization interval. The LTE of the Kilngas waste sample appeared to be near equilibrium with calcite, then became supersaturated with respect to both $CaCO_3$ phases. Neither carbonate or sulfate minerals were identified in the KG sample, and the solubility of Ca^{2+} did not seem to be controlled by either in long-term experiments. The mineral phases influencing the solubility of Ca^{2+} in KG are unknown but may possibly be CaO forms in the high-temperature residue and/or calcium feldspars. Carbonate phases may exercise some influence in short-term experiments as suggested by the ASTM-A extract of KG.

The possible sources of solution silicon and aluminum in the laboratory extracts and field leachates include the feldspars and clay minerals detected by X-ray diffraction (table 2). However, all the acidic LTE, ASTM-A, and field samples were undersaturated with respect to albite ($Na\{AlSi_3O_8\}$), anorthite ($Ca\{Al_2Si_2O_8\}$), adularia ($K\{AlSi_3O_8\}$), analcime ($Na\{AlSi_2O_6\}$), halloysite ($Al_4\{Si_4O_{10}\}\{OH\}_8$), illite (≈ K, Mg, aluminosilicate hydroxide), kaolinite ($Al_2Si_2O_5\{OH\}_4$), and montmorillonite (≈ Ca, Na, K, Mg, Fe, aluminosilicate hydroxide). The LTE and ASTM-A extracts of non-acidic materials, DMNS, DMOS, and KG, were also undersaturated with all the feldspar minerals considered by WATEQ2. The LTEs of the alkaline samples were initially supersaturated with respect to illite, montmorillonite, and kaolinite, then became either slightly supersaturated or undersaturated with respect to these clay minerals during the latter part of the equilibration period.

Figure 16 shows the silicon dioxide equilibria. All the samples fell within the range of silicon solubilities expected from either quartz, cryptocrystalline SiO_2, or amorphous SiO_2. To simplify the illustration, only the final subsamples of the LTEs are shown. Since quartz is a dominant mineral in the wastes, it can be expected that quartz would exert a major control on the solubility of H_4SiO_4. This relationship may have been partially obscured because glass containers were used in all of the extraction studies, shifting the silicon equilibria towards the less stable, amorphous SiO_2 boundaries. However, all the field leachate samples also fell along the amorphous SiO_2 boundaries.

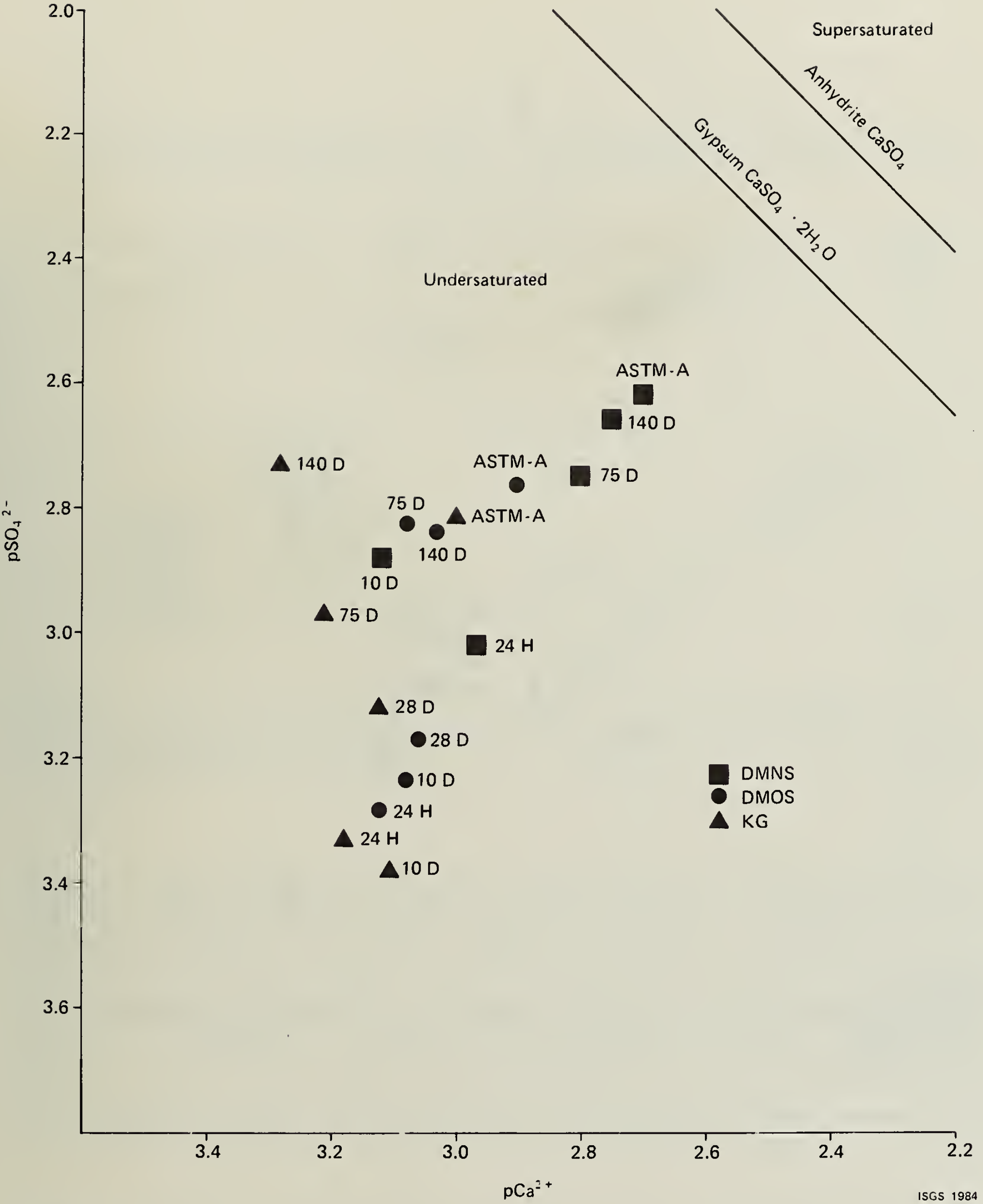


Figure 14
Calcium sulfate equilibria of the non-acidic laboratory extracts (ASTM-A and the long-term equilibrations).

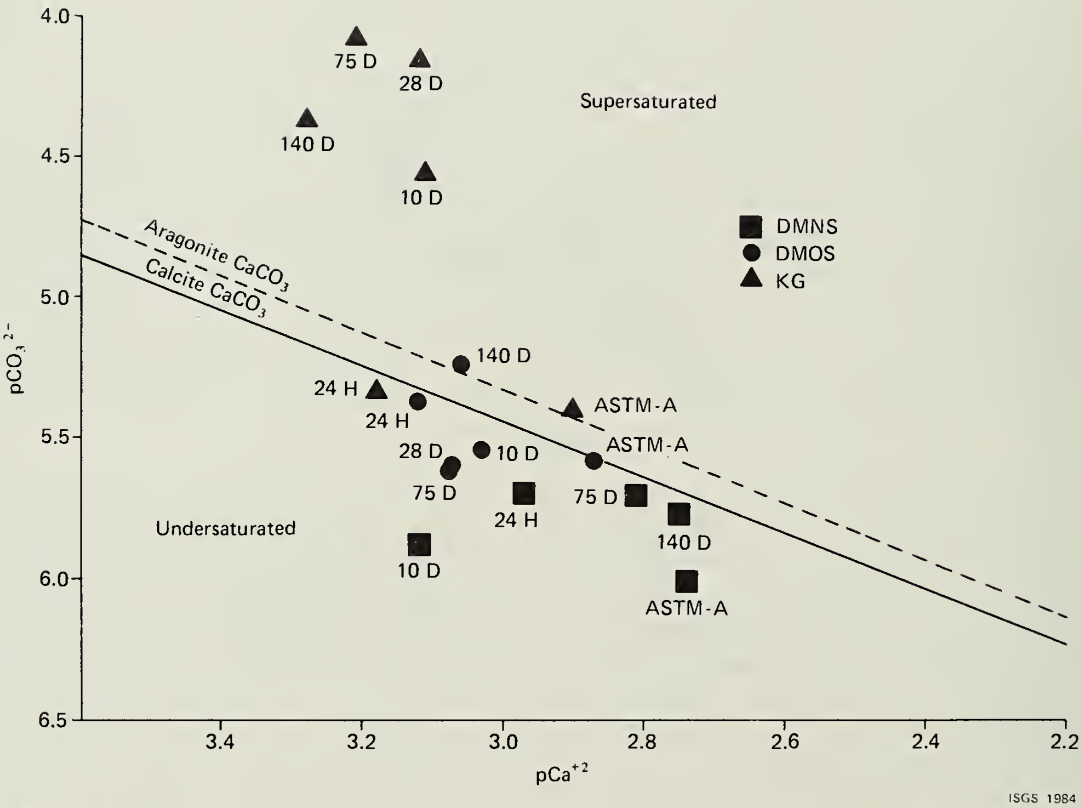
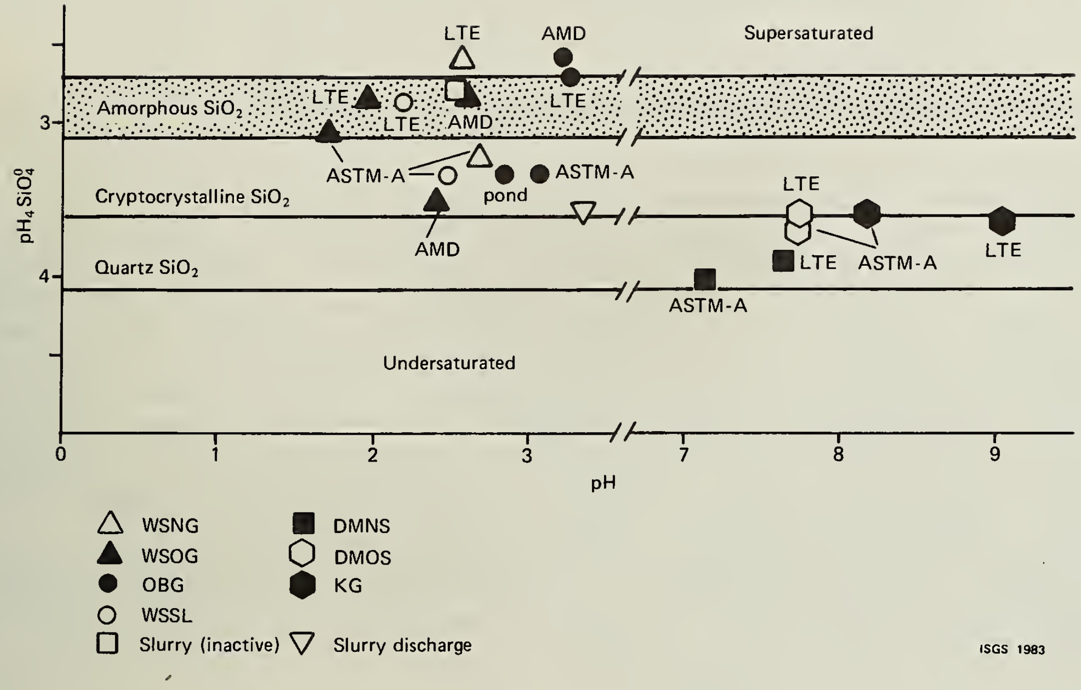


Figure 15
Calcium carbonate equilibria of the non-acidic laboratory extracts (ASTM-A and the long-term equilibrations).



ISGS 1983

Figure 16
Silicon dioxide equilibria of the laboratory extracts (ASTM-A and the long-term equilibrations) of all seven wastes and the field leachate samples.

Griffin et al. (1980) found that Al^{3+} activities in long-term extracts of coal solid wastes were dominated by metastable aluminum phases, (amorphous $Al(OH)_3$ and $AlOOH$) rather than aluminum containing minerals present in the solid wastes. In this study, all the acidic systems were undersaturated with respect to these particular metastable phases. In general, it appeared that most of the laboratory extracts and field samples were not in equilbrium with any known metastable phases of aluminum. Two field leachate samples (WSOG acid mine drainage and WSSL-discharge) were near equilibrium with a metastable $AlOHSO_4$ phase. The Al equilibria for these acidic systems remains unresolved.

Iron equilibria are often shown by constructing stability relationships of iron species by either holding Fe^{2+} or Fe^{3+} concentrations constant and varying Eh and pH. Griffin et al. (1980) constructed iron oxide and sulfide stability fields where Fe^{2+} aqueous = $10^{-6}M$ and total sulfur = $10^{-3}M$. Solution iron concentrations in this study varied from 0.21 mg/L Fe to 5625 mg/L Fe; thus, the classical iron-stability diagram based on an arbitrarily chosen Fe^{2+} or Fe^{3+} concentration may have little meaning.

Figure 17 shows the Fe^{3+} equilibria as a function of pH. While the ratio of Fe^{3+} to Fe^{2+} is influenced by Eh, the equilibrium Fe^{3+} activity of any iron mineral is independent of Eh. Solubility relationships may be derived by comparing the Fe^{3+} activities calculated by WATEQ2.

In general, the laboratory extracts and field leachates tended to plot near the maghemite boundary, a metastable phase of hematite (fig. 17). Consequently, all the aqueous samples were undersaturated with respect to amorphous ferric hydroxide. This disagrees with the work of Nordstrom et al. (1979) for field samples of acid mine waters in the West Shasta Mining District in northern California. Their work, also based on WATEQ2 modeling, indicated that iron equilibrium was influenced by $Fe(OH)_3$. Griffin et al. (1980) concluded that amorphous $Fe(OH)_3$ was probably a control on iron concentrations in some extracts; whereas maghemite solubility controls were operative in other systems. Reaction kinetics may partially explain some of the discrepancies between the studies. Note that while the LTE of OBG was initially in equilibrium with maghemite, the extract equilibrium shifted to magnetite after 77 days. A magnetite boundary is shown for $pFe^{2+} = 7.35$, the pFe^{2+} activity after 147 days, since the equilibria of magnetite is Eh dependent. The LTE of WSNG was near equilibrium with $Fe(OH)_3$ after 28 days of equilibration, then appeared to have equilibrated with maghemite.

The kinetic hypothesis was not confirmed, due to the fact that all the short-term ASTM-A extracts were near equilibrium with maghemite within only 48 hours; whereas the LTEs took months to reach the same phase boundary. The $Fe(OH)_3$-Fe_2O_3 question remains unresolved.

The field sample from the WSOG site was near equilibrium with maghemite; but both the ASTM-A and LTE extract of the solid sample taken from the WSOG site appeared to be approaching equilibrium with the more stable goethite (FeOOH) phase. Natrojarosite, $NaFe(SO_4)_2(OH)_6$, was identified in OBG by X-ray diffraction (table 2). The LTE of OBG may have also equilibrated with natrojarosite (S.I. = -0.221)[1]; while most of the other systems, including the field samples from the OBG area, were supersaturated with respect to natrojarosite. Nordstrom et al.(1979) also found that field samples of acid mine drainage were supersaturated with respect to natrojarosite. Coquimbite ($Fe_2(SO_4)_3 \cdot 9H_2O$) was detected by Mössbauer in WSNG and WSOG, but there are no thermodynamic data available on this iron sulfate phase, which precludes solubiity analysis.

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[1] S.I. or saturation indice is defined as the log of the ratio of the experimentally derived activity product to the equilibrium activity product.

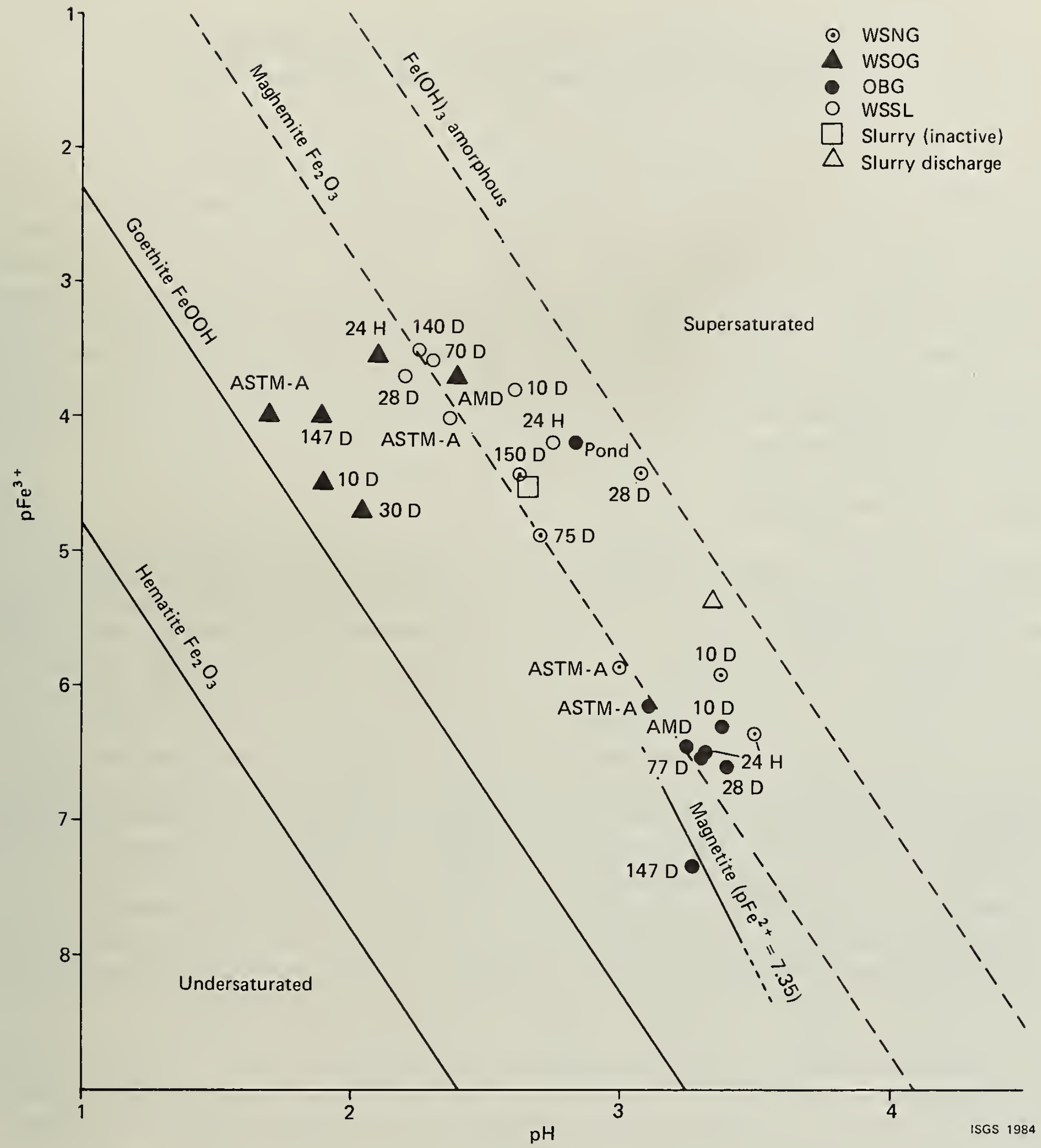

Figure 17
Fe^{3+} solubility equilibria as a function of pH for the acidic laboratory extracts (ASTM-A and the long-term equilibrations) and the field leachates.

