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GEOCHEMICAL PROPERTIES AND TOXICOLOGICAL EFFECTS ON AQUATIC LIFE OF COAL WASTES

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Final Report

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Southern Illinois University
Carbondale, Illinois 62901

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Southern Illinois University
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ABSTRACT

Seven coal-related waste samples (mining, cleaning, and gasification) were characterized chemically and mineralogically. Laboratory extracts of each sample, using a variety of different extraction methods, were used in both acute and chronic bioassays.

A coal slurry sample (coarse fraction) and two coal cleaning refuse samples were chemically and mineralogically similar, and generated acidic water-waste systems, both in the laboratory and in the field. Acidic laboratory extracts and field samples of acid mine drainage in the area where the solid samples were collected, tended to be in equilibrium with some type of 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. The 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 extractions suggest that some constituents (Al, Fe, SO_4) continued to be released by the acidic wastes after 22 weeks with no apparent associated change in pH.

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

All of the solid wastes contained a variety of organic compounds, many of which 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 fresh-water aquatic organisms; green sunfish (Lepomis cyanellus), 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 while the extracts from the acidic refuse and slurry samples were acutely toxic to all of the organisms. For all cases, pH was significantly correlated to mortality while Al, Fe, Mn, Ni, and Zn were significantly correlated to mortality 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 with the same test organisms were investigated with leachate samples from a relatively unweathered refuse sample and an older, more weathered refuse sample. The unweathered refuse sample generated a leachate that was acutely toxic while the leachate from the weathered refuse sample was not acutely toxic. No detrimental chronic effects were noted in organisms exposed to dilutions of the non-toxic leachate while low concentrations of the acutely toxic leachate produced lower hatchability for the Lepomis cyanellus and Pimephales promelas eggs, increased mortality with chronic exposure for Lepomis cyanellus, Daphnia, Physa, and reduced weight gain for Physa. Dilutions of a toxic, high-Fe leachate resulted in the precipitation of ferric hydroxide that was implicated as the major causative factor accounting for the physical and physiological toxic effects exhibited by all of the test organisms in these acutely sublethal concentrations. The toxicity of this leachate demonstrates the potential effects that these types of wastes can have on the aquatic ecosystem if they enter a receiving water in a natural setting.

SECTION 1

INTRODUCTION

During the late 1970's, shortages of natural gas, fuel oil, and gasoline dramatically demonstrated the need for the increased use of coal by the electric utilities. Predictions vary, but the National Coal Association forecasts an increase in coal usage from 787 million metric tons in 1976 to approximately 1.5 billion metric tons by 1985. However, past and current mining techniques have resulted in various types of coal solid wastes that have potentially harmful impacts on the environment. Moreover, coal conversion via gasification and liquefaction also produce solid wastes that may pose as environmental problems. ERDA (1977) concluded that there is the potential for coal solid wastes to create substantial leaching and re-vegetation problems. Abandoned mine spoil banks and coal preparation wastes pose similar problems (Byer 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 "bog" and 4,300 acres of slurry in Illinois alone. The impact on the aquatic environment of leachates from surface mine spoil banks, solid wastes generated during the cleaning of coal and in the production of synthetic fuels has not been adequately assessed.

This investigation is comprised of interrelated physical, chemical and biological analyses for a broad-based evaluation of the impact of abandoned spoil banks and coal solid wastes on the aquatic environment. The analytical synthesis of the data from this investigation would aid in control technology, development of reclamation and determine 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 practices for reclaimed surface mines (Cairns, 1978). However, in order to maximize the benefits and minimize the adverse effects of mining/reclamation methodologies, it is of mandatory importance 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 coal solid wastes from coal conversion and coal cleaning processes. The solid wastes from coal liquefaction and coal gasification will probably be re-deposited 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 (250 million ft³ of gas/day) gasification plant 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 and 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 pyritic minerals contained in coal solid wastes when 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 the majority of 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 31 of 60 chemical constituents measured in LURGI gasification and H-coal liquefaction wastes presented a potential hazard. Sixteen 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 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 (Vaughan 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 one of the primary post-production impacts to the environment of mineral development (Mason, 1978). Some environmental hazards to aquatic ecosystems related to surface mining have been well documented (Curry and Fowler, 1978). Best known are the problems of 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; Orcigri 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), and no bioassays of spoil bank leachates have been conducted and little is known with regard to chronic effects from any of the various types of coal waste leachates.

Toxicity tests or bioassays represent one of the best approaches for predicting the impacts of land disturbance, mining related wastes, or coal processing and utilization wastes on aquatic life (Preston, 1978). After determining whether or not a leachate or laboratory extract is toxic with bioassays, an analysis of the physico-chemical character of the leachate may identify the potential toxic components of the leachate and aid in the development of control technology and reclamation methodologies.

SECTION 2

CONCLUSIONS

1. 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 with the exception of higher sulfur contents. 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.
2. 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 adequate carbonate minerals to have any appreciable neutralizing influence. Laboratory extracts of the mine spoils tended to be neutral in pH while the Kilngas sample generated alkaline systems.
3. 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 same proximity as where the solid samples were collected.
4. The solid coal wastes contained a variety of organic compounds many of which are included on the EPA Priority Pollutant List. However, these compounds were found to be essentially insoluble in aqueous media.
5. All of the solid wastes contained elemental sulfur which was co-extracted with the organics by methylene chloride.
6. Acid mine drainage, albeit field effluent or laboratory extracts of solid samples tended to be in equilibrium with some type of CaSO_4 phase.

7. The concentrations of Al and Si in acid mine drainage does not appear to be controlled by the clay minerals or the feldspars present 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.
8. There is some evidence suggesting that acid mine drainage, albeit field or laboratory extracts may equilibrate with maghemite rather than an amorphous $\text{Fe}(\text{OH})_3$ phase. $\text{Fe}(\text{OH})_3$ solubility would overpredict Fe concentrations.
9. 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.
10. The non-toxic leachates were essentially neutral in pH and contained low concentrations of accessory elements. The toxic extracts from the coal cleaning wastes were all acidic ($\text{pH} < 3.5$) and contained concentrations of other elements which were both significantly correlated to mortality of the organisms and present at levels which exceeded recommended water quality standards.
11. 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.
12. Daphnia magna was generally considered to be the most sensitive organism in the acute toxicity studies, followed closely by Pimephales promelas, and then Lepomis cyanellus and Physa anatina. The dissolution of the calcium carbonate shell of Physa lent additional buffering capacity to

test solution waters, accounting, in part, for its greater tolerance to some solutions toxic to other organisms.