ACUTE STATIC BIOASSAYS OF EXTRACTS GENERATED FROM SAMPLES OF COAL SOLID WASTES

T. M. Skelly and J. J. Suloway

The major objective of the biological investigations was to determine whether extracts generated from samples of spoil banks (DMNS and DMOS), coal cleaning wastes (WSNG, WSOG, WSSL, and OBG), and a coal conversion waste (KG)--were acutely toxic to aquatic organisms. Other objectives included determining (1) the relative toxicities of the extracts that were shown to be acutely toxic, (2) the relative sensitivities of the four test organisms to the toxic extracts, and (3) any significant correlations between the acute toxicity of a solution and its physicochemical composition.

Methods and Materials

The LTE extracts, upon attaining steady-state concentrations, were decanted from the carboys and filtered through 0.45μ pore-size Millipore membranes. Samples were taken for physicochemical characterization and the remaining supernatant solution was used as the undiluted extract in the bioassays.

Each extract sample was assayed for acute toxicity with four species of aquatic organisms: green sunfish (*Lepomis cyanellus*), fathead minnow (*Pimephales promelas*), a crustacean (*Daphnia magna*), and a snail (*Physa anatina*). The acute toxicity tests were divided into two phases: a screening procedure and the LC-50 determination (the concentration that is lethal for 50% of the organisms). During the screening procedure, the test organisms were exposed to the extract diluted with soft reconstituted water (U.S. EPA, 1975). Graphic probit analysis (Litchfield and Wilcoxon, 1949) was used to determine the LC-50 values.

In acute bioassay tests, 1- to 2-day old *Daphnia*, 1- to 2-day old minnow fry, juvenile snails (shell length = 5.0 ± 0.5 mm), and yoke-sac green sunfish fry were exposed to the extracts in an environmental chamber maintained at a constant temperature ($20^{\circ} \pm 1^{\circ}C$) for a constant photoperiod (16L-8D). For each bioassay, 10 test organisms were placed in a 250-mL beaker containing 200 mL "full-strength" extract, diluted extract, or soft reconstituted water (control). Bioassays were conducted in quadruplicate for each of the four organisms; pH, temperature, and dissolved oxygen concentrations were monitored. Mortality data were collected at 24, 48, 72, and 96 hours, except for the *Daphnia* tests, which were terminated after 48 hours. After 96 hours, snails that appeared to be dead were placed in reconstituted water and checked within 24 hours to confirm mortality assessments. The test organisms were not fed and test solutions were not aerated during the bioassays. Four control solutions, each containing 200 mL of soft reconstituted water and 10 test organisms, were tested with each set of bioassays.

Regression analysis was used to determine differences between the mortality data sets by testing the hypothesis that the slopes of the lines describing each of the two data sets were equal and that the y-intercepts were also equal. Mortality data were regressed on physicochemical data using the General Linear Model procedure of the Statistical Analysis System. The IBM 4341 computer at the University of Illinois was used to perform the analyses.

Results

Acute toxicity of extracts. The screening procedures were conducted to determine if the undiluted extracts were acutely toxic. The mean initial pH of the control solutions (n = 108) was 7.91 ± 0.18 (range = 7.69 to 8.85), and the mean final pH was 7.72 ± 0.14 (range = 7.30 to 7.91). The mean initial dissolved oxygen was 7.94 ± 0.37 mg/L (range = 6.93 to 8.86 mg/L), and the mean final dissolved oxygen concentration was 8.56 ± 0.64 mg/L (range = 6.67 to 9.90 mg/L). The mean hardness, as determined by titration, was 29.6 ± 5.37 mg/L $CaCO_3$ (range = 15 to 35 mg/L). The mean survival of the test organisms exposed to the control solutions was 95.0, 97.0, 98.2 and 98.1 percent for Daphnia, Physa, Lepomis and Pimephales, respectively.

To examine the relationship between pH and mortality, static bioassays were conducted with reconstituted water ranging in pH from 3.0 to 9.0. The results of the screening procedures and the pH experiments are depicted in figure 18. The results of the pH experiments were similar to those of the screening procedures. The undiluted extracts and reconstituted water produced total mortality when the pH was below 6.0, 5.6, 5.4, and 3.5 for Pimephales, Daphnia, Lepomis and Physa. Undiluted extracts generated from the spoil bank (DMNS and DMOS) and Kilngas (KG) samples were not acutely toxic (mortality <5%) to Daphnia, Pimephales, Lepomis and Physa (fig. 18). Undiluted extracts produced by the LTE procedure from the coal cleaning waste samples (WSOG, WSNG, WSSL, and OBG) were acutely toxic to all four test organisms. These solutions were very acidic (pH <3.5). Some extracts produced total mortality within minutes after bioassays were initiated. All four test organisms were also sensitive to acidic reconstituted water. The order of sensitivity to low pH was Pimephales > Daphnia > Lepomis> Physa.

The LTE solutions from the refuse pile samples (WSNG, WSOG and OBG) and the slurry sample (WSSL) were evaluated for their relative acute toxicities in the LC-50 determinations. In addition, results from these bioassays were used to estimate both the amount of dilution necessary to eliminate mortality during an acute bioassay and the relative sensitivities of the test organisms to the LTE solutions. The LC-50 value is reported as the volume of solution/100 mL necessary to cause 50 percent mortality.

The LC-50 values, their 95-percent confidence intervals, and dilutions necessary to eliminate mortality are listed in table 18. The pH values

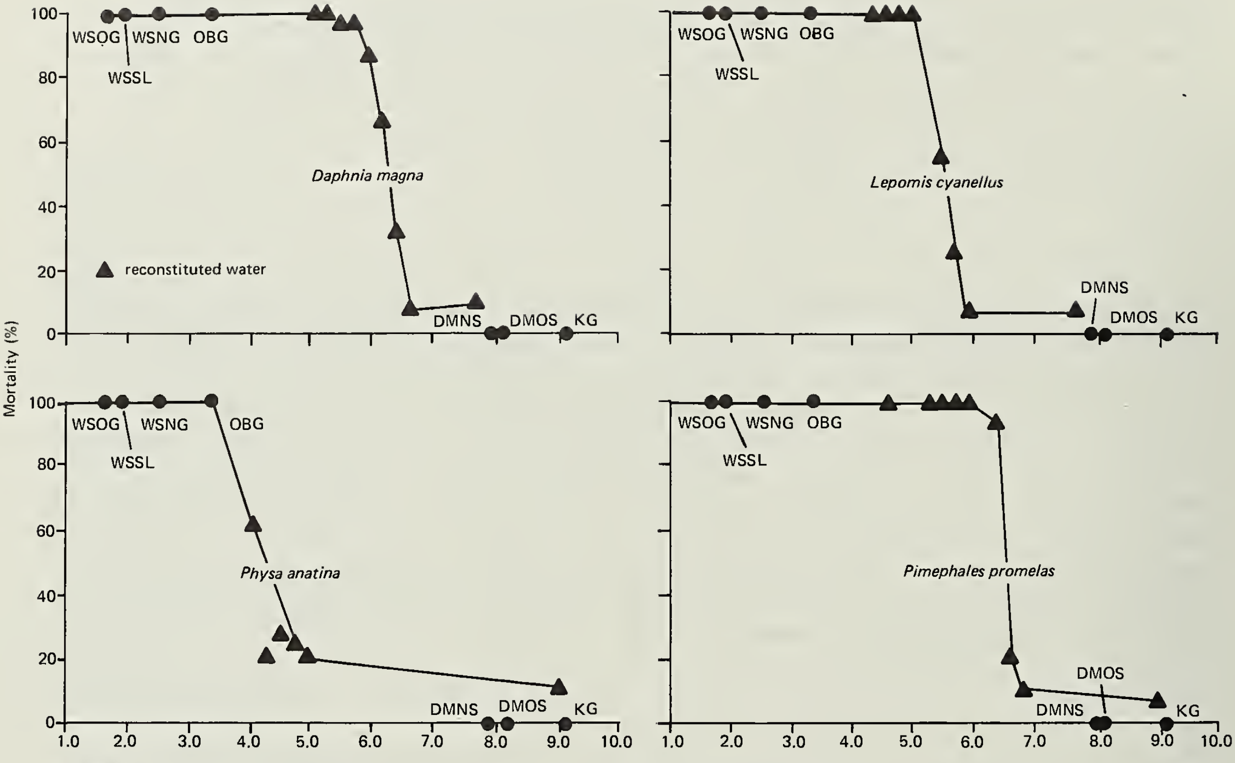

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Figure 18
Percent mortality of *Daphnia magna, Lepomis cyanellus, Physa anatina* and *Pimephales promelas* resulting from exposure to undiluted extracts generated from seven coal solid wastes and buffered solutions of reconstituted water.

listed are for the undiluted extracts before dilution with soft reconstituted water. There is an inverse relationship between toxicity and the LC-50 value: an increase in the toxicity corresponds to a decrease in the LC-50 value. Of the four extracts shown to be acutely toxic by the screening procedures, WSOG produced the most toxic solution and OBG produced the least toxic solution. The extracts produced from WSNG, WSOG,and WSSL were very toxic to all four test organisms: LC-50 values were less than 3.0 mL/100 mL.

Generally, acidic extracts or leachates (pH <5.0) were acutely toxic. With increasing acidity, there was an increase in the toxicity, a decrease in the LC-50 value, and an increase in the amount of dilution necessary to eliminate mortality. The most toxic extract, WSOG, required a dilution of 1:1000 in order for Daphnia to survive a 48-hour bioassay. All four acutely toxic extracts required a relatively large amount of dilution (>1:20) to eliminate mortality, except for OBG when tested with Physa. Physa was the most tolerant test organism with the highest relative LC-50 values and the lowest dilutions to eliminate mortality. Daphnia and Pimephales were the most sensititve to the toxic effects of the extracts (fig. 19). As the concentration of the extract increased, there was an increase in mortality for all species. The

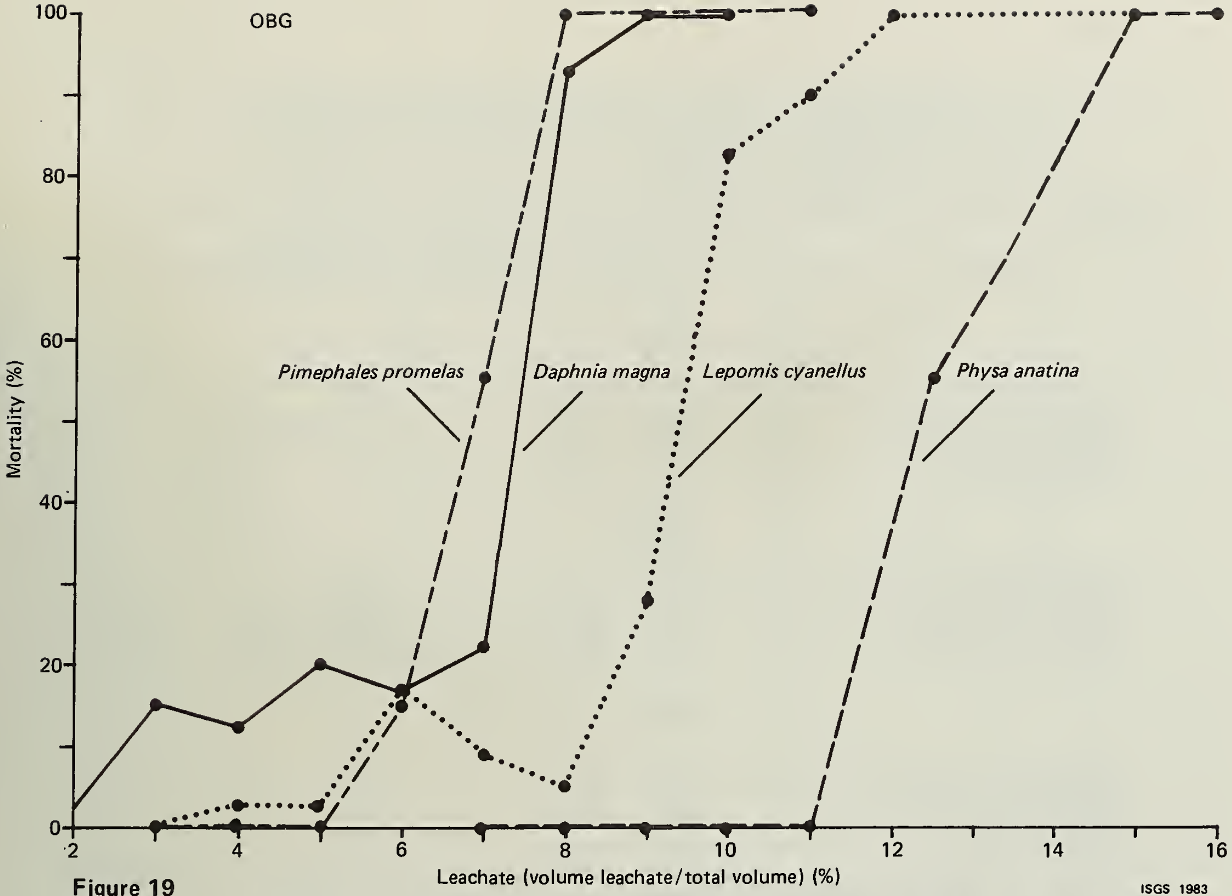

Figure 19
Relationships between the OBG extract and mortality for *Pimephales promelas, Daphnia magna, Lepomis cyanellus,* and *Physa anatina.*

mortality curve for Physa anathina is shifted to the right side of the figure, demonstrating the superior tolerance of snails to the solutions.

Relative toxicities of the four extracts were significantly different ($P \leq 0.01$) from one another in all cases for all four organisms (table 19). In 20 of 24 comparisons, the difference between the toxicity data sets were highly significantly different ($P < 0.001$ or 0.0001).

Generally, all four organisms were significantly different in their sensitivity to the extracts (table 20); however, Pimephales and Daphnia were similar in their tolerance to WSNG and OBG extracts, while Lepomis and Daphnia were similar in their tolerance to OBG. These results are supported by the 95-percent confidence intervals for the LC-50 values (table 18); for example, the 95-percent confidence intervals for the LC-50 of OBG to Daphnia (7.3 to 7.5) overlaps that for Lepomis (7.2 to 12.4). Physa, the most tolerant test organisms, was very significantly different in its tolerance in 7 of 12 comparisons (table 20).

Relative tolerances of test organisms. Daphnia and Pimephales were the species most sensitive to the toxic effects of the extracts. Lepomis cyanellus was less tolerant than Physa; however, it was more tolerant

Table 18. The LC-50 values, their 95 percent confidence intervals, and the amount of dilution necessary to eliminate mortality in static bioassays of extracts (WSOG, WSSL, WSNG and OBG) generated from the solid wastes.

Organism	pH	LC-50 mL/100mL	Dilution for zero percent mortality
WSOG			
Daphnia magna	1.67	0.36 ± .02	1:1000
Pimephales promelas	1.71	0.42 ± .004	1:263
Lepomis cyanellus	1.68	0.60 ± .02	1:200
Physa anatina	1.65	0.98 ± .05	1:154
WSSL			
Daphnia magna	2.09	0.77 ± .02	1:143
Pimephales promelas	2.21	0.84 ± .02	1:143
Lepomis cyanellus	2.06	0.96 ± .05	1:118
Physa anatina	2.05	1.65 ± .05	1:91
WSNG			
Daphnia magna	2.44	1.70 ± .02	1:57
Pimephales promelas	2.30	1.69 ± .02	1:65
Lepomis cyanellus	2.52	1.95 ± .08	1:57
Physa anatina	2.51	2.90 ± .09	1:44
OBG			
Daphnia magna	3.34	7.4 ± 0.1	>1:50
Pimephales promelas	3.33	6.8 ± 0.3	1:20
Lepomis cyanellus	3.36	9.5 ± 2.9	1:33
Physa anatina	3.37	14.2 ± 0.3	1:9

than *Daphnia* or *Pimephales promelas*. *Daphnia* has been shown to be more sensitive to cations than fish (Anderson, 1948).