13. One coal cleaning refuse leachate produced by a large volume generation procedure for the chronic bioassays was acutely toxic to the test organisms; however, another leachate produced by a different refuse sample using the long-term equilibration procedure was toxic while the leachate produced by the large volume procedure was not toxic, reflecting the differences in the generation procedures and possibly, sample heterogeneity.
14. Concentrations of the non-toxic refuse leachate produced by the large volume procedure showed no detrimental chronic effects.
15. Low concentrations of the toxic leachate by the large volume procedure produced refuse leachate caused toxic effects in the forms of 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.
16. Soluble ferrous iron in the toxic leachate converted to insoluble ferric species when the leachate was diluted. The ferric hydroxide precipitate was implicated as the major causative factor to the physical and physiological toxic effects exhibited by all test organisms for acutely sublethal concentrations of this leachate.
17. Low concentrations of the toxic leachate were shown to affect several life stages and species of aquatic organisms which 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 these types of wastes can have on the aquatic ecosystem should they enter a receiving water in a natural setting.

SECTION 3

RECOMMENDATIONS

1. 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. Investigations with emphasis parallel to the topics treated in this project need to be carried out with more thorough sampling of each type of waste (e.g. refuse, slurry, mine spoils, etc.) in order to gain a more accurate assessment of the environmental impact of coal utilization.
2. 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 and thus, 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.
3. 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 non-dilute systems such as acid mine drainage.
4. Coal solid wastes do not appear to contain significant 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.

5. 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.
6. Current EPA criteria state that 1.0 mg Fe/L is a safe concentration for freshwater aquatic life. A safe concentration of total iron in these studies for the protection of freshwater aquatic life, based on concentrations of total iron in solution, is suggested to lie between 0.29 and 0.64 mg Fe/L. 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.
7. The continuous-flow mini diluter system for toxicity testing should not be used with complex solutions that precipitate compounds like ferric hydroxide due to the coating effects of this precipitate which necessitates a regimental cleaning schedule to maintain proper flow rates. The system is superb for testing non-iron-containing leachates.
8. 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.

SECTION 4

METHODS AND MATERIALS

4.1 SAMPLE COLLECTION AND PREPARATION

Seven waste samples produced by coal utilization were collected. These included 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 sample of the Lawson Shale Member, a dark gray Pennsylvanian unit stratigraphically above the Herrin (No. 6) Coal Member. This shale comprises the largest unit of the overburden at the mine. The samples were collected from a vertical section at the strip mine. At the same location, a second spoil sample, DMOS, was taken from a road cut made through an 18 to 22 year old spoil mound, composed of largely the Lawson Shale.

Three 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. A sample of fresh cleaning waste was collected from an active preparation plant (WSNG) that was 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 activities associated with the Herrin Coal Member by shaft methods (Old Ben No. 9 Mine). The source preparation plant is no longer present.

Nineteen liters of solid waste from a Kilngas (KG) deep bed gasifier was supplied by Allis-Chalmers from their pilot plant in Milwaukee, Wisconsin. This operation is of a proprietary nature, therefore the specifications for fuel being used at the time the waste was generated could not be obtained. A description of the Kilngas process is given elsewhere (Illinois Institute of Natural Resources, 1979).

The collection of representative samples from coal refuse and spoil piles is extremely difficult. To take a sample representative of the entire waste pile would have been impractical and beyond the scope of the study. Moreover, sampling procedures leading to the collection of representative samples from waste piles are unknown. Therefore, an effort was made to collect a 25 Kg-sample from each waste pile by visually avoiding obviously anomalous materials.

It was considered more important to divide the collected bulk waste samples into representative subsamples than to attempt to collect an initial sample that would be representative of the entire waste pile.

All of the mining wastes were initially air-dried and ground to pass through a 9.53mm sieve. This sized material was then subdivided using a sample splitter until a series of representative subsamples were collected for each waste. Twelve subsamples for each waste were used for the solubility studies. An additional subsample for each waste was then further ground to pass through a 0.25mm 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 0.1mm to 1.5mm. Prior to analysis of the solid, the material was ground to pass through a 0.25mm sieve and split.

4.2 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). The primary purpose of low temperature ashing is to isolate the desired mineral residue from the organic matter in the samples. Low temperature ashing often facilitates the resolving capabilities of X-ray diffractometry. The samples were ashed on a LFE corporation Model LTA-504 radio-frequency asher. The ashed samples were qualitatively analyzed by X-ray diffraction with a Phillips Norelco X-ray diffractometer using copper K α radiation and a graphite monochromator. Further discussion of the method is given 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 which 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 Saporaschenko et al. (1980)

and Hinckley et al. (1980).

4.3 INORGANIC ANALYTICAL METHODS

Chemical analysis of the samples for Si, Al, Mg, Ca, K, Fe, Ti, and P were done by X-ray fluorescence spectrometry. 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. 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. A detailed discussion of sample preparation, detection limits and procedures for these techniques can be found in Harvey et al. (1983). The sulphur determinations were done by ASTM method D-2492 and total carbon determinations were carried out by ISO method 609-1975E.

Most of the 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 in a Fisher Scientific Company publication by the Jarrell-Ash Division (1978). Sulfate was done turbidimetrically (American Public Health Association, 1975). Alkalinity was determined by titrations with dilute sulfuric acid and oxidation-reduction potential (Eh), pH, and electrical conductance were measured by electrodes (U.S. EPA, 1979).

4.4 ORGANIC ANALYTICAL METHODS

The solid samples were air-dried and ground to pass a 0.25mm screen prior to organic analysis. The solid waste samples and laboratory extracts

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 Fig. 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).

Five liters of aqueous solutions (5 L) were extracted twice at a pH value of 2 and 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 above 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 in the extract that have boiling points between 100° and 300°C . 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°C 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

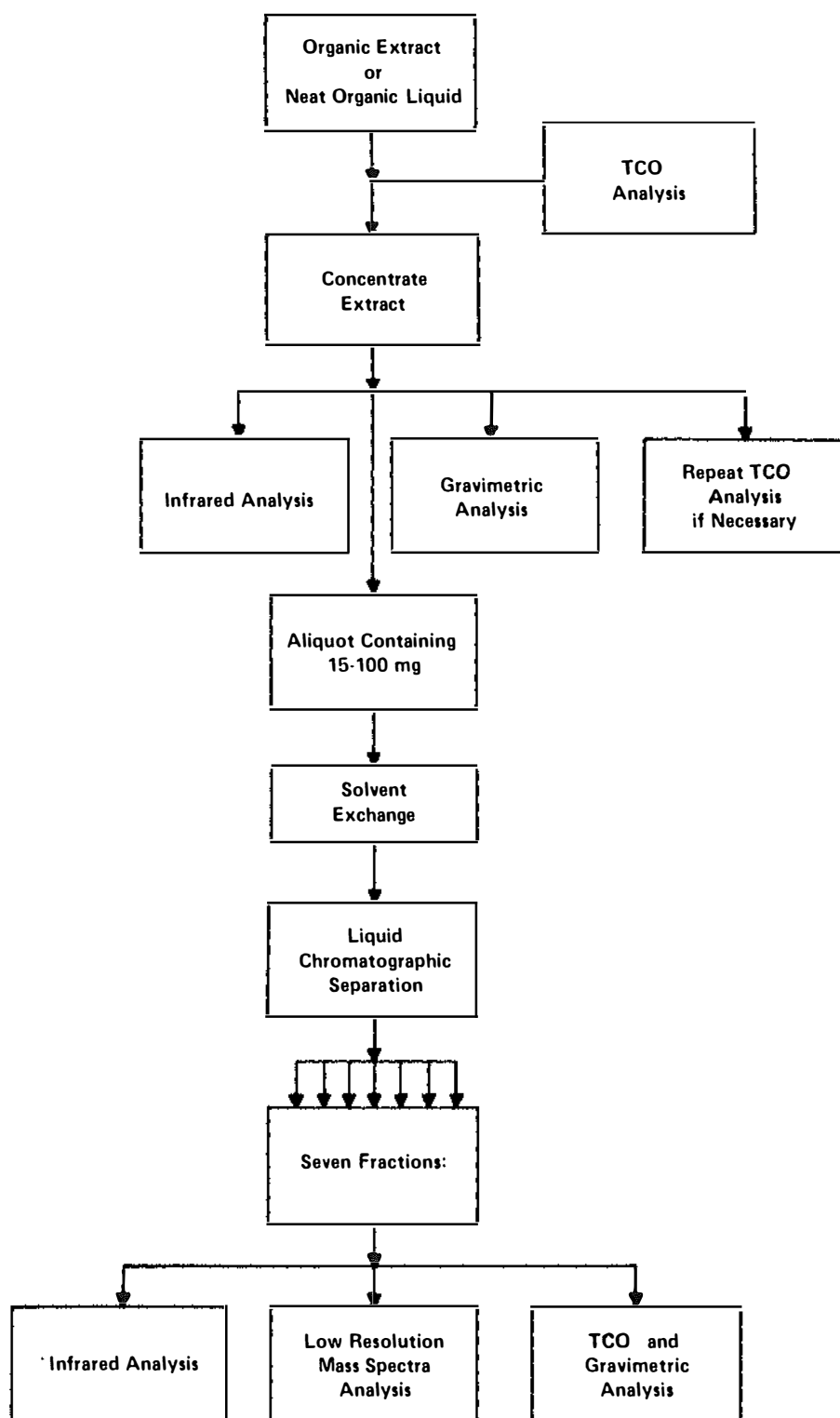


Figure 1. Organic analysis methodology.

material available, the IR spectrum was obtained using a neat smear of the sample between two NaCl plates. Where only smaller (~5 mg) amounts were available, the sample was dissolved in carbon tetrachloride (CCl₄) 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, 60-200 mesh, Grade 950 (Fisher Scientific Company) was used as adsorbent. The adsorbent was cleaned prior to use by sequential Soxhlet extractions with methanol, CH₂Cl₂, and pentane. The adsorbent was activated at 110°C 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, 4.6 x 250 mm HPLC column (Beckman Instruments, Inc., Berkely, 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

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, etc.) 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

phenols, toluene, and four polycyclic aromatic hydrocarbons was prepared and used as a reference standard (Fig. 2).

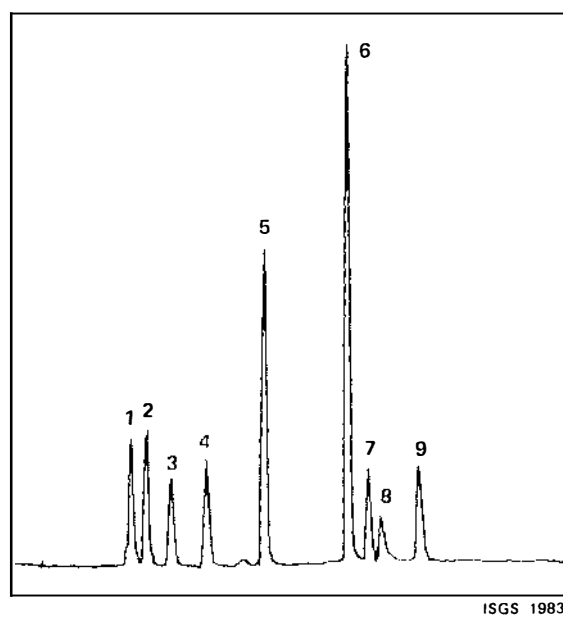


Figure 2. HPLC of a known mixture of phenols and polycyclic aromatic hydrocarbons referenced to toluene. Peak identification: 1. phenol; 2. *p*-cresol; 3. 2,3-dimethylphenol; 4. 2,4,5-trimethylphenol; 5. toluene; 6. phenanthrene; 7. pyrene; 8. chrysene; 9. benzo (α) pyrene.