There was a distinct threshold where the buffering capacity of the reconstituted water used for dilution was exhausted. Characteristically, above that threshold, the final pH of dilutions containing *Lepomis cyanellus*, *Pimephales promelas*, or *Daphnia* would increase 0.4 to 0.9 units above the initial pH. Below that point, pHs would remain constant or drop up to 0.5 units.

Dilutions containing *Physa anatina* showed an increased level of buffering, which for WSOG, existed throughout the pH range tested. Solutions containing *Physa* increased in pH by 0.3 to 1.6 units from the initial values. It was theorized that the shell of the snail, composed of calcium carbonate, was being dissolved in these acidic dilutions, thereby adding to the buffering capacity of the test solutions and raising the pH. An experiment was performed with the equilibrated WSOG

Table 19. Differences in the acute toxicities of extracts generated from four coal solid wastes (WSNG, WSOG, OBG and WSSL) as determined by an analysis of covariance. The levels of significant difference are listed and were obtained by analyzing mortality data of 48- and 96-hour bioassays using *Daphnia magna*, *Pimephales promelas*, *Lepomis cyanellus* and *Physa anatina*.

	WSNG vs WSOG	WSNG vs WSSL	WSNG vs OBG	WSOG vs WSSL	WSOG vs OBG	OBG vs WSSL
Pimephales	0.0001	0.0001	0.0001	0.01	0.01	0.001
Daphnia	0.0001	0.0001	0.001	0.0001	0.0001	0.0001
Physa	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Lepomis	0.01	0.01	0.001	0.001	0.0001	0.0001

0.01 = significant difference.
0.001 = highly significant difference.
0.0001 = very highly significant difference.

Table 20. Differences in sensitivities of *Daphnia magna*, *Pimephales promelas*, *Lepomis cyanellus* and *Physa anatina* to extracts generated from four coal solid wastes (WSNG, WSOG, OBG and WSSL) as determined by an analysis of covariance. The levels of significant difference are listed and were obtained by analyzing mortality data of 48- and 96-hour static bioassays.

	Pimephales vs Daphnia	Pimephales vs Lepomis	Pimephales vs Physa	Daphnia vs Lepomis	Daphnia vs Physa	Lepomis vs Physa
WSNG	N.S.	0.001	0.0001	0.05	0.001	0.01
WSOG	0.001	0.01	0.0001	0.0001	0.0001	0.0001
OBG	N.S.	0.05	0.0001	N.S.	0.001	0.001
WSSL	0.01	0.01	0.001	0.0001	0.0001	0.0001

N.S. = difference not statistically significant at 0.05 level.
0.05 = significant difference.
0.01 = significant difference.
0.001 = highly significant difference.
0.0001 = very highly significant difference.

extract using snail shells (with the animals removed) to determine if this could have been the cause of the observed increases in pH values. In all dilutions within the range of concentration toxic to Physa, the pH rose by 0.3 to 0.7 pH units in 96 hours due to shells alone. The pH of control solutions dropped by 0.1 to 0.2 units. These dilutions were all below the buffering cutoff point for WSOG.

The snail shell does contribute to the buffering capacity of the dilution water. This increased buffering capacity is partially responsible for the relatively increased tolerance of the snails to the acute toxicity of the extracts generated from the coal solid waste samples.

Chemical characterization of the diluted extracts. After the acute static bioassays were completed, subsamples of all test solutions were filtered, preserved with nitric acid, and stored for analysis. To determine which constituents were concentrated enough to be potentially hazardous, we analyzed samples that produced partial mortality as well samples containing the lowest concentration at which total mortality occurred and the highest concentration at which no mortality occurred. The mortality data were regressed on the physicochemical data using a multiple regression procedure (Nie et al., 1975).

The results of the multiple and linear regressions are included in tables C-1 through C-15 in Appendix C. Ranges of concentration of each chemical constituent in the test solutions and the recommended water-quality level for each chemical constituent are also given. Subsamples of the test solutions of WSNG during the Daphnia bioassays were not analyzed. Table 21 summarizes the results listed in Appendix C. The chemical constituents listed were found to be significantly correlated to mortality ($P < 0.05$) and present in concentrations exceeding recommended water quality levels (U.S. EPA, 1976). Calcium was not included in table 21 since it is not toxic at the concentrations measured in the test solutions.

For all extracts and all test organisms, the pH of the test solutions is significantly correlated to mortality and exceeds the recommended water-quality level ($pH < 6.5$). Only eight physicochemical parameters other than pH are listed in table 21. Aluminum, Fe, Mn, and Ni appeared to be significantly correlative to mortality. Zinc was highly correlated with mortality in test solutions of OBG.

More physicochemical parameters were correlated to mortality in the bioassys using Lepomis cyanellus and Physa anatina than in those using Daphnia magna and Pimephales promelas. This difference was probably due to the fact that Lepomis and Physa exhibited higher levels of tolerance, thus the solutions were more concentrated in their bioassays.

Discussion

Nontoxic leachates. Several authors (Beyer and Hutnik, 1969; Barnhisel and Rotromel, 1974; Hood et al., 1979; Klimstra and Jewell, 1973; Mason,

Table 21. Chemical constituents found to be significantly correlated to mortality and to exceed recommended water quality levels in test solutions prepared from extracts (OBG, WSNG, WSOG and WSSL) generated from coal solid wastes.

	Test Organism			
Extract	*Daphnia magna*	*Pimephales promelas*	*Lepomis cyanellus*	*Physa anatina*
OBG	pH Mn Ni Zn	pH Mn Ni Zn	pH Al Mn Ni SO_4	pH Al Mn Ni Zn
WSNG	pH	pH Mn Zn	pH Al Fe Mn Ni	pH Al Fe Mn Ni
WSOG	pH Fe	pH	pH Fe Pb	pH Al Fe
WSSL	pH Cd Ni	pH	pH Fe	pH Al Fe Mn Ni

1978; and many others) have cited spoil banks as sources of problem leachates. The laboratory extracts generated from the spoil bank samples (DMNS and DMOS) in this study were essentiallly neutral in pH, contained relatively low concentrations of accessory elements, and were not acutely toxic (mortality ≤5%).

The steady state extract generated from the Kilngas solid waste (KG) was alkaline (pH 9.0), contained relatively low concentrations of accessory elements, and was not acutely toxic. Similar results were obtained in a study testing laboratory extracts generated from Lurgi gasification ashes (Suloway et al., 1981).

Toxic leachates. The extracts generated from the coal cleaning refuse samples (OBG, WSNG, and WSOG) and the slurry sample (WSSL) were acidic (pH <3.5), contained relatively high concentrations of some accessory elements, and were acutely toxic to all four test organisms. Because of the complexity of the chemical composition of the systems and the undetermined synergistic and antagonistic effects of the chemical constituents composing the solutions, it was not possible to identify the chemical constituents directly responsible for the observed mortality; however, certain tentative conclusions can be drawn.

The mortality caused by the OBG extract can be attributed, in part, to the low pH of the test solutions, since the pH of some test solutions was below the tolerance levels established during the pH experiments with reconstituted water. The pHs of the most concentrated test solutions were approximately 5.0. Reconstituted water with a pH of 5.0 will cause total mortality in Daphnia, Pimephales, and Lepomis bioassays and 20 percent mortality in Physa bioassays. Also the concentration of Zn in some OBG test solutions exceeded the LC-50 values established for Daphnia by Biesinger and Christensen (1972), for Pimephales by Benoit and Holcombe (1978), and for Physa by Patrick (1968). Relatively high concentrations of aluminum were measured in the OBG test solutions; however, LC-50 values for aluminum have not been established for the test organisms.

As was the case in the OBG test solutions, the pH values of the most concentrated test solutions for the WSNG waste exceeded the tolerance levels of all four test organisms. Also the concentration of Zn measured in the WSNG bioassays using Pimephales exceeded the LC-50 value for Zn established by Benoit and Holcombe (1978).

In addition to toxic pH levels, the WSOG test solutions contained concentrations of Fe that exceed the LC-50 value for Daphnia (Biesinger and Christensen, 1972). The WSSL test solutions were characterized by toxic pH levels.

CHRONIC BIOASSAYS OF LEACHATES GENERATED FROM COAL CLEANING REFUSE SAMPLES

T. M. Skelly and J. J. Suloway

The major objectives of these biological investigations were to determine (1) what concentrations of leachates generated from two coal cleaning refuse samples (OBG and WSNG) caused sublethal, toxic effects in chronic bioassays using Pimephales promelas, Lepomis cyanellus, Daphnia magna and Physa anatina; (2) the relative sensitivities of the four test organisms to the leachates; (3) the relative sensitivities of the parameters measured (such as growth, reproduction, mortality) during the bioassays, and (4) any significant correlations between the chronic toxicity of a leachate and its physicochemical composition.

Methods and Materials

The composition of the leachates generated from samples of OBG and WSNG by the large volume generation (LVG) procedure was continuously monitored. This particular procedure was used to generate the leachate because of an anticipated need for large volumes of solution for the chronic bioassays. After about 1 year, the leachates were first assayed for acute toxicity with the four test organisms; these toxicity tests were divided into phases: (1) the screening procedure, and (2) the LC-50 determination. Methodologies for these acute tests were identical to those in the discussion of acute static bioassays.

The effects of chronic exposure to sublethal concentrations of leachates from OBG and WSNG were determined using a continuous flow mini-diluter exposure system modified from a design proposed by Benoit et al. (1981). The system delivered 12.5 mL/min of five concentrations and a control solution to each of four replicate chambers. During the bioassays using fish and snails, the chambers contained 700 mL of test solution; while during the bioassays using Daphnia, the test chambers contained approximately 500 mL of test solution. The dilution water, which was a blend of dechlorinated tap and deionized water, was passed through an ultraviolet filter before use and heated to the test temperature at each diluter. Water temperature for all fish and snail bioassays was maintained at 25.0°C; Daphnia experiments were conducted at 22.5°C. All tests were held under a constant (16L-8D) photoperiod. The four species of test organisms were exposed to dilutions of the OBG leachate at concentrations of 10, 5, 2.5, 1.25, 0.63 and 0.0 (control) percent (by volume) of the undiluted OBG leachate, and 0.1, 0.05, 0.025, 0.0125, 0.00625 and 0.0 percent of the WSNG leachate.

Fathead minnows were tested for 32 days (4 days as embryos and 28 days post-hatch). To initiate these embryo-larval chronic bioassays, 30 eggs were placed in screened egg cups in each chamber. The egg cups were mechanically, slowly rocked to facilitate oxygen transfer and cleaning of the fish eggs. When hatching was completed, the total number of hatched individuals was recorded, and the number of larval fish per chamber was reduced to 15. Fish were fed live, brine shrimp nauplii (Artemia salina) three times per day. Dead fish and debris were siphoned from each exposure chamber every morning before the first feeding. When the test was terminated, fish were killed with ice water and measured for total length and weight.

Green sunfish were tested for 29 days (1 day as embryos and 28 days post-hatch) with WSNG. The green sunfish bioassay with OBG was terminated after 14 days because of insufficient leachate. Test procedures were the same as those used in the fathead minnows bioassays.

Daphnia magna experiments for both OBG and WSNG were conducted for 28 days; 5 individual Daphnia were maintained separately within stainless steel cages in each exposure chamber. Tests were initiated with 2- to 26-hour-old Daphnia. Daphnia were fed a blended solution of trout chow and baker's yeast 3 times per day. When the Daphnia grew large and reproduced (Daphnia are parthenogenic), the number of progeny were counted and removed. Total length of each adult was measured at test termination.

The snail experiments with OBG and WSNG were conducted for 28 days. All snails were measured for shell length and weight prior to and after the exposure period. At test initiation, 15 snails (shell length = 5.0 ±

0.5 mm) were placed into each of the 24 exposure chambers. Several behavioral parameters were monitored 3 times per day, 3 days per week. The number of snails out of the water, snails taking on air, and mating behavior were noted. Egg masses deposited by the snails were counted and removed each day. Occasionally, an egg mass went undetected, in which case the juvenile snails were removed. Snails were fed a gelatinous plug of wheatgerm, dry milk, and cerophyll (Standon, 1951) once per day, every other day.

During each chronic bioassay for all test species, mortality, water temperature, and the pH of the undiluted leachate were monitored daily. Diluter flow rates were measured twice daily and adjusted as necessary.

Twice per week, water samples were taken from one-half of the exposure chambers. By sampling alternate replicates, A and C, then B and D, all exposure chambers were sampled once a week. Approximately 100 mL of test solution was siphoned for each sample. These samples were analyzed initially for pH and dissolved oxygen, then preserved for inorganic constituent analysis after filtering.

Since an iron precipitate formed when the WSNG leachate was diluted, the capillary tubes in the dilution apparatus were cleaned every 4 hours. Also, the toxicant dilution water cell and mixing cell were replaced daily to help maintain proper flow rates. Other cells in the dilution apparatus were replaced as required. During replacement, the dilutor was shut down for approximately 45 minutes.

Results

Acute toxicity of the leachates. Acute toxicity tests were conducted in the second year to determine the range of concentrations of leachates that should be used during the chronic toxicity tests. First, screening procedures were conducted to determine if the undiluted leachates were acutely toxic (table 22). Undiluted OBG leachate was not acutely toxic to any species of test organism; the pH range of undiluted OBG during the second year (pH 5.70 to 6.04) was much higher than that measured in the leachate generated during the first year of the study (pH 3.33 to 3.37). Undiluted WSNG generated during the second year of the study was acutely toxic to the three species of test organisms tested. The relative sensitivity of the test organisms was the same as that observed in the first year of the study; Pimephales and Daphnia were the most sensitive and Physa was the most tolerant species. The pH range of undiluted WSNG was higher in the second year (pH 3.49 to 3.98) than that measured in the first year (pH 2.30 to 2.51); however, the LC-50 values calculated for WSNG using data collected during Daphnia and Pimephales bioassays were considerably lower in the second year than those calculated in the first year. In contrast, LC-50 values calculated for WSNG using data collected during Physa bioassays in the first and second years were similar, despite the fact that the pH of the undiluted

Table 22. Results of the acute bioassays of WSNG and OBG conducted by the LTE and LVG procedures.

	Procedure			
	LTE		LVG	
Organism	pH	LC-50 mL/100 mL	pH	LC-50 mL/100 mL
		OBG		
Pimephales	3.33	6.8 ± 0.3	5.74	>100[1]
Daphnia	3.34	7.4 ± 0.1	5.62	>100
Lepomis	3.36	9.4 ± 2.9	6.04	>100
Physa	3.37	14.2 ± 0.3	5.70	>100
		WSNG		
Pimephales	2.30	1.69 ± 0.02	3.56	0.240 ± 0.010
Daphnia	2.44	1.70 ± 0.02	3.49	0.335 ± 0.018
Lepomis	2.52	1.95 ± 0.08	3.51	-[2]
Physa	2.51	2.90 ± 0.09	3.98	3.20 ± 0.20

[1] undiluted OBG was not acutely toxic to any of the species of test organisms during acute bioassays.

[2] green sunfish larvae were not available for acute bioassays.

leachate was considerably higher in the second year (pH 2.51 vs. pH 3.98).

As was the case in the first year of the study, WSNG was a more toxic leachate than OBG. Since 0.1 percent was the highest conentration of WSNG at which no toxic effects were observed during the acute bioassays, this concentration was selected to be used as the highest concentration of WSNG for the chronic bioassays. Since even undiluted OBG was not acutely toxic, a relatively high concentration of OBG (10%) was selected as the highest concentration of OBG for the chronic bioassay. This concentration was selected primarily because a limited amount of undiluted OBG was generated during the second year.

Chronic toxicity of the leachates. The results of the chronic bioassays of WSNG using *Pimephales promelas* are summarized in table 23. One-way Analysis of Variance (ANOVA) was used to analyze the significance of differences in length and weight. Chi-square analysis was used to analyze the significance of differences in hatchability and survival. Growth as measured by length ($F_{5,308} = 0.0003$, $P > 0.10$) and weight ($F_{5,308} = 0.0039$, $P > 0.10$) was not significantly affected by the dilutions of the WSNG leachate. The mean lengths ranged from a high of 21.6 mm in both the control and the 0.05-percent concentration, to 20.7 mm in the highest concentration, 0.1 percent. A similar trend was observed in the mean weights, with the lowest weight measured in the

Table 23. Lengths, weights, mortality, and hatching percentages for fathead minnows exposed to five concentrations of WSNG leachate and a control. Data were obtained during 32-day, embryo-larval bioassays conducted in flow-through mini-diluters.

Concentration of leachate (%)	N[1]	Total length $\bar{X} \pm SD^2$(mm)	Weight (g) $\bar{X} \pm SD$	Mortality (%)	Hatchability (%)
0.10	54	20.7 ± 1.59	0.073 ± 0.017	8.3	84.0
0.05	47	21.6 ± 1.78	0.087 ± 0.023	8.3	91.7
0.025	57	21.2 ± 1.85	0.085 ± 0.022	4.8	98.3
0.0125	51	21.1 ± 1.86	0.085 ± 0.022	5.0	89.3
0.00625	49	21.4 ± 1.60	0.083 ± 0.018	11.5	95.7
0.00 (control)	56	21.6 ± 1.44	0.085 ± 0.018	5.0	99.2

[1] number of data
[2] mean ± one sample standard deviation

Table 24. Lengths, weights, mortality, and hatching percentages for green sunfish exposed to five concentrations of WSNG leachate and a control. Data were obtained during 29-day, embryo-larval bioassays conducted in flow-through mini-diluters.

Concentration of leachate (%)	N[1]	Total length $\bar{X} \pm SD^2$(mm)	Weight (g) $\bar{X} \pm SD$	Mortality (%)	Hatchability (%)
0.10	24	16.9 ± 1.45	0.060 ± 0.016	45.0	56.0
0.05	43	16.5 ± 1.44	0.059 ± 0.012	21.7	74.5
0.025	40	16.2 ± 1.16	0.054 ± 0.012	26.7	78.1
0.0125	40	15.8 ± 1.80	0.049 ± 0.014	29.5	63.1
0.00625	44	16.2 ± 0.97	0.053 ± 0.010	21.7	76.0
0.00 (control)	43	16.4 ± 0.79	0.056 ± 0.009	23.3	80.7

[1] number of data
[2] mean ± one sample standard deviation

strongest concentration and the highest mean weight measured in the chambers with a 0.05-percent concentration of WSNG. There was no significant difference in the amount of mortality of fathead minnow larvae exposed to various concentrations of the WSNG leachate. The highest mortality (11.5%) occurred in the lowest concentration of WSNG. The lowest mortality (4.8%) was observed in the third highest concentration, 0.025 percent. The only parameter measured during the chronic bioassays of WSNG using fathead minnows in which a significant difference was observed was hatchability. The hatchability in the control (99.2%) was significantly higher than that measured in test solutions of 0.10 percent leachate (hatchability = 84.0%, $P < 0.001$), 0.05 percent leachate (hatchability = 91.7%, $P < 0.025$), and 0.015 percent leachate (hatchability = 89.3%, $P < 0.005$).

Table 25. Lengths, mortality, and reproductive success of Daphnia magna exposed to five concentrations of WSNG leachate and a control. Data were obtained during 28-day, chronic bioassays conducted in flow-through mini-diluters.

Concentration of leachate (%)	Progeny/Adult $\overline{X} \pm SD^1$	First day of reproduction	Mortality (%)	Total length $\overline{X} \pm$ SD (mm)
0.10	0.0 ± 0.0	--	75.0	--
0.05	8.5 ± 4.4	18	75.0	3.5 ± 0.22
0.025	10.5 ± 7.1	12	40.0	3.7 ± 0.28
0.0125	16.0 ± 12.0	11	50.0	3.7 ± 0.37
0.00625	20.0 ± 13.9	13	30.0	3.7 ± 0.31
0.00 (control)	24.2 ± 12.5	11	15.0	4.0 ± 0.33

[1] mean ± standard deviation

The results of the chronic bioassyas of WSNG using Lepomis cyanellus are summarized in table 24. The same parameters were measured and the same statistical analyses were used as those reported for fathead minnows. Again the growth parameters, mean length ($F_{5,229} = 0.004$, $P > 0.10$) and mean weight ($F_{5,229} = 0.0046$, $P > 0.10$) were not significantly different between treatments. In fact, the largest fish were those found in the chamber dosed with the highest concentration of WSNG. There was a significant increase in the amount of mortality in the highest concentration over that found in the control ($\chi^2 = 9.58$, $P < 0.005$). The hatchability in the control (90.7%) was significantly higher than that measured in the test solutions of 0.10-percent leachate (hatchability = 56.0% $P < 0.005$) and 0.0125-percent leachate (hatchability = 63.1%, $P < 0.005$).

The results of the chronic bioassays of WSNG using Daphnia magna are summarized in table 25. The leachate had several dramatically detrimental effects on the Daphnia. The 75-percent mortality observed in chambers exposed to 0.10- and 0.05-percent leachate was significantly higher than the 15-percent mortality observed in the controls, as determined by chi-square contingency analysis. The mortality in the other treatments (30% to 50%) was also higher than that observed in the controls, but the difference was not statistically significant because of the small sample sizes. Reproduction, as measured by the mean number of progeny per adult, was significantly reduced in the three highest concentrations (0.10%, 0.05%, and 0.025% WSNG) from that observed in the control. The reproduction at doses of 0.0125 and 0.00625 percent WSNG was also reduced, but the difference was not statistically significant. The first day of reproduction also appeared to be delayed at the higher concentrations. The mean total length of Daphnia adults was not significantly reduced by exposure to different concentrations of WSNG ($F_{4,47} = 0.0014$, $P > 0.10$).

Table 26. Shell lengths, weights, mortality, and egg mass production of Physa anatina exposed to five concentrations of WSNG leachate and a control. Data were obtained during 28-day, flow-through bioassays.

Concentration of leachate (%)	N[1]	Shell length $\bar{X} \pm SD^2$(mm)	Weight (g) $\bar{X} \pm SD$	Mortality (%)	Egg mass production $\bar{X} \pm SD$
0.10	33	5.4 ± 0.40	0.018 ± .003	30.0	89.3 ± 27.0
0.05	49	5.4 ± 0.50	0.020 ± .005	13.3	133.3 ± 12.7
0.025	49	5.7 ± 0.73	0.022 ± .007	15.0	106.3 ± 17.3
0.0125	43	5.8 ± 0.48	0.023 ± .005	18.3	108.5 ± 24.2
0.00625	45	5.9 ± 0.80	0.026 ± .009	18.3	99.0 ± 14.1
0.00 (control)	46	5.9 ± 0.56	0.025 ± .006	8.3	119.3 ± 22.1

[1] number of data

[2] mean ± one sample standard deviation

The results of the chronic bioassays of WSNG using Physa anatina are summarized in table 26. One-way ANOVA was used to analyze the significance of differences in length and weight between treatments. Although mean shell length increased with decreasing concentration of WSNG, and although the mean shell length of individuals exposed to the control was greater than those exposed to the higher concentrations of WSNG, the differences were not statistically significant ($F_{5,259} = 2.113$, $P > 0.05$). However, the differences in mean weight were significant ($F_{5,229} = 8.89$, $P < 0.001$). The mean weight data was further analyzed using a Student-Newman-Keuls test. The results of this analysis demonstrated that the mean weight of the controls was significantly greater than that of those individuals exposed to 0.1-percent WSNG ($P < 0.001$), 0.05-percent WSNG ($P < 0.001$), and 0.025-percent WSNG ($P < 0.05$). The mortality observed in the different treatments was also significantly different ($\chi^2 = 13.07$, df = 5, $P < 0.025$). Specifically, the mortality in the controls was significantly less than that observed in the 0.1-percent WSNG treatment ($\chi^2 = 8.80$, df = 1, $P < 0.005$). Reproduction as measured by egg mass production, was not significantly affected by exposure to WSNG ($F_{5,223} = 2.237$, $P > 0.05$).

Few significant differences were observed in the chronic bioassays of OBG. The results of the chronic bioassays of OBG using fathead minnows are summarized in table 27. Growth, as measured by mean length and weight, was lowest in the controls. Mean total length of those individuals exposed to the highest concentration of OBG (10%) was signficantly greater than the controls ($P < 0.001$). No significant differences were seen in mean weights of the snails exposed to the various concentrations of OBG. Mortality was low (<10%) and hatchability was nearly complete (>93%) in the chronic bioassyas of OBG using Pimephales promelas. No significant differences in mortality or hatchability were observed between the various concentrations of OBG and the control.

Table 27. Lengths, weights, mortality, and hatching percentages for fathead minnows exposed to five concentrations of OBG leachate and a control. Data were obtained during 32-day, embryo-larval bioassays conducted in flow-through mini-diluters.

Concentration of leachate (%)	N[1]	Total length $\bar{X}$ ± SD[2] (mm)	Weight (g) $\bar{X}$ ± SD	Mortality (%)	Hatchability (%)
10.0	61	24.2 ± 1.63	0.133 ± .031	0.0	93.2
5.0	49	23.5 ± 1.59	0.131 ± .029	8.3	98.3
2.5	51	23.3 ± 1.98	0.013 ± .037	6.7	93.9
1.25	57	23.7 ± 1.95	0.140 ± .037	3.3	98.3
0.625	53	23.1 ± 2.28	0.127 ± .037	10.0	98.3
0.00 (control)	49	23.1 ± 1.37	0.126 ± .025	1.7	97.3

[1] number of data

[2] mean ± one sample standard deviation

Table 28. Lengths, weights, mortality and hatching percentages for green sunfish exposed to five concentrations of OBG leachate and a control. Data were obtained during 14-day, embryo-larval bioassays conducted in flow-through mini-diluters.

Concentration of leachate (%)	N[1]	Total length $\bar{X}$ ± SD[2] (mm)	Weight (g) $\bar{X}$ ± SD	Mortality (%)	Hatchability (%)
10.0	33	8.4 ± 0.71	-[3]	18.3	96.6
5.0	39	8.3 ± 0.87	-[3]	8.3	98.3
2.5	30	8.4 ± 0.85	-[3]	30.0	99.1
1.25	39	8.2 ± 0.84	-[3]	13.3	98.3
0.625	39	8.2 ± 0.72	-[3]	10.0	96.7
0.00 (control)	41	8.2 ± 0.97	-[3]	10.0	99.2

[1] number of data

[2] mean ± one sample standard deviation

[3] not measured

The green sunfish chronic bioassys of OBG were terminated after 14 days because of insufficient leachate. Only total length, mortality, and hatchability were recorded. The results of these chronic bioassays are summarized in table 28. Mean length did not differ significantly between treatments ($F_{5,205} = 0.5276$, $P > 0.10$). Mortality showed no discernible trend. The only significant difference for green sunfish was the higher mortality for individuals exposed to a leachate concentration of 2.5-percent OBG than for those in the control solution ($\chi^2 = 6.17$, df = 1, $P < 0.025$). Hatchability for eggs in all treatments was nearly complete (>96.5%) during the bioassays of OBG using green sunfish; no significant differences in hatchability among treatments were observed.

Table 29. Lengths, mortality and reproductive success of Daphnia magna exposed to five concentrations of OBG leachate and a control. Data were obtained during 28-day, chronic bioassays conducted in flow-through mini-diluters.

Concentration of leachate (%)	Progeny/Adult $\bar{X} \pm SD^1$	First day of reproduction	Mortality (%)	Total length $\bar{X} \pm SD$ (mm)
10.0	56.6 ± 35.2	10	35.0	4.0 ± 0.38
5.0	66.3 ± 19.3	10	15.0	4.3 ± 0.17
2.5	56.5 ± 21.0	12	35.0	4.1 ± 0.27
1.25	52.5 ± 22.8	12	30.0	4.0 ± 0.20
0.625	71.5 ± 15.0	12	35.0	4.2 ± 0.06
0.00 (control)	70.0 ± 47.8	11	35.0	4.0 ± 0.32

[1] mean ± one sample standard deviation

The results of the chronic bioassays of OBG using Daphnia magna are listed in table 29. Reproduction, measured as number of progeny produced per adult, was greatest in the controls and the lowest concentration of OBG; however, due to the large variability in production of progeny, this difference was not significant ($F_{5,67} = 0.8699$, $P > 0.10$). Also, the first day of reproduction did not vary among treatments (between day 10 and day 12). Mortality was high (15% to 35%) in all treatments; there were no significant differences between mortality observed in the controls and in the other treatments ($\chi^2 = 3.305$, df = 5, $P > 0.10$). Mean total length of adult Daphnia showed no discernible trend. The only significant difference in total length was between the control and those individuals exposed to the concentration of 5.0-percent leachate ($P < 0.05$).

The results of the Physa bioassays of OBG are summarized in table 30. Growth of Physa, as measured by mean shell length ($F_{5,308} = 0.00067$, $P > 0.10$) and mean weight ($F_{5,308} = 0.0022$, $P > 0.10$), was not significantly affected by the OBG leachate. Observed mortality ($\chi^2 = 1.03$, df= 5, $P > 0.10$) and egg mass production ($F_{5,18} = 0.9890$, $P > 0.10$) did not differ significantly among the treatments and control.

Discussion

The chronic bioassays were designed to supplement acute toxicity data by determining the sublethal effects--changes in growth, reproduction,and mortality--associated with chronic exposure to dilute concentrations of two toxic leachates generated from the refuse wastes samples OBG and WSNG.

The full strength OBG leachate generated by the LVG procedure was not acutely toxic to any of the organisms tested, unlike the OBG LTE solution. The differences in the effects of the OBG solutions (table 22) were attributable to differences in the solution generation procedures, which produced dissimilar solutions. The particle size of the OBG waste that was used in the LTE experiment was ≤9.53 mm; it was

Table 30. Shell lengths, weights, mortality, and egg mass production of Physa anatina exposed to five concentrations of OBG leachate and a control. Data were obtained during 28-day, flow-through bioassays.

Concentration of leachate (%)	N[1]	Shell length $\overline{X}$ ± SD[2] (mm)	Weight (g) $\overline{X}$ ± SD	Mortality (%)	Egg mass production $\overline{X}$ ± SD
10.0	52	5.0 ± 0.56	0.012 .003	8.3	54.5 ± 5.7
5.0	55	5.2 ± 0.54	0.013 .003	6.7	62.5 ± 12.1
2.5	52	5.2 ± 0.58	0.014 .004	6.7	61.0 ± 7.7
1.25	51	5.2 ± 0.65	0.013 .005	5.0	75.5 ± 31.0
0.625	49	5.3 ± 0.62	0.014 .005	15.0	66.0 ± 5.5
0.00 (control)	55	5.2 ± 0.70	0.013 .005	5.0	55.8 ± 16.4

[1] number of data

[2] mean ± one sample standard deviation

necessary to sieve the sample in order to mix the solution without damaging the stirring motors. In contrast, the OBG sample used in the LVG procedure was not sorted, but loaded into the Agro^R tank in the same physical state as it was in the field. The unsorted sample contained boulder-sized clasts mixed with other coarse-grained particles. The rate of pyrite oxidation in the samples and the subsequent formation of H_2SO_4 would increase with increasing surface area. This may be the major factor accounting for the lower pH and consequent toxicity of the LTE extract of OBG relative to that of the leachate from the LVG procedure. Refuse pile heterogeneity is also a likely factor.

Because there was a limited quantity of OBG leachate, it was assayed as a 10-percent solution for the highest concentration for chronic exposure to determine if any long-term effects might be associated with exposure to this nontoxic leachate in acute experiments.

The organisms exposed to the OBG leachate were generally not detrimentally affected by dosages of this nontoxic solution. In fact, Pimephales promelas, the fish exposed to the highest concentration of OBG were larger than the controls, suggesting that this leachate provided a favorable growth medium. The chemical composition of the test solutions (tables 31 to 34) was quite innocuous, which accounts for its relative lack of toxic effects.

The WSNG leachate generated by the LVG procedure was quite toxic throughout the course of this investigation. Although the WSNG leachate generated changed in chemical composition with time, its toxicity was still very great. Its low pH of 3.49 to 3.98 was partially responsible for the toxicity during the screening procedures and LC-50 determinations. The pH of 7.8 to 8.5 during the chronic tests was not near the lethal limits for organisms, and yet mortality (Lepomis, Daphnia, Physa), lowered hatchability (Lepomis cyanellus, Pimephales promelas), reduced reproduction (Daphnia), and reduced weight gain (Physa) were all associated with chronic exposure to the WSNG leachate.

Table 31. Ranges of mean physicochemical parameter values (mg/L) for replicate concentrations of OBG during chronic bioassays for fathead minnow (Pimephales promelas).

	OBG Concentrations (%)					
Parameter	10.0	5.0	2.5	1.25	0.625	0.0
pH(units)	7.757-7.850	7.990-8.053	8.180-8.257	8.090-8.338	8.324-8.415	8.425-8.481
Dissolved oxygen	5.78-6.21	5.83-6.13	5.73-5.99	5.71-6.01	5.82-6.08	5.51-6.21
Al	0.19-0.23	0.20-0.26	0.22-0.25	0.21-0.26	0.21-0.26	0.24-0.27
B	0.48	0.46	0.45	0.44-0.45	0.44-0.45	0.43-0.45
Ba	0.02	0.02-0.03	0.02-0.03	0.02-0.03	0.02-0.03	0.02-0.03
Ca	70.7-88.2	35.9-37.7	25.3-26.6	19.1-20.4	16.1-17.2	13.0-13.5
K	1.8-2.0	1.7-2.1	1.6-2.2	1.7-2.3	1.8-1.9	1.9-2.3
Mg	12.8-13.2	11.3-11.5	10.6-10.8	10.2-10.4	10.2-10.2	9.9-10.0
Mn	0.27-0.34	0.12-0.15	0.06-0.08	0.02-0.03	0.01	<0.01
Na	30.2-31.5	31.9-32.9	32.5-33.2	32.6-34.1	32.3-34.3	33.0-34.3
Si	3.94-4.12	3.17-3.22	2.78-3.00	2.59-2.87	2.53-2.76	2.39-2.66
Zn	0.06-0.33	0.03-0.06	0.05-0.10	0.02-0.04	0.01-0.06	<0.01-0.01
As	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Be	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Cd	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Co	<0.004	<0.003	<0.003	<0.003	<0.003	<0.003
Cr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Mo	<0.01-0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pb	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Sb	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Se	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Sn	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
V	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12

Table 32. Ranges of mean physicochemical parameter values (mg/L) for replicate concentrations of OBG during chronic bioassays for green sunfish (*Lepomis wanellus*).