SECTION 5

MINERALOGICAL CHARACTERIZATION¹

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 itself. Coal preparation wastes consist primarily of shale clasts, fragments, and nodules; pyritic coal; pyrite lenses and nodules; and underclay fragments. Obviously the type of material in mining spoils will be greatly influenced by the local geology at the mining site.

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 of predominantly clay minerals with lesser amounts of quartz, and iron sulfides. They also found marcasite, calcite, and gypsum in some samples existing as minor components. 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 ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) was present in refuse samples WSNG and WSOG

¹Authors: W. R. Roy and R. M. Schuller

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

	WSNG	WSOG	OBG	WSSL	DMNS	DMOS	KG
<u>Nonferrous Minerals</u>							
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		
<u>Ferrous Minerals</u>							
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

and that hematite was present in refuse OBG. Neither of these minerals were identified by Bush et al. (1974, 1975) or Wewerka et al. (1978) in their refuse samples. Griffin et al. (1980) reported a similar masking difficulty which 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 the presence of 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.

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 is largely a reflection of the composition of the Lawson Shale, a micaceous, and calcareous gray shale. While DMNS is made up of entirely the Lawson Shale, visual inspection of hand samples of DMOS revealed pre-mining soils, weathered and unweathered flakes of the Lawson Shale, and carbonate fragments. The mineralogical composition 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 which are 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 which are commonly found in coal fly ash (Roy et al., 1981), another high temperature residue of coal. However, while feldspars appear to be rare in coal fly ash, they were present in the Kilngas waste sample. Griffin et al. (1980) found that Lurgi ash samples were mineralogically similar to coal ashes but that they also contained feldspars. The Mössbauer spectrum was characteristic of a water quenched bottom ash (slag) in that the absorptions were broad and unresolved. Most of the iron may be 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.

SECTION 6

INORGANIC CHEMICAL CHARACTERIZATION¹

6.1 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 that six of the seven wastes were composed of primarily aluminosilicates and 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 while Al_2O_3 ranged from 7.88 percent to 9.66 percent. Comparisons between these three refuse samples and two samples studied by Griffin et al. (1980) and the three samples by Wewerka et al. (1978) suggest that SiO_2 in 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 while SO_3 varied from about 1 percent to nearly 34 percent SO_3 . 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 percent) of the sulfur in WSNG existed as pyritic sulfur while only 0.30 percent was in the form of sulfate sulfur. WSOG is about 20 years old and about 63.4 percent of the S in this sample occurred as pyritic sulfur

¹Author: W. R. Roy

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

	<u>Wewerka et al. (1978)</u>			<u>Griffin et al. (1980)</u>		<u>This work</u>			<u>Range in composition</u>
	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 ₂ O ₃	13.23	9.62	13.91	10.68	18.33	8.36	7.88	9.66	7.88-18.33
Fe ₂ O 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 ₂ O	0.15	0.11	0.40	0.33	0.49	0.14	0.25	0.95	0.11- 0.95
K ₂ O	2.09	2.04	2.53	1.81	3.11	1.98	1.95	2.05	1.81- 3.11
P ₂ O 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

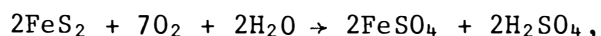
Table 4: Major and minor constituent composition
of the two spoil samples, the slurry
sample, and the Kilngas waste.

	DMNS	DMOS	WSSL	KG	Average coal fly ash composition (Roy and Griffin, 1982)	Slag (Griffin et al., 1980)
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 ₂ O ₃	15.82	13.14	4.41	22.09	23	15.98
Fe ₂ O 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 ₂ O	0.73	0.57	0.14	0.41	1.8	0.80
K ₂ O	4.18	3.54	0.96	3.10	2.0	2.43
P ₂ O 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		-

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

while there was 1.49 percent more sulfate sulfur than the younger WSNB sample. The oldest refuse sample, OBG (about 50 years old) contained only 6.87 percent pyritic sulfur while the majority of the sulfur (88.5 percent) occurred as sulfate compounds. The apparent shift from pyritic forms of sulfur to sulfate forms with the increasing age of the wastes may be due to the more or less continual solubilization and leaching of the pyrite in the refuse piles with time 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) may be written as,



which would account for this apparent trend.

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) ranged from about 6 percent to 0.15 percent. The amount of calcium (as percent Ca) nearly equals the amount of inorganic carbon (as percent CO₃) suggesting that the calcium existed as carbonates. 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 concentrations 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 WSNB, WSOB 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 percent) occurred in pyritic 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 presented in this report may represent the first such published data on this shale. Study of Paleozoic shales in Illinois by the Illinois State Geological Survey include the work by Lamar (1948), Grim, Bradley, and White (1957), and Kosanke et al. (1960) but do not contain analytical data for the Lawson Shale. The stratigraphic equivalent of the shale in Indiana has also not received attention by the Indiana Geological Survey (Shaver et al., 1970). However, it should be noted that there was little stratigraphic control with respect to sampling and 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 was comprised 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 contained a low SiO_2 content (15.51 percent) relative to most geological materials but a SO_3 concentration (10.56 percent) within the range of 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 of the same was also comparable to other high temperature combustion residues (Table 4). Comparisons between the composition of the KG sample (Table 4) and 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 in that the concentrations of some major and minor constituents fell between the ranges in composition established by fly ash and the slag sample.

6.2 TRACE CONSTITUENTS

The concentrations of trace constituents in the three refuse samples WSNB, WSOB and OBB are listed in Table 6 along with data for other refuse samples for comparisons. As with most natural materials, the trace constituent composition of refuse is variable. Arsenic varied from 12 to 94 mg/kg in refuse samples, V from 4 to 86 mg/kg, and Zn from 39 to 500 mg/kg.

Since the central concept of coal cleaning is to concentrate the coal from the noncarbonaceous materials, e.g. silicates, sulfides, oxides, phosphates, etc., those trace constituents which generally occur with inorganic phases are concentrated in cleaning wastes relative to the concentrations of these same constituents in the material as 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 via present coal cleaning techniques. The arithmetic means of As, Co, Ni and Pb in Illinois Basin coal refuse samples were found to be over twice the arithmetic means (Gluskoter et al., 1977) of the same constituents in Illinois Basin coals.

The trace constituent compositions of the two spoil samples, DMNS and DMOS (Table 7) are very similar with the exception of F and Mn. Barium, F, Mn, Sr, Zn, concentrations exceeded 200 mg/kg and were the predominant trace constituents in these two samples. The trace constituent composition of the slurry sample was broadly similar to that of the refuse samples WSNB, WSOB and OBB, although the concentrations of As, Ce and F were significantly lower than those in Illinois Basin coal refuse. The trace

	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: (cont'd).

	<u>Wewerka et al. (1978)</u>			<u>Griffin et al. (1980)</u>		<u>This work</u>			<u>Range in composition</u>	
	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 (concentrations in mg/kg.

Sample	WSSL	DMOS	DMNS	KG
<u>Constituent</u>				
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

constituent composition of the Kilngas sample was broadly comparable to the other six wastes with the exception of the relatively high levels of Cr and Ni. Chromium levels of this magnitude (1531 mg/kg) are generally not associated with coal utilization solids wastes (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.

SECTION 7

AQUEOUS SOLUBILITY OF THE SOLID WASTES¹

Solubility studies by laboratory extraction or leaching procedures are currently considered the best available approach for assessing the potential impact of leachate streams from solid wastes on the environment. Presently, there are more than 50 different extraction methods cited in the literature although many are essentially variations of the "shake-test". Some of these procedures were designed to simulate a particular disposal scenario that are often not applicable to more than one type of waste or disposal technique.

It would be expeditious if one single 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 of the objectives of this investigation was to generate aqueous extracts from selected coal utilization wastes using five extraction procedures that have recently received wide attention 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 ASTM-A method, (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.

¹Authors: W. R. Roy, I. G. Krapac, R. M. Schuller

ASTM-A and ASTM-B.

The ASTM methods (American Society for Testing and Materials, 1979) are titled Method-A (Water shake extraction) and Method-B (acid shake extraction). Both 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. The procedures are designed as a rapid means of obtaining a solution for the evaluation of the extractable materials from the wastes.

The ASTM procedures recommend using the waste materials in the physical form in which they would be 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") 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 in grams of the sample used. 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. Leaching of plastisizers from the plastic lids that could have resulted as an interferent during organic analysis of the samples was avoided by use of the Teflon liners. The slurries were shaken for 48 hours at 100 strokes per minute using a large capacity reciprocal shaker. The slurries were allowed to settle for one hour after shaking. After settling, pH, oxidation-reduction potential, specific conductance, and alkalinity measurements were made immediately after opening the bottles. The slurries were then filtered through Whatman^R Qualitative I filter paper then subsequently through

Millipore 0.45 μ m 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 with the exception that a sodium acetate-acetic acid buffer solution (pH 3.5 ± 0.1) was the extraction media.

U.S. EPA EP

The EP also was intended to serve as a quick test for identifying wastes that are capable of posing potential pollution hazards (U.S. EPA, 1980). The EP method required that the solid sample be prepared by grinding to pass through a 9.53 mm (3/8") standard sieve. Identical wide mouth gallon glass bottles with Teflon lined lids as used 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 - 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^oC equal in weight to the initial solid sample. Sample filtration and preparation procedures were identical to those used for the ASTM methods.

CAP

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 CO₂ gas. The CO₂ saturated water had a pH of 4.1. The extract was shaken for 48 hours and was carried out similarly to the ASTM methods. The rationale for using CO₂ 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 CO₂ than the atmosphere above the soil due to the aerobic metabolism of micro-organisms and the decay of soil organic matter. Also, carbonic acid was used as an acidic extract since carbonic acid itself is not toxic to the organisms used in the bioassays. It would have been difficult to assess the biological toxicity of the extracts due to solutes if the aqueous medium used to solublize the sample was also toxic such as the sodium acetate used in ASTM-B.

LTE

The long-term equilibration procedure (LTE) that was used in this study was developed by Griffin et al. (1980) for coal solid wastes samples. 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 (a 10% slurry wt./vol.) 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 metastable chemical

equilibrium conditions develop. Samples of the extracts were periodically taken and analyzed over the 21 weeks to monitor the changes in chemical composition of the solutions.

LVG

A large volume generation (LVG) procedure 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 (Section 6), acute toxicity of extracts, and accessibility of obtaining large amounts of the material.

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 insure that the drainage system would remain permeable. After the placement of the stone and refuse, each tank was filled with 6.53 kL (725 gal) of deionized water, completely saturating the solid waste (Fig. 3). A pump was connected to an outlet at the bottom of each tank which 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

¹by definition, solutions formed by shake procedures such as the ASTM-A, EP, etc., 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.

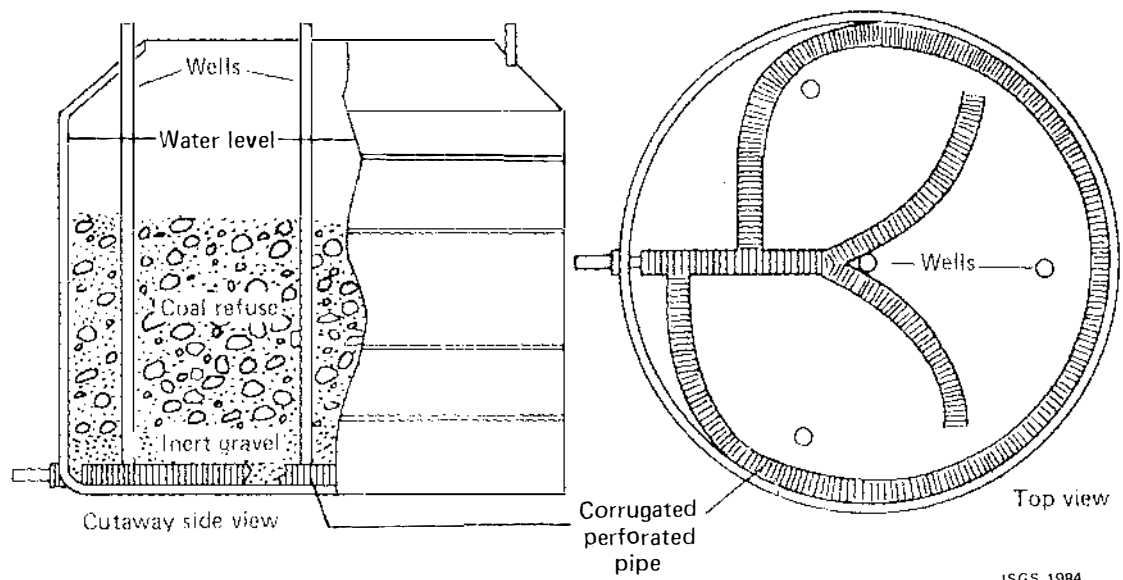


Figure 3. Cutaway side and top view of one of the Agro^R tanks set up to generate a large volume of coal waste leachate.