	OBG Concentrations (%)					
Parameter	10.0	5.0	2.5	1.25	0.625	0.0
pH(units)	7.745-7.902	7.976-8.149	8.138-8.346	8.224-8.467	8.274-8.544	8.320-8.592
Dissolved oxygen	7.43-7.82	7.37-7.69	7.53-8.35	7.38-7.81	7.26-7.76	7.52-7.98
Al	0.12-0.16	0.13-0.16	0.12-0.15	0.14-0.15	0.13-0.17	0.15-0.17
B	0.39-0.79	0.36-0.81	0.35-0.81	0.34-0.81	0.34-0.81	0.33-0.81
Ba	0.03	0.03	0.03	0.03	0.03-0.10	0.03
Ca	58.2-73.4	32.6-34.6	22.9-24.4	17.2-18.5	13.8-15.4	11.0-12.3
K	<2.14	<2.2-2.2	<2.07-2.09	<2.14	<2.09-2.64	<2.66-2.66
Mg	10.8-11.4	9.6-10.2	8.9-9.5	8.6-9.2	8.4-9.1	8.3-8.8
Mn	0.23-0.24	0.12	0.06-0.07	0.03-0.04	0.01-0.02	<0.01
Na	25.6-26.6	26.9-27.6	27.2-27.6	27.2-28.0	27.5-29.0	27.0-28.4
Si	3.83-4.56	3.09-3.90	2.73-3.55	2.58-3.36	2.47-3.19	2.38-3.14
Zn	<0.06	<0.05	<0.04-0.05	<0.04-0.07	<0.05	<0.04
As	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Be	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Cd	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Co	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Fe	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Sb	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Se	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Sn	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
V	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18

Table 33. Ranges of mean physicochemical parameter values (mg/L) for replicate concentrations of OBG during chronic bioassays for the crustacean, *Daphnia magna*.

	OBG Concentrations (%)					
Parameter	10.0	5.0	2.5	1.25	0.625	0.0
pH(units)	7.722-7.874	7.932-8.100	8.110-8.272	8.327-8.425	8.252-8.481	8.447-8.505
Dissolved oxygen	6.95-7.54	7.02-7.25	7.00-7.44	6.88-7.38	6.83-7.22	6.77-7.35
Al	<0.11-.14	<0.11-0.13	<0.14-0.14	0.14-0.16	0.14-0.17	0.16-0.18
B	0.38-0.58	0.36-0.56	0.35-0.56	0.34-0.56	0.34-0.55	0.34-0.56
Ba	0.027-0.029	0.028-0.030	0.028-0.030	0.030-0.036	0.028-0.031	0.028-0.031
Ca	61.7-67.7	33.7-35.0	21.2-23.3	17.0-17.6	14.2-14.4	11.2-11.4
K	<2.1	<2.2	<2.4	<2.4	<2.2	<2.0
Mg	10.8-11.0	9.5-9.6	8.8-8.9	8.6	8.4-8.5	8.3-8.4
Mn	0.17-0.20	<0.07-0.07	<0.03	<0.01-0.02	<0.01	<0.01
Na	25.2-25.6	25.5-26.9	26.5-27.0	26.4-27.7	27.0-27.8	27.2-28.0
Si	3.68-4.05	2.99-3.41	2.66-2.98	2.47-2.82	2.38-2.76	2.30-2.72
Zn	<0.10	<0.12	<0.06	<0.08	<0.04	<0.06
As	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Be	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cd	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Co	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Sb	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Se	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sn	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
V	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15

Table 34. Ranges of mean physicochemical parameter values (mg/L) for replicate concentrations of OBG during chronic bioassays for the snail, *Physa anatina*.

	OBG Concentrations (%)					
Parameter	10.0	5.0	2.5	1.25	0.625	0.0
pH (units)	7.790-7.879	8.036-8.212	8.220-8.406	8.360-8.534	8.392-8.608	8.450-8.672
Dissolved oxygen	7.44-7.70	7.41-7.62	7.48-8.22	7.37-8.22	7.34-7.61	7.28-7.71
Al	0.130-0.152	0.142-0.165	0.150-0.176	0.152-0.176	0.150-0.169	0.157-0.178
B	0.442-0.644	0.416-0.638	0.417-0.631	0.411-0.630	0.407-0.633	0.405-0.633
Ba	0.018-0.026	0.020-0.027	0.020-0.028	0.020-0.028	0.020-0.030	0.021-0.032
Ca	67.7-68.6	34.2-35.2	24.2-25.3	18.4-19.0	15.7-16.1	12.4-13.0
Fe	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
K	<0.20	<1.9-2.0	<2.0	<1.9-2.3	<2.1	<2.2
Mg	12.0-12.1	10.6-10.9	9.9-10.2	9.6-9.9	9.9-9.7	9.4-9.5
Na	28.4-28.9	29.4-29.9	29.7-30.7	23.7-30.8	30.2-31.1	30.9-31.5
Si	4.03-4.44	3.28-3.74	2.96-3.36	2.74-3.15	2.66-3.12	2.57-3.00
As	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Be	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Cd	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Co	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Se	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sb	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Pb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Sn	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
V	<0.14	<0.15	<0.15	<0.15	<0.15	<0.15
Zn	<0.07-0.21	<0.13	<0.08-0.17	<0.32	<0.33	<0.14-0.14

Although there may have been some synergistic effects of various chemical constituents in WSNG, iron appeared to be the only chemical present at toxic levels in chronic-test solutions (tables 35 to 38). Acid mine drainage often contains high levels of ferrous iron (Fe^{2+}) that oxidizes to ferric iron (Fe^{3+}) and precipitates as ferric hydroxide {$Fe(OH)_3$} as the pH is elevated and oxygenation takes place (Smith and Sykora, 1976), for example, when mine drainage enters a receiving water.

Mixing WSNG with dilution water in these experiments raised the pH and formed a precipitate, predominantly a ferric hydroxide phase. The presence of this visible, yellow flocculent, also reflected by the turbidity values of solutions (tables 35 to 38), represented both a physical and physiological interference to the functional processes of the organisms.

The lowered hatchability of both green sunfish and fathead minnow eggs was probably due to suffocation, as the precipitate would attach to eggs and block oxygen transfer. Small masses of ferric hydroxide suspensions are similar in size to the pores in the chorion of fathead minnow eggs. Consequently, clogging these pores by ferric hydroxide particles would reduce oxygen diffusion across the chorion and cause embryo mortality (Smith et al., 1973). Eggs in this study were suspended in egg cups and rocked in exposure chambers, which may have helped keep some eggs free of the precipitate. If eggs had rested on the chamber bottoms, hatchability would probably have been further reduced. The gills of fish that hatched and died were often covered with a layer of ferric hydroxide, suggesting interference with respiration.

Growth of surviving fish appeared to be little affected by the different concentrations of WSNG; although the highest concentration of WSNG produced high mortality of green sunfish. These results support previous evidence that different life stages and species can be differentially affected by chronic exposure to ferric hydroxide suspensions (Smith et al., 1973; Smith and Sykora, 1976; Sykora et al. 1972, 1975).

Daphnia mortality and reproductive problems were common at the highest concentrations of WSNG, the problems were probably a result of consuming the ferric hydroxide precipitate, as these crustaceans are filter feeders on particulate matter in water. The gut of these Daphnia (easily visible in these translucent organisms) was often a yellow-gold color, similar to the color of ferric hydroxide precipitate.

Consumption of precipitate may also have been responsible for reduced growth and increased mortality in the highest WSNG concentrations for Physa. These snails often consumed the precipitate as was evident from their orange fecal material.

The WSNG concentrations of 0.1, 0.05, and 0.025 percent, which corresponded to total solution iron concentrations of 3.37 to 8.1 mg/L, 1.43 to 4.37 mg/L, and 0.79 to 1.40 mg/L, were toxic in some form to all organisms tested. Significant differences in development were observed in both fish species in their exposure to 0.0125-percent WSNG relative to control solutions. These WSNG solutions were characterized by iron concentrations of 0.42 to 0.58 mg/L total solution iron. Concentration of total iron in solutions of 0.00625-percent WSNG (the "no effect" concentration) used in green sunfish and fathead minnow tests ranged from 0.26 to 0.29 mg/L. Add to these values an estimation of the amount of iron present as a precipitate (based on a mean value of 3881 mg/L total iron in the full strength WSNG leachate) and a safe concentration of total iron therefore would be between 0.29 and 0.64 mg Fe/L.

These chronic bioassays have demonstrated that a 0.0125-percent solution of WSNG (an acutely toxic, sublethal concentration) will cause toxic effects in fathead minnows and green sunfish. These tests also show that other low concentrations of this leachate are toxic to various organisms in the aquatic food chain--specifically, to a crustacean, a snail, and two fish species. Disruption of a single element in the aquatic food chain could modify an entire aquatic ecosystem. The toxicity shown here for the WSNG leachate demonstrates the potential effects of these wastes should they ever enter a receiving water in a natural setting.

SUMMARY

- The coal slurry (coarse fraction) and refuse samples were chemically and mineralogically similar; aluminosilicates mixed with organic and inorganic sulfur and carbonaceous matter. The composition of the mine spoil samples was typical of shale, although higher in sulfur. The Kilngas sample resembled other high-temperature coal residues, such as slag and fly ash, except for higher Cr and Ni concentrations. Arsenic, Co, Ni, Pb, Si and Sb were concentrated in the refuse samples, presumably associated with sulfide minerals.

- The slurry (coarse fraction) and the refuse in the mining areas studied have the capacity for producing very acidic effluent and do not appear to contain sufficient carbonate minerals to have any appreciable neutralizing influence. Laboratory extracts of the mine spoils tended to be neutral in pH; whereas the Kilngas sample generated alkaline systems.

- Laboratory extractions of the slurry and refuse samples indicated that Al, Mn, Ni, SO_4, and Zn are in soluble forms and may leach out in appreciable quantities. Elevated levels of these same constituents were detected in field samples taken in the proximity of the solid sample.

- The solid coal wastes contained various organic compounds; many are included on the EPA Priority Pollutant List. However, these compounds were found to be essentially insoluble in aqueous media.

Table 35. Ranges of mean physicochemical parameter values (mg/L) for replicate concentrations of WSNG during chronic bioassays for fathead minnows, *Pimephales promelas*.

	WSNG Concentrations (%)					
Parameter	0.10	0.05	0.025	0.0125	0.00625	0.0
pH(units)	7.770-7.868	8.021-8.056	8.151-8.176	8.130-8.287	8.254-8.307	8.313-8.367
Dissolved oxygen	7.53-7.85	7.44-7.77	7.50-7.79	6.98-7.80	7.40-7.62	7.26-7.45
Turbidity (JTU)	12.3-20.0	6.7-9.0	3.6-4.8	2.2-3.2	2.0-4.4	1.3-1.8
Al	0.17-0.20	0.16-0.19	0.16-0.19	0.16-0.20	0.16-0.19	0.16-0.17
B	0.34-0.46	0.34-0.46	0.34-0.45	0.34-0.45	0.34-0.46	0.35-0.46
Ba	0.024-0.027	0.024-0.026	0.026	0.026-0.027	0.026-0.027	0.026-0.030
Ca	9.30-9.94	8.95-9.68	8.85-9.61	8.82-9.52	8.86-9.55	8.89-9.51
Co	0.07-0.10	0.03-0.04	<0.02-0.03	<0.02-0.02	<0.02	<0.02
Fe	3.37-4.44	1.74-1.89	0.92-0.94	0.42-0.58	0.26-0.29	<0.02
K	<2.20	<2.18	<2.10	<2.16	<2.05	<2.28
Mg	9.10-9.70	8.72-9.40	8.52-9.27	8.52-9.28	8.54-9.26	8.58-9.16
Mn	0.040-0.059	0.025-0.030	0.010-0.014	0.008	<0.008	<0.008
Na	25.7-27.7	25.0-27.4	25.3-27.1	25.9-31.6	25.3-29.4	25.6-27.2
Si	2.48-2.78	2.45-2.70	2.45-2.67	2.44-2.67	2.44-2.72	2.45-2.69
As	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Be	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cd	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Pb	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Sb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Se	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sn	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
V	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
Zn	<0.02-0.03	<0.02	<0.02	<0.02	<0.02	<0.02

Table 36. Ranges of mean physicochemical parameter values (mg/L) for replicate concentrations of WSNG during chronic bioassays for green sunfish, *Leponis cyanellus*.

	WSNG Concentrations (%)					
Parameter	0.10	0.05	0.025	0.0125	0.00625	0.0
pH(units)	7.801-7.874	8.042-8.159	8.254-8.284	8.319-8.377	8.396-8.426	8.444-8.496
Dissolved oxygen	7.74-7.90	7.35-7.79	7.56-7.90	7.32-7.54	7.28-7.69	7.39-7.62
Turbidity (JTU)	15.0-18.0	7.4-12.1	4.5-13.7	2.5-3.1	2.2-2.4	1.1-2.5
Al	0.17-0.28	0.16-0.18	0.16-0.19	0.16-0.18	0.16-0.17	0.17-0.17
B	0.36-0.46	0.36-0.45	0.35-0.46	0.35-0.46	0.34-0.45	0.34-0.46
Ba	0.026-0.027	0.024-0.026	0.026-0.027	0.026-0.027	0.025-0.027	0.026-0.027
Ca	9.26-10.06	9.01-9.85	8.77-9.62	8.64-9.64	8.70-9.57	8.74-9.48
Co	<0.07-0.18	0.02-0.05	0.02-0.05	<0.02	<0.02	<0.02
Fe	3.54-6.60	1.43-2.13	0.79-0.98	0.42-0.52	0.26-0.27	<0.02
K	<2.32	<2.14	<2.66	<2.71	<2.62	<2.14
Mg	9.18-9.74	8.84-9.43	8.02-9.32	8.48-9.21	8.48-9.18	8.53-9.04
Mn	0.041-0.067	0.023-0.031	0.010-0.017	<0.006-0.008	<0.010	<0.010
Na	25.9-27.0	25.8-27.2	25.5-27.3	25.5-29.7	26.0-27.6	25.0-27.6
Si	2.50-2.87	2.47-2.76	2.45-2.70	2.44-2.70	2.42-2.68	2.42-2.70
Zn	0.02-0.05	<0.02	<0.02	<0.02	<0.02	<0.02
As	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
Be	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cd	<0.08-<0.91	<0.08-<0.91	<0.08-<0.91	<0.08-<0.91	<0.08-<0.91	<0.08-<0.91
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Pb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Sb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Se	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sn	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
V	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08

Table 37. Ranges of mean physicochemical parameter values (mg/L) for replicate concentrations of WSNG during chronic bioassays for the crustacean, *Daphnia magna*.

	WSNG Concentrations (%)					
Parameter	0.10	0.05	0.025	0.0125	0.00625	0.0
pH(units)	7.760-7.888	8.027-8.074	8.174-8.203	8.275-8.293	8.314-8.328	8.382-8.449
Dissolved oxygen	7.72-8.42	7.72-8.66	7.83-8.20	7.82-8.70	7.83-8.51	7.96-8.68
Turbidity (JTU)	21.7-51.4	6.7-10.8	3.8-4.4	2.6-2.8	1.9-2.0	1.1-1.2
Al	0.24-0.35	0.18-0.27	0.17-0.20	0.16-0.20	0.14-0.17	0.15-0.19
B	0.34-0.46	0.35-0.46	0.34-0.45	0.34-0.44	0.34-0.47	0.35-0.46
Ba	0.026-0.029	0.025-0.029	0.025-0.026	0.024-0.027	0.024-0.027	0.024-0.036
Ca	9.4-10.2	9.0-9.9	8.8-9.8	8.7-9.7	8.3-9.6	8.8-9.6
Co	0.11-0.31	0.02-0.12	<0.03-0.04	<0.02-0.02	<0.02	<0.01
Fe	5.64-8.16	1.81-4.37	1.10-1.40	0.57-0.74	<0.25-0.61	<0.04
K	<2.54	<2.00	<2.46	<2.40	<2.00	<2.26
Mg	9.34-9.80	8.76-9.56	8.44-9.36	8.29-9.26	8.10-9.21	8.61-9.14
Mn	0.079-0.084	0.027-0.047	0.012-0.022	0.010-0.018	0.008-0.018	<0.008
Na	26.5-27.0	25.8-27.4	24.7-26.8	24.1-27.1	25.8-26.7	25.8-26.8
Si	2.68-2.78	2.52-2.70	2.44-2.66	2.45-2.60	2.43-2.64	2.44-2.65
As	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Be	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Cd	<0.38	<0.38	<0.38	<0.38	<0.38	<0.38
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Sb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Se	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sn	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
V	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
Zn	<0.08	<0.05	<0.03	<0.03	<0.03	<0.03

Table 38. Ranges of mean physicochemical parameter values (mg/L) for replicate concentrations of WSNG during chronic bioassays for the snail, *Physa anatina*.

	WSNG Concentrations (%)					
Parameter	0.10	0.05	0.025	0.0125	0.00625	0.0
pH(units)	7.776-7.828	8.036-8.056	8.213-8.228	8.328-8.356	8.366-8.406	8.390-8.462
Dissolved oxygen	7.70-8.29	7.50-8.00	7.68-8.12	7.51-8.07	7.57-8.22	7.78-8.00
Turbidity (JTU)	20.9-30.8	7.1-8.8	3.8-4.4	2.68-2.94	2.1-2.3	1.1-1.5
Al	0.19-0.22	0.17-0.20	0.17-0.19	0.14-0.18	0.16-0.19	0.14-0.18
B	0.36-0.47	0.36-0.47	0.36-0.47	0.36-0.46	0.36-0.46	0.36-0.46
Ba	<0.026-0.027	0.026-0.027	0.026-0.027	0.026-0.029	0.026-0.027	0.026-0.029
Ca	9.3-9.9	9.0-9.6	8.9-9.5	8.9-9.5	8.9-9.7	8.8-9.4
Fe	4.34-5.54	1.72-2.14	0.82-0.96	0.38-0.54	0.19-0.32	<0.07
K	<2.1	<2.2	<2.5	<2.2	<2.4	<2.0
Mg	9.23-9.88	8.93-9.37	8.78-9.34	8.63-9.21	8.60-9.35	8.58-9.06
Mn	0.06-0.08	<0.02-0.03	<0.02	<0.01	<0.01	<0.01
Na	26.6-27.3	26.8-28.1	26.4-28.1	25.8-28.4	26.8-27.5	26.3-26.7
Si	2.60-2.84	2.56-2.78	2.57-2.76	2.56-2.75	2.49-2.74	2.53-2.74
As	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Be	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cd	<0.55	<0.55	<0.55	<0.55	<0.55	<0.55
Co	<0.10	<0.04	<0.03	<0.02	<0.02	<0.02
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Mo	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ni	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Se	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Pb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Sn	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
V	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Zn	<0.04-0.04	<0.02	<0.40	<0.50	<1.60	<0.02

- All the solid wastes contained elemental sulfur that was co-extracted with the organics by methylene chloride.