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 from the four monitoring wells to assess the compositional variability within the tanks.

Representative subsamples of each of 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. However, in most cases, 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). Gullledge 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. However, this comparison was made with data from another study (Marten, 1974) and not leachates collected 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 make many generalizations about solubility trends from evaluating the short-term procedures in this study. Differences in the amount soluble 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 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 is essentially soluble in all seven wastes by all four short-term procedures. The slurry sample released substantial amounts (greater than 35 percent of the matrix concentration) of Mn, Ni, and Zn irrespective of the extraction procedure. These anomalously high solubilities warrant further study.

Unlike the short-term extracts, the long-term equilibrates (LTEs) permitted the study of changes in chemical composition with time. These

Table 8: Range in pH and percent extracted of the total available in the solid by the four short-term procedures for the four different waste types.

	<u>Coal cleaning refuse</u> (WSNG, WSOG, and OBG)	<u>Mine spoil</u> (DMNS, DMOS)	<u>Slurry</u> (WSSL)	<u>KilnGas</u> (KG)
pH	1.62- 4.27	5.07- 7.57	2.43- 3.88	5.00- 8.10
<u>percent extracted</u>				
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

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

LTEs were carried out for 20 to 21 weeks at which time the experiments were terminated and the resulting extracts were 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 while 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). Roy and Griffin (1983) 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 (Roy, Griffin, and Skelly, 1983).

The pHs of the LTE extracts of the seven wastes (Fig. 4) were essentially 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 Fe 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 WSSI after 20 weeks. Sulfate concentrations (Fig. 6) appeared to reach steady state conditions after about a week in the alkaline solutions, but continued 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

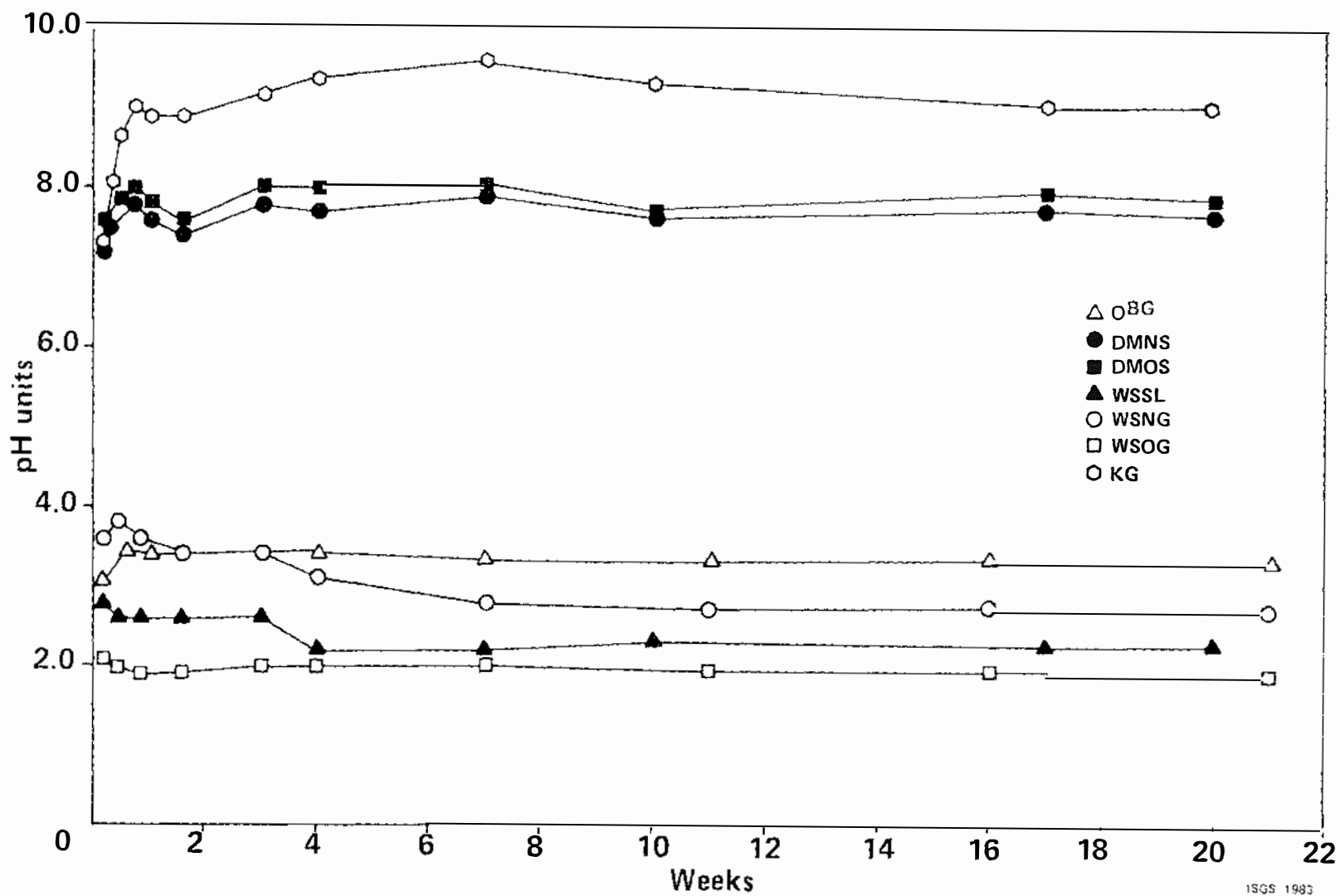
Table 9: Chemical analysis of the long-term equilibrates (LTEs) after 147 days of equilibration (concentrations in mg/L).

	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

¹relative to a normal hydrogen electrode

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

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



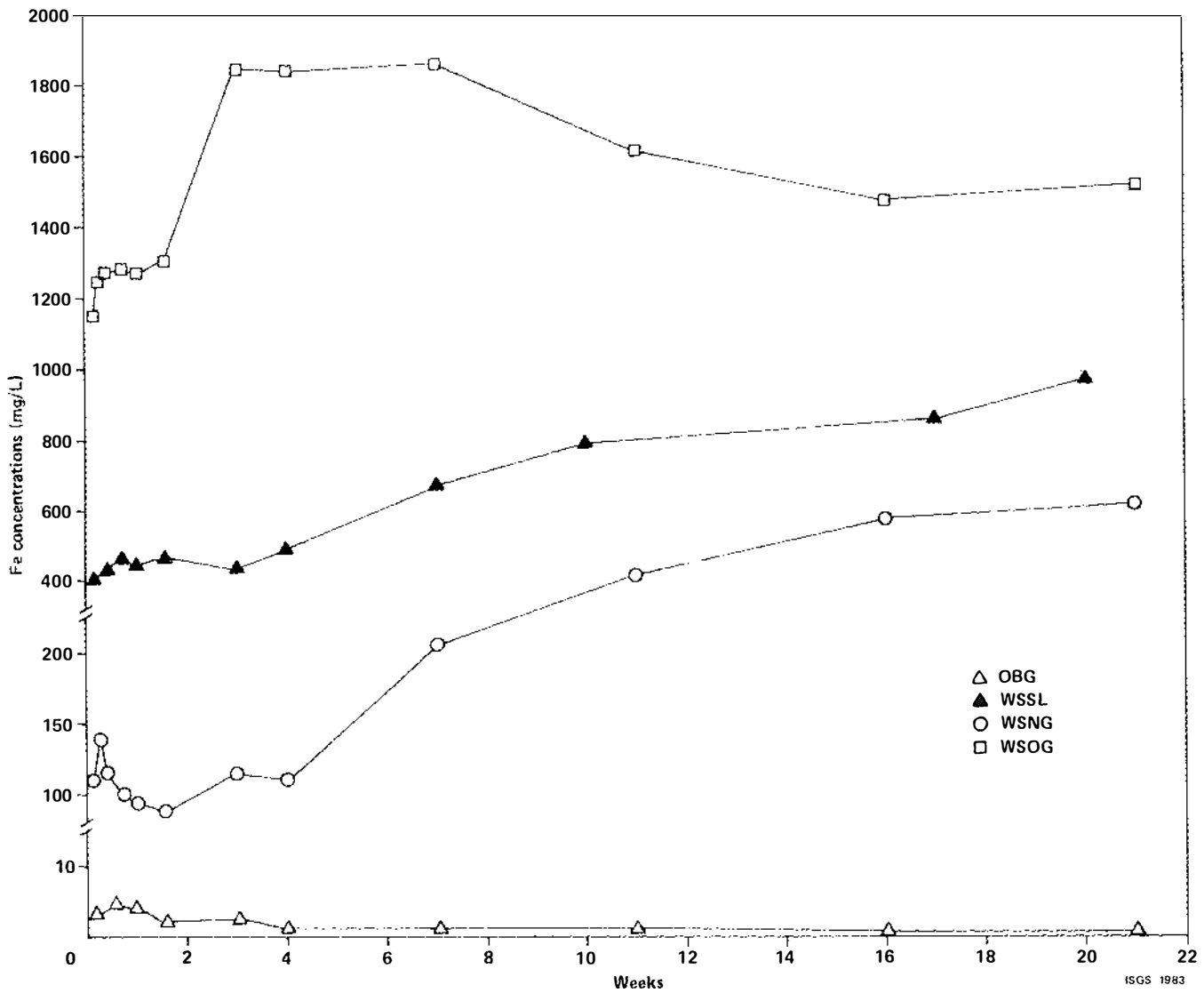


Figure 5. Changes in total Fe concentrations with time for the four acidic long-term equilibrations.