- Acid mine drainage, whether field effluent or laboratory extracts of solid samples, tended to be in equilibrium with some type of $CaSO_4$ phase.

- The concentrations of Al and Si in acid mine drainage do not appear to be controlled by the clay minerals or the feldspars in the refuse samples. The laboratory and field solutions tended to be in equilibrium with some type of SiO_2 phase, while the solution chemistry of Al remains unresolved.

- There is some evidence suggesting that acid mine drainage, whether field or laboratory extracts, may equilibrate with maghemite rather than an amorphous $Fe(OH)_3$ phase. $Fe(OH)_3$ solubility would over-predict Fe concentrations.

- Extracts generated from samples of spoil banks and a coal gasification waste were not acutely toxic to the crustacean, _Daphnia magna_, fathead minnows (_Pimephales promelas_), green sunfish (_Lepomis cyanellus_), and the snail, _Physa anatina_ whereas, the undiluted extracts produced by a long-term equilibration procedure from all of the coal cleaning wastes studied were acutely toxic to all four test organisms, requiring as much as a 1:1000 dilution to eliminate mortality.

- The nontoxic leachates were essentially neutral in pH and contained low concentrations of accessory elements. The toxic extracts from the coal cleaning wastes were all acidic ($pH < 3.5$) and contained concentrations of other elements that were both significantly correlated to mortality of the organisms and present at levels exceeding recommended water quality standards.

- The most toxic extracts were those with the lowest pH. The most acidic leachates, therefore, had the lowest LC-50 value and required the greatest amounts of dilution to eliminate mortality.

- _Daphnia magna_ was generally considered to be the most sensitive organism in the acute toxicity studies, followed closely by _Pimephales promelas_, then _Lepomis cyanellus_ and _Physa anatina_. The dissolution of the calcium carbonate shell of _Physa_ lent additional buffering capacity to test solution waters, accounting partly, for its greater tolerance to some solutions toxic to other organisms.

- One coal cleaning refuse leachate produced by a large-volume generation procedure for the chronic bioassays was acutely toxic to the test organisms. Another leachate produced by a different refuse sample using the long-term equilibration procedure was toxic, whereas the leachate produced by the large-volume procedure was not toxic, reflecting the differences in the generation procedures, and possibly, sample heterogeneity.

- Concentrations of the nontoxic refuse leachate produced by the large-volume procedure showed no detrimental chronic effects.

- Low concentrations of the toxic refuse leachate produced by the large-volume procedure caused toxic effects: decreased hatchability for *Lepomis cyanellus* and *Pimephales promelas* eggs; increased mortality with chronic exposure for *Lepomis cyanellus*, *Daphnia*, and *Physa*; and reduced weight gain in *Physa*.

- Soluble ferrous iron in the toxic leachate converted to insoluble ferric species when the leachate was diluted. Ferric hydroxide precipitate was the major factor implicated in the physical and physiological effects exhibited by all test organisms subjected to acutely toxic, sublethal concentrations of this leachate.

- Low concentrations of the toxic leachate were shown to affect several life stages and species of aquatic organisms that represent several trophic levels in aquatic ecosystems. Given that the disruption of a single element in an aquatic food chain can have dramatic consequences on an aquatic system, the toxicity of this leachate is demonstrative of the potential effects that this type of waste can have on the aquatic ecosystem, if it enters a receiving water in a natural setting.

RECOMMENDATIONS

- A limitation of this type of project and the earlier work of Griffin et al. (1980), is that single grab samples were used; such samples may or may not be representative of the deposit under study. Recent work by Krapac, Smyth, and Griffin (1983) showed that two refuse piles in southwestern Illinois are heterogeneous with respect to water soluble constituents via laboratory extractions. Similar investigations need to be carried out with more thorough sampling of each type of waste (e.g. refuse, slurry, mine spoils) to gain a more accurate assessment of the environmental impact of coal utilization.

- Laboratory extractions of coal solid wastes resemble field leachates in terms of their prevalent chemical character but may or may not duplicate the chemical composition of leachates quantitatively. Coal by-products and their associated leachates are extremely variable; therefore, it is not recommended that additional work be conducted to attempt to design extraction procedures applicable to all types of coal wastes where the objective is to produce quantitative facsimiles.

- The solubility relationships in both the field leachates and laboratory extracts remains only partially understood. Additional work is needed to characterize both the crystalline and X-ray amorphous phases in the solid phases, particularly at concentration levels below typical X-ray diffractometry detection limits. The computer-assisted model WATEQ2 should not be used indiscriminately in its present form with nondilute systems such as acid mine drainage.

- Coal solid wastes do not appear to contain sufficient amounts of water-soluble organic compounds to pose serious environmental problems. A more complete and quantitative investigation would be useful in evaluating the validity of this conclusion.

- Given the low pH and elemental composition of many coal cleaning waste leachates, these complex fluids should be characterized and treated as potentially toxic-forming substances.

- Current EPA criteria state that 1.0 mg/L Fe is a safe concentration for freshwater aquatic life. These studies suggest a safe concentration of total iron lies between 0.29 and 0.64 mg/L Fe. In light of this research and other studies (Smith et al., 1979) further investigation into the mechanisms of iron toxicity related to formation of hydroxide precipitates is warranted.

- The continuous-flow mini-diluter system for toxicity testing should not be used with complex solutions that precipitate compounds like ferric hydroxide; the coating effects of this precipitate necessitates a regimental cleaning schedule to maintain proper flow rates. The system is superb for testing non-iron-containing leachates.

- These toxicity tests have been performed using extracts generated in the laboratory. Further tests should be initiated to study leachates collected from actual field locations.

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APPENDIX-A

COMPILATION OF CHEMICAL ANALYSES OF ALL EXTRACTS

Table A-1. Chemical composition of extracts generated from samples of WSNG (concentrations in mg/L).

	Extraction procedures.					
	ASTM-A[2]	ASTM-B[2]	EP[2]	CAP[2]	LTE[3]	LVG[4]
pH	3.15	4.25	3.24	2.92	2.66	3.29
Eh (mV)[5]	+551	+439	+578	+500	+686	+500
EC (dSm^{-1})	3.0	5.5	1.2	3.5	3.4	9.4
Al	18.7	8.68	3.20	21.9	41.9	115
As	<0.25	<0.07	0.13	0.35	0.57	10.7
Ba	<0.01	Si[6]	<0.01	<0.01	<0.001	<0.001
Be	0.03	0.02	0.01	0.03	0.03	0.2
Ca	264	258	48.9	231	262	416
Cd	0.06	0.05	0.07	0.39	0.48	1.4
Cl	1.6	2.7	1.9	1.8	6.5	-[1]
Cr	<0.06	<0.01	<0.02	<0.02	0.09	<0.01
Cu	<0.29	0.03	<0.003	<0.003	0.03	<0.004
F	3.6	1.3	0.8	3.6	-[1]	-[1]
Fe	629	419	151	684	623	3825
K	<11.3	10.9	2.04	5.71	7.21	6.68
Mg	55.4	58.0	11.8	52.3	49.8	497
Mn	5.63	6.00	0.99	4.96	4.73	Si[6]
Mo	<0.07	<0.01	<0.03	<0.03	<0.02	<0.01
Na	27	1147	<0.94	<0.94	<0.55	<2.6
NH$_4$	1.9	1.4	-[1]	-[1]	-[1]	-[1]
Ni	2.48	2.37	0.44	2.31	1.95	13.4
Pb	<0.37	<0.01	<0.01	<0.03	<0.01	<0.04
Sb	<0.38	<0.06	<0.02	<0.02	<0.02	<0.03
Se	0.33	<0.05	<0.05	<0.05	<0.06	<0.08
Si	11.1	16.3	<0.12	4.13	143	51.0
Sn	<0.10	<0.02	<0.06	<0.06	<0.05	<0.04
SO$_4$	2007	2067	897	3022	3042	10,436
V	0.06	0.02	<0.12	0.30	<0.02	Si[6]
Zn	1.36	1.42	0.70	1.47	5.43	54.0

[1] not determined.

[2] average of three replicates.

[3] sample taken after 147 days of equilibration.

[4] sample taken after 133 days of leaching.

[5] relative to normal hydrogen electrode.

[6] concentration could not be determined due to spectral interferences.

Table A-2. Chemical composition of extracts generated from sample of WSOG (concentrations in mg/L).

	Extraction procedures				
	ASTM-A^2	ASTM-B^2	EP^2	CAP^2	LTE^3
pH	1.75	2.18	2.12	1.62	1.92
Eh (mV)^4	+655	+647	664	+655	695
EC (dSm^{-1})	17.7	11.9	6.3	17.4	10.9
Al	384	214	42.9	180	69.8
As	<0.01	1.77	0.71	2.65	Si^5
Ba	<0.01	Si^5	<0.01	<0.01	0.006
Be	0.01	0.01	<0.01	<0.006	0.01
Ca	287	193	50.2	249	123
Cd	0.15	Si^5	0.42	2.28	1.26
Cl	6.5	2.5	<1.0	2.0	2.9
Cr	Si^5	<0.01	<0.02	<0.02	0.10
Cu	<0.29	<0.03	<0.53	Si^5	0.51
F	<0.5	<0.5	<0.5	<0.5	<0.5
Fe	5483	3544	787	2434	2552
K	36.9	18.2	9.01	32.4	52.7
Mg	15.1	10.6	2.19	9.61	3.26
Mn	Si^5	2.64	Si^5	Si^5	<0.05
Mo	<0.07	<0.01	<0.03	<0.03	<0.02
Na	<27	1038	<0.84	<0.94	<0.55
NH$_4$	<1.0	<1.0	–^{1}	–^{1}	–^{1}
Ni	Si^2	<0.01	<0.01	<0.01	0.34
Pb	<0.01	<0.06	0.61	<0.01	1.67
Sb	<0.38	<0.06	0.06	<0.02	<0.02
Se	<0.33	<0.05	<0.05	<0.05	<0.06
Si	23.1	20.9	<0.08	11.8	103.1
Sn	<0.10	<0.02	<0.05	<0.06	<0.05
SO$_4$	18,782	12,797	4115	17,910	8721
V	<0.01	0.84	0.37	2.11	<0.08
Zn	0.38	1.22	0.10	0.47	Si^5

[1] not determined.

[2] average of three replicates.

[3] sample taken after 21 weeks of equilibration.

[4] relative to normal hydrogen electrode.

[5] could not be determined due to spectral interferences.

Table A-3. Chemical composition of extracts generated from samples of OBG (concentrations in mg/L).

	Extraction procedures					
	ASTM-A[2]	ASTM-B[2]	EP[2]	CAP[2]	LTE[3]	LVG[4]
pH	3.12	4.27	3.49	3.06	3.27	4.68
Eh (mV)[5]	+644	+566	+655	+638	+797	+591
EC (dSm^{-1})	3.0	5.7	1.6	3.0	2.2	2.3
Al	158	49.7	22.5	120	64.5	2.21
As	<0.01	<0.07	0.08	0.31	<0.14	<0.06
Ba	0.02	0.03	<0.01	0.01	0.004	<0.001
Be	0.01	<0.001	<0.01	<0.006	0.006	<0.001
Ca	754	632	246	546	458	567
Cd	0.05	0.03	0.01	0.04	0.02	<0.02
Cl	12.7	11.9	1.4	7.1	15.8	-[1]
Cr	<0.06	0.02	<0.02	<0.02	<0.02	<0.01
Cu	<0.29	<0.03	0.01	0.02	0.01	<0.004
F	3.7	2.1	0.7	2.9	-[1]	-[1]
Fe	12.5	4.46	2.23	13.2	0.21	0.08
K	<1.1	<2.4	<0.2	<0.2	0.44	<0.80
Mg	71.9	67.8	13.4	58.7	25.3	36.8
Mn	7.64	5.85	1.31	5.44	2.35	3.55
Mo	<0.07	<0.01	<0.02	<0.03	<0.02	<0.01
Na	<1.7	1282	<0.80	<0.94	3.60	4.63
NH$_4$	<1.0	1.0	-[1]	-[1]	-[1]	-[1]
Ni	0.43	0.27	0.07	0.30	0.22	0.05
Pb	<0.37	<0.06	<0.02	<0.02	<0.01	<0.04
Sb	<0.38	<0.06	<0.02	<0.02	<0.02	<0.03
Se	<0.33	<0.05	0.05	<0.05	<0.06	<0.08
Si	13.7	16.8	0.98	9.26	51.2	14.1
Sn	<0.10	<0.02	<0.04	<0.06	<0.05	<0.04
SO$_4$	2153	2253	755	2179	1383	1595
V	<0.20	<0.02	<0.08	<0.12	<0.06	<0.05
Zn	11.5	6.78	2.31	7.87	4.59	0.88

[1] not determined.

[2] average of three replicates.

[3] sample taken after 147 days of equilibration.

[4] sample taken after 150 days of leaching.

[5] relative to normal hydrogen electrode.

Table A-4. Chemical composition of extracts generated from samples of the WSSL (concentrations in mg/L).

	Extraction procedures				
	ASTM-A[2]	ASTM-B[2]	EP[2]	CAP[2]	LTE[3]
pH	2.43	3.88	2.81	2.48	2.24
Eh (mV)[4]	+636	+448	+631	+613	+855
EC (dSm^{-1})	5.6	6.4	2.1	5.4	4.6
Al	63.5	37.0	11.2	70.1	27.4
As	0.42	0.17	0.23	0.86	0.58
Ba	<0.02	<0.01	<0.01	<0.01	0.002
Be	0.04	0.03	<0.01	0.03	0.02
Ca	188	155	31.3	169	60.4
Cd	0.14	0.16	0.13	0.94	0.64
Cl	5.2	2.2	<1.0	1.5	<1.0
Cr	<0.11	<0.08	<0.02	<0.05	<0.02
Cu	<0.29	<0.03	0.14	Si[5]	0.58
F	2.0	<0.5	<0.5	<0.5	-[1]
Fe	1411	965	264	1274	971
K	<11.3	<2.4	0.26	0.31	0.60
Mg	89.3	98.6	15.6	84.5	32.5
Mn	19.3	19.2	2.66	16.3	6.42
Mo	<0.07	<0.01	<0.03	<0.03	<0.02
Na	<27	1184	<0.94	<0.94	<0.94
NH_4	<1.0	<1.0	-[1]	-[1]	-[1]
Ni	2.28	2.01	0.28	1.65	0.91
Pb	<0.37	<0.06	<0.02	<0.02	0.01
Sb	0.38	<0.06	0.10	<0.02	<0.02
Se	<0.33	<0.05	0.05	0.05	<0.06
Si	11.2	16.8	0.08	2.62	55.2
Sn	<0.10	<0.02	<0.06	<0.06	<0.05
SO_4	5135	2670	516	5934	3001
V	0.28	<0.08	0.09	0.83	<0.08
Zn	7.67	8.09	1.25	6.57	2.99

[1] not determined.

[2] average of three replicates.

[3] sample taken after 147 days of equilibration.

[4] relative to normal hydrogen electrode.

[5] could not be determined due to spectral interferences.

Table A-5. Chemical composition of extracts generated from samples of DMNS (concentrations in mg/L).

	Extraction procedures				
	ASTM-A[2]	ASTM-B[2]	EP[2]	CAP[2]	LTE[3]
pH	6.94	5.41	5.19	6.14	7.56
Eh (mV)[4]	+535	+476	+503	+497	+545
EC (dSm^{-1})	1.0	7.0	1.3	1.6	0.8
Alkalinity	107	–[1]	–[1]	–[1]	–[1]
Al	<0.88	<0.11	<0.08	<0.08	<0.07
As	<0.25	<0.07	<0.04	<0.04	<0.07
Ba	0.04	0.26	0.06	0.06	0.02
Be	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	165	1238	197	323	144
Cd	<0.03	<0.01	<0.01	<0.01	<0.01
Cl	2.9	3.1	<1.0	2.3	2.1
Cr	<0.06	<0.01	<0.02	<0.02	<0.02
Cu	<0.29	<0.03	<0.01	<0.01	<0.01
F	<0.05	<0.05	<0.05	<0.05	–[1]
Fe	0.07	<0.19	<0.07	<0.07	<0.05
K	<11.3	12.7	3.24	10.1	6.30
Mg	37.6	113	19.8	46.2	25.5
Mn	2.09	24.4	3.93	6.14	0.15
Mo	<0.07	<0.01	<0.03	<0.03	<0.02
Na	<27	1155	1.82	7.06	3.94
NH_4	<1.0	1.1	–[1]	–[1]	–[1]
Ni	<0.06	0.52	0.07	0.14	<0.05
Pb	<0.37	<0.06	<0.02	<0.02	<0.01
Sb	<0.38	<0.06	<0.02	<0.02	<0.02
Se	<0.33	0.05	<0.05	<0.05	<0.06
Si	3.07	14.8	0.31	2.96	3.45
Sn	<0.10	0.06	<0.06	<0.06	<0.05
SO_4	509	440	86	474	427
V	<0.02	<0.02	<0.12	<0.12	<0.06
Zn	<0.20	0.27	0.26	<0.07	0.33

[1] not determined.

[2] average of three replicates.

[3] sample taken after 147 days of equilibration.

[4] relative to normal hydrogen electrode.

Table A-6. Chemical composition of extracts generated from samples of DMOS (concentrations in mg/L).

	Extraction procedures				
	ASTM-A[2]	ASTM-B[2]	EP[2]	CAP[2]	LTE[3]
pH	7.57	5.64	5.07	6.24	7.77
Eh (mV)[4]	+494	+495	+577	+491	+536
EC (dSm^{-1})	0.6	7.3	1.5	1.5	0.57
Alkalinity	67	–[1]	–[1]	–[1]	80
Al	<0.88	<0.11	<0.08	<0.08	<0.07
As	<0.25	<0.07	<0.04	<0.04	<0.07
Ba	0.04	0.62	0.18	0.11	0.04
Be	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	96.9	1320	259	271	67.0
Cd	<0.03	<0.01	<0.01	<0.01	<0.01
Cl	3.2	3.6	<1.0	2.4	4.1
Cr	<0.06	<0.01	<0.02	<0.02	<0.02
Cu	<0.29	<0.03	<0.01	<0.01	<0.01
F	0.7	0.5	<0.5	<0.5	–[1]
Fe	<0.06	1.44	<0.07	<0.07	<0.05
K	<11.3	8.1	2.33	4.97	2.59
Mg	26.4	177	40.9	58.0	21.5
Mn	<0.05	7.06	1.38	0.67	<0.01
Mo	<0.07	<0.01	<0.03	<0.03	0.05
Na	<27	1182	2.13	9.56	5.53
NH_4	<1.0	<1.0	–[1]	–[1]	–[1]
Ni	<0.06	0.10	0.03	<0.02	<0.05
Pb	<0.37	<0.06	0.02	<0.02	<0.01
Sb	<0.38	<0.06	0.03	0.04	<0.02
Se	<0.33	<0.05	<0.05	<0.05	<0.06
Si	4.44	19.3	2.76	7.39	7.25
Sn	<0.10	0.07	0.11	0.08	<0.05
SO_4	315	253	58.3	291	245
V	<0.20	<0.02	<0.12	<0.12	<0.06
Zn	0.18	0.13	0.33	<0.07	0.11

[1] not determined.

[2] average of three replicates.

[3] sample taken after 147 days of equilibration.

[4] relative to normal hydrogen.

Table A-7. Chemical composition of extracts generated from samples of KG (concentrations in mg/L).

	Extraction procedures				
	ASTM-A[2]	ASTM-B[2]	EP[2]	CAP[2]	LTE[3]
pH	8.10	4.86	5.00	6.17	9.02
Eh (mV)[4]	+516	+533	+594	+484	+446
EC (dSm^{-1})	0.6	0.5	0.3	1.2	0.6
Alkalinity	35	-[1]	-[1]	-[1]	88
Al	<0.88	2.87	<0.08	<0.08	<0.07
As	<0.25	<0.07	<0.04	<0.04	<0.07
Ba	0.02	0.20	0.03	0.06	0.004
Be	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	78.8	327	33.3	197	40.8
Cd	<0.03	0.01	<0.01	0.01	<0.01
Cl	2.8	2.6	1.0	2.4	3.6
Cr	<0.06	0.11	<0.02	<0.02	<0.02
Cu	<0.29	1.53	0.11	0.02	<0.01
F	<0.5	<0.5	<0.5	<0.5	-[1]
Fe	0.33	2.53	<0.07	<0.07	<0.05
K	<11.3	12.3	1.51	5.64	4.48
Mg	16.3	187	6.72	59.1	40.8
Mn	<0.05	1.65	0.10	0.44	<0.01
Mo	<0.07	<0.01	<0.03	<0.03	0.12
Na	<27	1192	1.51	5.58	4.00
NH_4	<1.0	<1.0	-[1]	-[1]	-[1]
Ni	<0.06	3.00	0.40	1.18	<0.05
Pb	<0.37	<0.06	<0.02	<0.02	<0.01
Sb	<0.38	<0.06	<0.02	<0.02	<0.02
Se	<0.33	<0.05	<0.05	<0.05	0.06
Si	4.19	39.6	1.41	9.82	7.06
Sn	0.10	0.03	<0.06	<0.06	<0.05
SO_4	251	266	85	267	314
V	<0.20	<0.02	<0.12	<0.12	<0.06
Zn	0.09	0.70	0.39	0.09	0.42

[1] not determined.

[2] average of three replicates.

[3] sample taken after 147 days of equilibration.

[4] relative to normal hydrogen electrode.

APPENDIX-B

INTERELEMENT INTERFERENCES IN INDUCTIVELY COUPLED ARGON PLASMA (ICAP) APPLIED TO HIGH-IRON SOLUTIONS

W. R. Roy and I. G. Krapac

Argon supported inductively coupled plasma (ICAP) is among the state-of-the-art analytical methods for multielemental analyses. Quantitative simultaneous elemental determinations can be quickly made from aqueous solutions. These capabilities include measurements of constituents such as arsenic or boron, which are not easily performed by conventional atomic absorption or emission techniques at trace levels.

Complex solutions such as the high-iron laboratory extracts of the coal solid wastes yielded spectral interferences that greatly hindered the determination of certain trace elements. Iron has many emission lines, many of which lie close to the primary or international spectral lines of other elements. This situation is illustrated in figure B-1. The ICAP used in this study (Jarrell-Ash 975 ICAP AtomComp) uses the 259.99 nm wavelength for Fe and the 238.89 nm wavelength for Co; however, there are two iron emission lines at 238.863 nm and 238.940 nm. The spectral band pass of the exit slit is typically 0.03 nm. This means that the detector views a wavelength region of approximately 0.03 nm on either side of the analytical wavelength. In other words, the detector cannot resolve signals emanating from the cobalt line from those coming from the near-by iron lines as suggested by figure B-1. As the iron in solution increases, so will its addition to the cobalt signal, producing a greater apparent concentration of Co. While Co was the element most susceptible to spectral interferences by iron, several other elements were also influenced by the presence of iron (table B-1), aluminum, and silicon. The magnitude of the apparent concentrations depends on the concentration of the interfering element and specific wavelengths studied. Ediger et al. (1980) found that apparent concentrations of Cr ranged from 0.1 to 0.8 mg/L using a 1000 mg/L Fe solution at wavelengths ranging from 205.55 to 284.32 nm for the determination of Cr.

Spectral interferences are not unique to ICAP but are common problems in any spectroscopic technique. To overcome this problem in ICAP spectroscopy, empirical correction factors are derived from single-element solutions at different concentrations as outlined by Marciello and Ward (1978). These factors are used, via computer software, to subtract out artifact emissions generated by major aqueous species that enhance the emission spectra of other constituents at trace levels. These correction factors vary from instrument to instrument and many such factors have been reported and used in generating trace constituent data.

Table B-1. Interelement interferences generated by iron at a concentration of 100 mg/L Fe.

Element effected	Wave length (nm)	Apparent concentration (mg/L)	Typical detection limit[1] (mg/L)
Co	238.89	2.51	0.003
Al	308.22	0.77	0.03
Mn	257.01	0.46	0.007
B	249.77	0.42	0.003
Sn	189.99	0.24	0.03
Ba	455.4	0.11	0.001
Cu	324.75	0.11	0.003
Sb	206.53	0.06	0.01
Pb	220.35	0.06	0.01
Zn	206.20	0.05	0.04
V	292.4	0.03	0.02
Cr	267.72	0.03	0.01
Ni	231.60	0.03	0.02
Be	313.04	0.02	0.003

[1] twice the standard deviation of 10 determinations of an acidified solution of deionized water.

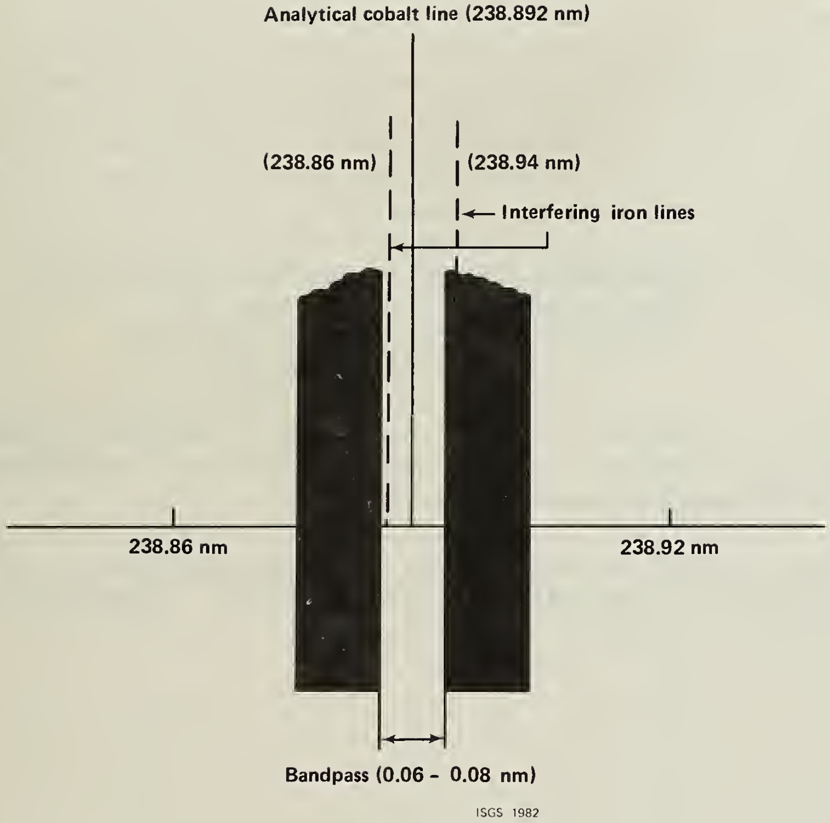

Figure B-1
Relationship between the spectral bandpass, analytical cobalt emission line, and two interfering iron lines.

In the course of the project, correction factors were derived and tested. The apparent concentration of some elements, such as, including cobalt, were also reduced by adjusting the position of the band pass to partially exclude the iron lines relative to the analytical line. Comparisons of corrected concentrations with analytical results from conventional atomic absorption indicated that these empirical correction factors were capable of eliminating the interferences for most of the trace elements. It was found, however, that determinations of V, Mn, B, and Co at concentrations less than 1 mg/L were still unreliable in some solutions containing Fe in concentrations exceeding 100 mg/L. Consequently, data for these elements were frequently omitted in the analytical results reported in this study. Refining the analytical capabilities of ICAP for trace elements in the presence of iron is a current area of study by the authors. It is recommended that determinations of trace constituents in complex solutions be routinely checked by independent methods and/or by different sample preparation procedures.

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APPENDIX-C

COMPILATION OF CHEMICAL ANALYSES OF ACUTE BIOASSAY TEST SOLUTIONS AND CORRELATIONS BETWEEN CONSTITUENT CONCENTRATION AND MORTALITY

Table C-1. Chemical composition of acute bioassay test solutions generated from OBG waste and the correlations between the concentrations of various chemical constituents and mortality in *Daphnia magna*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r^c
pH_i	4.9 - 7.1	6.5 - 9.0[d]	0.707	-0.84 (0.001)
pH_f	5.0 - 7.7	6.5 - 9.0[d]	0.097	-0.93 (0.001)
Al	<0.06 - 0.87	1.0	0.069	0.75 (0.001)
As	<0.04	0.05	----	----
B	<0.04 - 0.22	25	<0.001	0.77 (0.001)
Ba	<0.001 - 0.006	2.5	<0.001	0.18
Be	<0.001 - 0.006	0.055	0.001	0.03
Ca	15.5 - 49.3	16	0.010	0.76 (0.001)
Cd	<0.08	0.001	0.011	0.04
Cr	<0.01	0.25	0.012	-0.31
Cu	<0.004	0.05	0.008	0.21
Fe	<0.02	0.25	----	----
Mg	6.6 - 8.69	87	0.001	0.51 (0.001)
Mn	<0.005 - 0.250	0.1	0.004	0.77 (0.001)
Mo	<0.01	7	----	----
Ni	<0.01 - 0.03	0.01	<0.001	0.42 (0.01)
Pb	<0.02	0.05	<0.001	-0.15
Sb	<0.02	0.02	----	----
Se	<0.04	0.25	0.008	0.04
Si	0.90 - 4.97	----	0.017	0.85 (0.001)
Sn	<0.02	----	0.013	-0.15
SO_4	86 - 234	250	----	0.84 (0.01)
V	<0.1	----	----	----
Zn	<0.08 - 1.09	0.1	0.002	0.28 (0.05)

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-2. Chemical composition of acute bioassay test solutions generated from OBG waste and the correlations between the concentrations of various chemical constituents and mortality in *Lepomis cyanellus*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r^c
pH_i	4.8 - 6.8	6.5 - 9.0[d]	0.413	-0.64 (0.001)
pH_f	4.8 - 7.6	6.5 - 9.0[d]	0.001	-0.74 (0.001)
Al	<0.06 - 3.16	1.0	0.331	0.92 (0.001)
As	<0.04	0.05	0.006	-0.03
B	0.05 - 0.38	25	<0.001	0.71 (0.001)
Ba	<0.001 - 0.005	2.5	0.018	0.05
Be	<0.001 - 0.004	0.055	0.030	0.17
Ca	23.1 - 46.3	16	0.002	0.67 (0.001)
Cd	<0.003	0.001	----	----
Cr	<0.02	0.25	<0.002	-0.12
Cu	<0.004	0.05	0.018	0.35 (0.05)
Fe	<0.02 - 0.09	0.25	0.058	0.36 (0.01)
Mg	6.66 - 9.68	87	0.022	0.57 (0.001)
Mn	0.09 - 0.331	0.1	0.016	0.73 (0.001)
Mo	<0.02	7	0.009	0.04
Ni	0.01 - 0.04	0.01	0.002	0.51 (0.001)
Pb	<0.06	0.05	----	----
Sb	<0.04	0.2	0.002	-0.03
Se	<0.04	0.25	0.003	0.12
Si	1.69 - 7.72	----	0.003	0.77 (0.001)
Sn	<0.02	----	0.014	-0.13
SO_4	102 - 267	250	----	0.96 (0.001)
V	<0.1	----	----	----
Zn	0.25 - 2.62	0.1	0.011	0.15

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-3. Chemical composition of acute bioassay test solutions generated from OBG waste and the correlations between the concentrations of various chemical constituents and mortality in *Pimephales promelas*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r[c]
pH_i	5.0 - 6.7	6.5 - 9.0[d]	0.673	-0.82 (0.001)
pH_f	5.0 - 7.5	6.5 - 9.0[d]	0.115	-0.93 (0.001)
Al	<0.06 - 0.96	1.0	0.058	0.63 (0.001)
As	<0.04	0.05	----	----
B	<0.04 - 0.17	25	<0.001	0.52 (0.01)
Ba	<0.004	2.5	0.006	0.26
Be	<0.001	0.055	----	----
Ca	27.0 - 48.6	16	0.013	0.58 (0.001)
Cd	<0.08	0.001	0.003	0.00
Cr	<0.01	0.25	0.014	0.26
Cu	<0.004	0.05	0.005	0.26
Fe	<0.04	0.25	----	----
Mg	7.44	87	0.051	-0.02
Mn	0.106 - 0.299	0.1	0.012	0.69 (0.001)
Mo	<0.01	7	----	----
Ni	<0.01 - 0.03	0.01	0.005	0.78 (0.001)
Pb	<0.02	0.05	----	----
Sb	<0.04	0.2	----	----
Se	<0.04	0.25	----	----
Si	1.67	----	0.011	0.75 (0.001)
Sn	<0.02	----	----	----
SO_4	91 - 173	250	----	----
V	<0.1	----	----	----
Zn	<0.01 - 1.33	0.1	0.008	0.54

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-4. Chemical composition of acute bioassay test solutions generated from OBG waste and the correlations between the concentrations of various chemical constituents and mortality in *Physa anatina*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r[c]
pH_i	4.6 - 4.8	6.5 - 9.0[d]	0.118	-0.34 (0.05)
pH_f	4.8 - 5.1	6.5 - 9.0[d]	0.023	-0.32 (0.05)
Al	0.69 - 2.73	1.0	0.182	0.66 (0.001)
As	<0.06	0.05	----	----
B	0.27 - 0.47	25	0.208	0.39 (0.01)
Ba	<0.02	2.5	0.028	0.46 (0.01)
Be	<0.02	0.055	----	----
Ca	61.0 - 73.1	16	0.033	0.26
Cd	<0.01	0.001	0.007	0.48 (0.01)
Cr	<0.02	0.25	0.116	0.36 (0.05)
Cu	<0.01 - 0.04	0.05	0.041	-0.06
Fe	<0.02 - 0.08	0.25	0.085	0.31 (0.05)
Mg	9.20 - 10.5	87	<0.005	0.37 (0.05)
Mn	0.3 - 0.4	0.1	0.017	0.47 (0.01)
Mo	<0.02	7	0.033	0.20
Ni	0.03 - 0.05	0.01	<0.001	0.47 (0.01)
Pb	<0.02	0.05	----	----
Sb	<0.02	0.02	0.027	-0.16
Se	<0.05	0.25	<0.001	0.21
Si	5.74	----	0.006	0.44 (0.01)
Sn	<0.02	----	----	----
SO_4	245 - 315	250	----	----
V	<0.03	----	----	----
Zn	0.52 - 1.40	0.1	0.013	0.51 (0.001)

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-5. Chemical composition of acute bioassay test solutions generated from WSNG waste and the correlations between the concentrations of various chemical constituents and mortality in *Lepomis cyanellus*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r[c]
pH_i	4.0 - 5.2	6.5 - 9.0[d]	0.580	-0.76 (0.001)
pH_f	3.9 - 5.6	6.5 - 9.0[d]	<0.001	-0.82 (0.001)
Al	<0.04 - 1.20	1.0	0.179	0.93 (0.001)
As	<0.06	0.05	0.069	-0.26
B	<0.08	25	----	----
Ba	<0.01	2.5	0.018	-0.03
Be	<0.02	0.055	0.010	0.26
Ca	13.2 - 16.5	16	0.002	0.72 (0.001)
Cd	<0.01	0.001	0.014	0.26
Cr	<0.02	0.25	----	----
Cu	<0.02	0.05	0.031	0.54 (0.01)
Fe	0.38 - 1.10	0.25	0.047	0.90 (0.001)
Mg	7.71 - 8.33	87	0.027	0.73 (0.001)
Mn	0.11 - 0.17	0.1	0.001	0.76 (0.001)
Mo	<0.02	7	----	----
Ni	0.04 - 0.06	0.01	0.015	0.72 (0.001)
Pb	<0.04	0.05	----	----
Sb	<0.04	0.02	----	----
Se	<0.04	0.25	----	----
Si	1.30 - 2.08	----	<0.001	0.81 (0.001)
Sn	<0.02	----	----	----
SO_4	88 - 128	250	----	0.83 (0.05)
V	<0.04	----	----	----
Zn	0.07 - 1.33	0.1	0.003	0.03

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-6. Chemical composition of acute bioassay test solutions generated from WSNG waste and the correlations between the concentrations of various chemical constituents and mortality in *Pimephales promelas*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r[c]
pH_i	5.0 - 5.7	6.5 - 9.0[d]	0.219	-0.47 (0.001)
pH_f	5.3 - 7.1	6.5 - 9.0[d]	0.122	-0.80 (0.001)
Al	<0.04 - 0.36	1.0	0.001	0.55 (0.001)
As	<0.06	0.05	----	----
B	<0.08	25	0.018	0.20
Ba	<0.01	2.5	----	----
Be	<0.02	0.055	----	----
Ca	12.1 - 15.6	16	0.011	0.23
Cd	<0.01	0.001	----	----
Cr	<0.02	0.25	----	----
Cu	<0.03	0.05	0.047	0.51 (0.001)
Fe	<0.08	0.25	0.130	0.44 (0.001)
Mg	6.31 - 8.54	87	0.105	-0.01
Mn	0.07 - 0.16	0.1	0.010	0.38 (0.01)
Mo	<0.03	7	----	----
Ni	<0.02 - 0.05	0.01	0.021	0.10
Pb	<0.03	0.05	0.090	-0.30
Sb	<0.05	0.2	----	----
Se	<0.05	0.25	----	----
Si	0.99 - 1.50	----	0.010	-0.05
Sn	<0.03	----	0.013	0.18
SO_4	83 - 92	250	----	----
V	<0.03	----	----	----
Zn	0.07 - 1.07	0.1	0.093	0.45 (0.001)

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-7. Chemical composition of acute bioassay test solutions generated from WSNG waste and the correlations between the concentrations of various chemical constituents and mortality in *Physa anatina*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r[c]
pH_i	3.5 - 4.3	6.5 - 9.0[d]	0.267	-0.52 (0.001)
pH_f	4.3 - 6.0	6.5 - 9.0[d]	0.015	-0.66 (0.001)
Al	<0.04 - 1.63	1.0	0.242	0.93 (0.001)
As	<0.06	0.05	----	----
B	<0.07 - 0.13	25	0.005	0.64 (0.001)
Ba	0.002 - 0.005	2.5	0.022	0.62 (0.001)
Be	<0.003 - 0.009	0.055	0.198	0.70 (0.001)
Ca	16.9 - 27.3	16	0.015	0.68 (0.001)
Cd	<0.06	0.001	----	----
Cr	<0.01	0.25	0.002	-0.14
Cu	<0.006 - 0.029	0.05	0.018	0.67 (0.001)
Fe	0.26 - 1.63	0.25	0.013	0.87 (0.001)
Mg	7.45 - 9.24	87	0.003	0.64 (0.001)
Mn	0.13 - 0.24	0.1	0.001	0.68 (0.001)
Mo	<0.009	7	----	----
Ni	0.04 - 0.08	0.01	0.001	0.42 (0.05)
Pb	<0.03	0.05	----	----
Sb	<0.02	0.2	0.130	-0.34
Se	<0.06	0.25	----	----
Si	1.54 - 2.90	----	<0.001	0.71 (0.001)
Sn	<0.03	----	----	----
SO_4	104 - 141	250	----	0.36 (0.05)
V	<0.06	----	----	----
Zn	0.11 - 0.84	0.1	0.011	0.15

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water (U.S. EPA, 1976).

Table C-8. Chemical composition of acute bioassay test solutions generated from WSOG waste and the correlations between the concentrations of various chemical constituents and mortality in *Daphnia magna*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r^c
pH_i	4.9 - 7.0	6.5 - 9.0[d]	0.672	-0.82 (0.001)
pH_f	4.9 - 7.8	6.5 - 9.0[d]	0.080	-0.94 (0.001)
Al	<0.06 - 0.18	1.0	<0.001	0.41 (0.01)
As	<0.04	0.05	----	----
B	<0.04	25	----	----
Ba	<0.001	2.5	<0.001	0.04
Be	<0.001	0.055	0.020	-0.28 (0.05)
Ca	7.70 - 9.16	16	0.002	0.26 (0.05)
Cd	<0.01	0.001	----	----
Cr	<0.01	0.25	----	----
Cu	<0.004	0.05	----	----
Fe	<0.02 - 10.1	0.25	0.029	0.83 (0.001)
Mg	6.30 - 6.84	87	0.013	0.09
Mn	<0.005 - 0.042	0.1	<0.001	0.32 (0.05)
Mo	<0.01	7	----	----
Ni	<0.01	0.01	0.006	-0.03
Pb	<0.02	0.05	0.086	-0.15
Sb	<0.02	0.2	----	----
Se	<0.04	0.25	0.004	-0.15
Si	0.40 - 40	----	0.002	0.38 (0.01)
Sn	<0.02	----	----	----
SO_4	52 - 85	250	----	0.73 (0.01)
V	<0.1	----	<0.001	0.01
Zn	<0.01 - 0.37	0.1	0.015	0.06

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water (U.S. EPA, 1976).

Table C-9. Chemical composition of acute bioassay test solutions generated from WSOG waste and the correlations between the concentrations of various chemical constituents and mortality in *Lepomis cyanellus*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r^c
pH_i	4.6 - 5.9	6.5 - 9.0[d]	0.556	-0.75 (0.001)
pH_f	4.5 5.5	6.5 - 9.0[d]	0.014	-0.63 (0.001)
Al	<0.06 - 0.60	1.0	0.059	0.71 (0.001)
As	<0.06	0.05	0.035	0.39 (0.05)
B	<0.08	25	0.022	0.28
Ba	<0.002	2.5	0.044	0.39 (0.05)
Be	<0.003	0.055	0.001	0.60 (0.001)
Ca	8.33 - 9.18	16	0.007	0.70 (0.001)
Cd	<0.006	0.001	----	----
Cr	<0.01	0.25	----	----
Cu	<0.006 - 0.017	0.05	0.066	0.42 (0.05)
Fe	3.92 - 11.3	0.25	0.004	0.87 (0.001)
Mg	6.12 - 6.82	87	0.008	0.09
Mn	0.011 - 0.037	0.1	0.035	0.67 (0.001)
Mo	<0.009	7	----	----
Ni	<0.02	0.01	0.083	0.40 (0.05)
Pb	<0.03 - 0.08	0.05	0.024	0.49 (0.001)
Sb	<0.04	0.2	----	----
Se	<0.06	0.25	----	----
Si	0.25 - 0.54	----	0.006	0.75 (0.001)
Sn	<0.04	----	----	----
SO_4	73 - 101	250	----	----
V	<0.06	----	0.015	0.28
Zn	<0.01 - 0.15	0.1	<0.001	0.15

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-10. Chemical composition of acute bioassay test solutions generated from WSOG waste and the correlations between the concentrations of various chemical constituents and mortality in *Pimephales promelas*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r^c
pH_i	4.7 - 5.4	6.5 - 9.0[d]	0.349	-0.59 (0.01)
pH_f	4.9 - 6.7	6.5 - 9.0[d]	0.161	-0.87 (0.001)
Al	<0.06	1.0	0.058	0.34
As	<0.06	0.05	----	----
B	<0.07	25	----	----
Ba	<0.004	2.5	<0.001	-0.28
Be	<0.003	0.055	----	----
Ca	7.99 - 9.70	16	0.010	0.37
Cd	<0.006	0.001	----	----
Cr	<0.01	0.25	----	----
Cu	<0.006	0.05	<0.001	-0.19
Fe	<0.02 - 0.08	0.25	0.012	-0.14
Mg	5.75 - 7.31	87	0.015	-0.28
Mn	<0.008	0.1	----	----
Mo	<0.009	7	----	----
Ni	<0.01	0.01	----	----
Pb	<0.03 - 0.04	0.05	0.105	0.62 (0.01)
Sb	<0.02	0.2	----	----
Se	<0.06	0.25	----	----
Si	0.20 - 0.38	----	0.171	0.33
Sn	<0.03	----	----	----
SO_4	69 - 77	250	----	----
V	<0.06	----	----	----
Zn	0.03 - 0.79	0.1	0.068	0.07

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-11. Chemical composition of acute bioassay test solutions generated from WSOG waste and the correlations between the concentrations of various chemical constituents and mortality in *Physa anatina*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r^c
pH_i	3.4 - 4.9	6.5 - 9.0[d]	0.147	-0.48 (0.001)
pH_f	3.9 - 6.2	6.5 - 9.0[d]	0.018	-0.74 (0.001)
Al	<0.06 - 1.13	1.0	0.364	0.87 (0.001)
As	<0.06	0.05	0.002	-0.02
B	<0.07	25	----	----
Ba	<0.003 - 0.009	2.5	<0.001	0.38 (0.01)
Be	<0.001 - 0.009	0.055	0.040	0.35 (0.05)
Ca	12.3 - 19.8	16	0.003	0.73 (0.001)
Cd	<0.006	0.001	----	----
Cr	<0.01 - 0.02	0.25	0.060	0.34 (0.05)
Cu	<0.006 - 0.022	0.05	<0.001	0.50 (0.001)
Fe	4.15 - 18.5	0.25	0.002	0.72 (0.001)
Mg	6.69 - 7.28	87	0.005	0.70 (0.001)
Mn	0.013 - 0.065	0.1	0.019	0.49 (0.001)
Mo	<0.009	7	----	----
Ni	<0.02	0.01	0.022	0.24
Pb	<0.03 - 0.08	0.05	<0.001	0.27
Sb	<0.02	0.2	0.008	-0.07
Se	<0.06	0.25	----	----
Si	0.34 - 0.88	----	<0.001	0.78 (0.001)
Sn	<0.03	----	----	----
SO_4	83 - 161	250	----	0.83 (0.001)
V	<0.06	----	----	----
Zn	<0.01 - 2.06	0.1	0.147	0.53 (0.001)

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-12. Chemical composition of acute bioassay test solutions generated from WSSL waste and the correlations between the concentrations of various chemical constituents and mortality in *Daphnia magna*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r[c]
pH_i	5.2 - 5.9	6.5 - 9.0[d]	0.252	-0.51 (0.001)
pH_f	5.9 - 7.0	6.5 - 9.0[d]	0.147	-0.78 (0.001)
Al	<0.06	1.0	----	----
As	<0.06	0.05	----	----
B	<0.07	25	----	----
Ba	<0.002 - 0.004	2.5	0.008	0.10
Be	<0.003	0.055	0.034	-0.17
Ca	7.90 - 8.62	16	0.036	0.44 (0.01)
Cd	<0.006 - 0.015	0.001	0.258	0.52 (0.001)
Cr	<0.01	0.25	----	----
Cu	<0.006	0.05	----	----
Fe	<0.08	0.25	0.073	0.26
Mg	1.65 - 2.03	87	0.040	0.22
Mn	0.046 - 0.068	0.1	<0.001	0.51 (0.001)
Mo	<0.009	7	----	----
Ni	<0.01 - 0.02	0.01	0.054	0.31 (0.05)
Pb	<0.03	0.05	----	----
Sb	<0.02	0.2	----	----
Se	<0.06	0.25	----	----
Si	0.21 - 0.52	----	0.001	0.35 (0.05)
Sn	<0.03	----	----	----
SO_4	46 - 74	250	----	----
V	<0.06	----	----	----
Zn	0.01 - 0.10	0.1	0.011	0.22

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-13. Chemical composition of acute bioassay test solutions generated from WSSL waste and the correlations between the concentrations of various chemical constituents and mortality in *Lepomis cyanellus*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r^c
pH_i	3.9 - 5.1	6.5 - 9.0[d]	0.451	-0.67 (0.001)
pH_f	3.9 - 5.8	6.5 - 9.0[d]	<0.001	-0.76 (0.001)
Al	<0.06 - 0.33	1.0	0.364	0.93 (0.001)
As	<0.04	0.05	----	----
B	<0.04	25	0.039	-0.13
Ba	<0.001 - 0.002	2.5	<0.001	-0.25
Be	<0.001	0.055	0.043	-0.14
Ca	8.52 - 9.10	16	<0.001	0.30
Cd	<0.08	0.001	----	----
Cr	<0.03	0.25	----	----
Cu	<0.03	0.05	0.017	0.51 (0.01)
Fe	0.10 - 0.28	0.25	0.021	0.43 (0.05)
Mg	6.82 - 7.12	87	<0.001	0.36 (0.05)
Mn	0.05 - 0.09	0.1	0.046	0.45 (0.05)
Mo	<0.02	7	----	----
Ni	<0.03	0.01	<0.001	0.15
Pb	<0.04	0.05	----	----
Sb	<0.03	0.2	----	----
Se	<0.04	0.25	<0.001	-0.17
Si	0.47 - 0.74	----	0.005	0.73 (0.001)
Sn	<0.02	----	----	----
SO_4	73 - 89	250	----	----
V	<0.03	----	----	----
Zn	<0.01 - 1.51	0.1	0.010	-0.11

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-14. Chemical composition of acute bioassay test solutions generated from WSSL waste and the correlations between the concentrations of various chemical constituents and mortality in *Pimephales promelas*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r^c
pH_i	4.9 - 5.9	6.5 - 9.0[d]	0.348	-0.59 (0.001)
pH_f	5.5 - 7.0	6.5 - 9.0[d]	0.317	-0.89 (0.001)
Al	<0.06	1.0	----	----
As	<0.06	0.05	0.038	-0.16
B	<0.07	25	----	----
Ba	<0.002	2.5	<0.001	-0.02
Be	<0.003	0.055	0.018	-0.04
Ca	8.25 - 9.08	16	0.026	-0.08
Cd	<0.06	0.001	----	----
Cr	<0.02	0.25	0.101	-0.16
Cu	<0.006 - 0.009	0.05	0.032	0.22
Fe	<0.02 - 0.32	0.25	<0.001	-0.31
Mg	6.46 - 7.44	87	<0.001	-0.24
Mn	0.050 - 0.072	0.1	0.063	0.45 (0.05)
Mo	<0.02	7	----	----
Ni	<0.01 - 0.02	0.01	0.028	0.06
Pb	<0.04	0.05	----	----
Sb	<0.03	0.2	----	----
Se	<0.06	0.25	----	----
Si	0.31 - 0.57	----	0.015	0.68 (0.001)
Sn	<0.03	----	----	----
SO_4	70 - 76	250	----	----
V	<0.06	----	----	----
Zn	0.02 - 0.91	0.1	<0.001	-0.06

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).

Table C-15. Chemical composition of acute bioassay test solutions generated from WSSL waste and the correlations between the concentrations of various chemical constituents and mortality in *Physa anatina*.

	Range of concentration in test solutions (mg/L)	Recommended water quality levels (mg/L)[a]	r^2 Change[b]	r[c]
pH_i	3.1 - 3.7	6.5 - 9.0[d]	0.204	-0.45 (0.001)
pH_f	3.2 - 5.0	6.5 - 9.0[d]	0.002	-0.69 (0.001)
Al	<0.06 - 1.01	1.0	0.161	0.90 (0.001)
As	<0.04	0.05	0.037	-0.17
B	<0.04	25	0.047	0.27 (0.05)
Ba	0.001 - 0.007	2.5	0.040	0.68 (0.001)
Be	<0.001	0.055	----	----
Ca	12.4 - 23.6	16	0.029	0.86 (0.001)
Cd	<0.01	0.001	----	----
Cr	<0.01	0.25	----	----
Cu	<0.03	0.05	0.025	0.50 (0.001)
Fe	0.21 - 3.66	0.25	0.222	0.72 (0.001)
Mg	6.25 - 28.2	87	0.001	0.32 (0.05)
Mn	0.09 - 0.245	0.1	0.033	0.25 (0.05)
Mo	<0.02	7	0.002	0.02
Ni	0.01 - 0.04	0.01	0.019	0.74 (0.001)
Pb	<0.04	0.05	----	----
Sb	<0.03	0.2	----	----
Se	<0.04	0.25	0.003	-0.03
Si	0.71 - 2.11	----	0.001	0.85 (0.001)
Sn	<0.02	----	----	----
SO_4	77 - 160	250	----	0.90 (0.001)
V	<0.10	----	0.007	-0.07
Zn	<0.01 - 1.68	0.1	0.081	-0.17

[a] MATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

[b] contribution to multiple regression of chemical composition on mortality.

[c] linear regression value (statistical significance).

[d] from Quality Criteria for Water. (U.S. EPA, 1976).