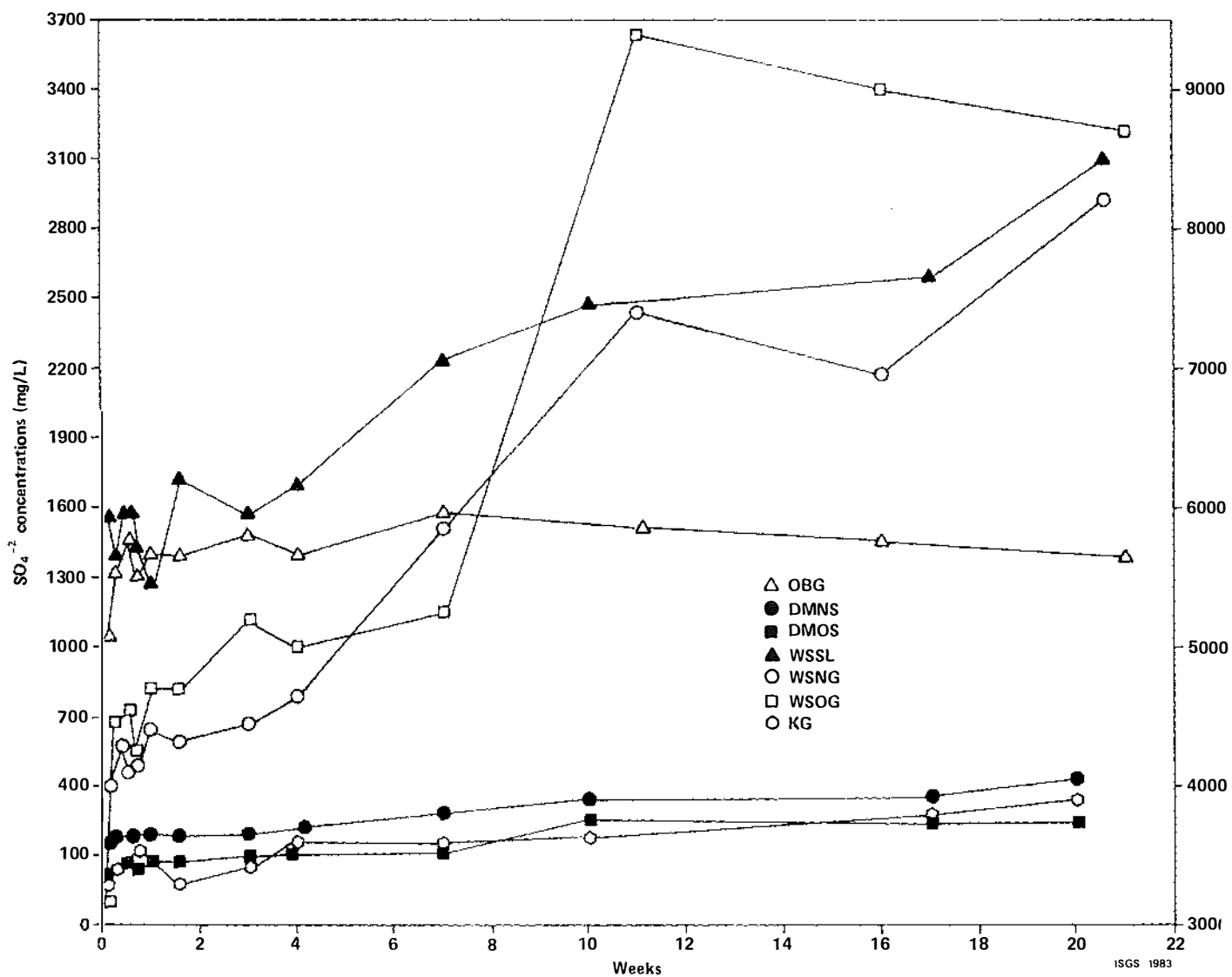


Figure 6. Changes in SO_4^{2-} concentrations with time for all seven long-term equilibrations.

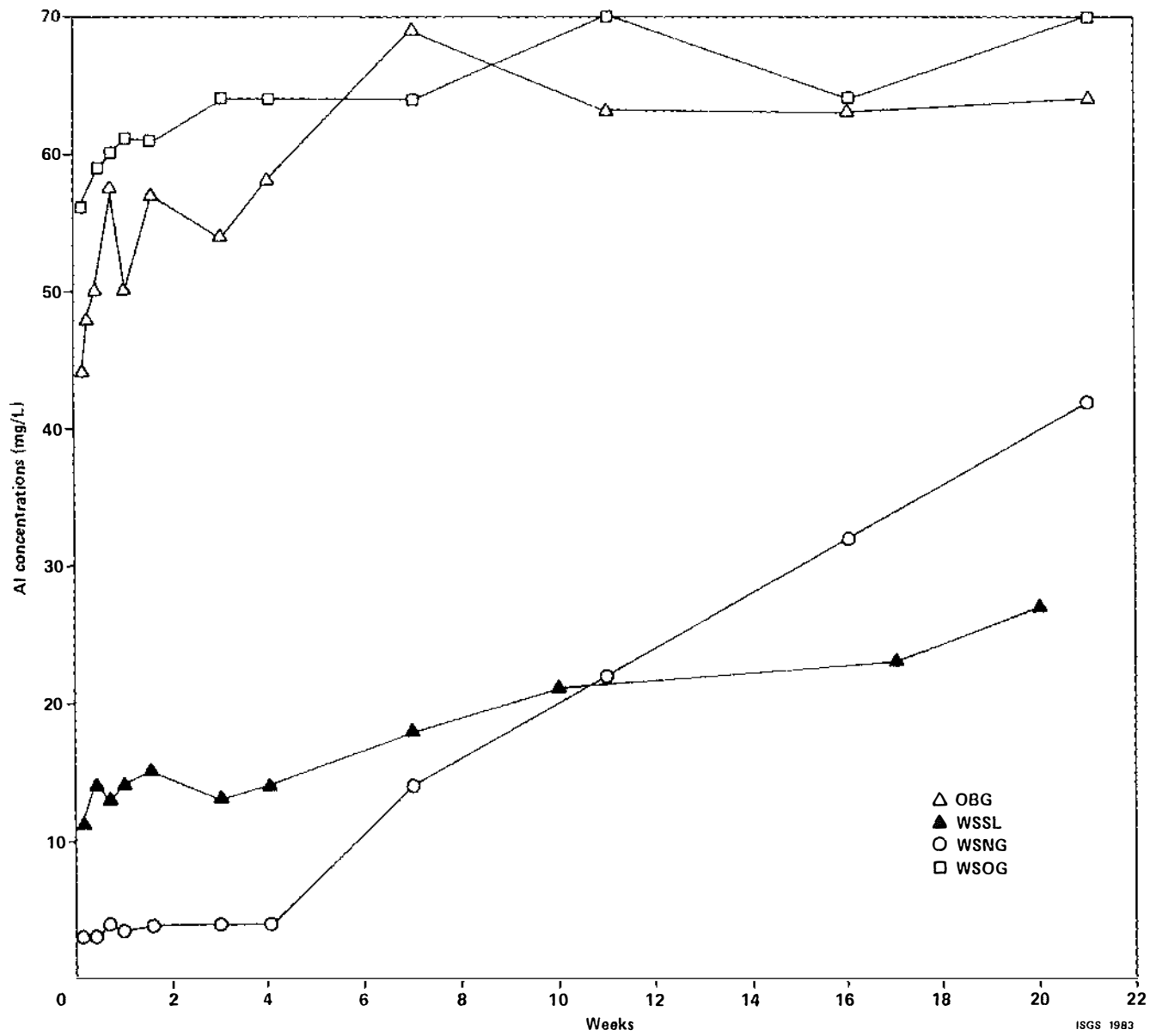


Figure 7. Changes in Al concentrations with time for the acidic long-term equilibrations.

interval. The amount of solution Si in the WSNG and WSSL extracts (Fig. 8) paralleled Al in that the Si concentrations had not reached invariant levels but were steadily increasing. In contrast, the amount of soluble Si 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 while the alkaline systems appeared to have reached steady state conditions with respect to the ionic composition of the solutions.

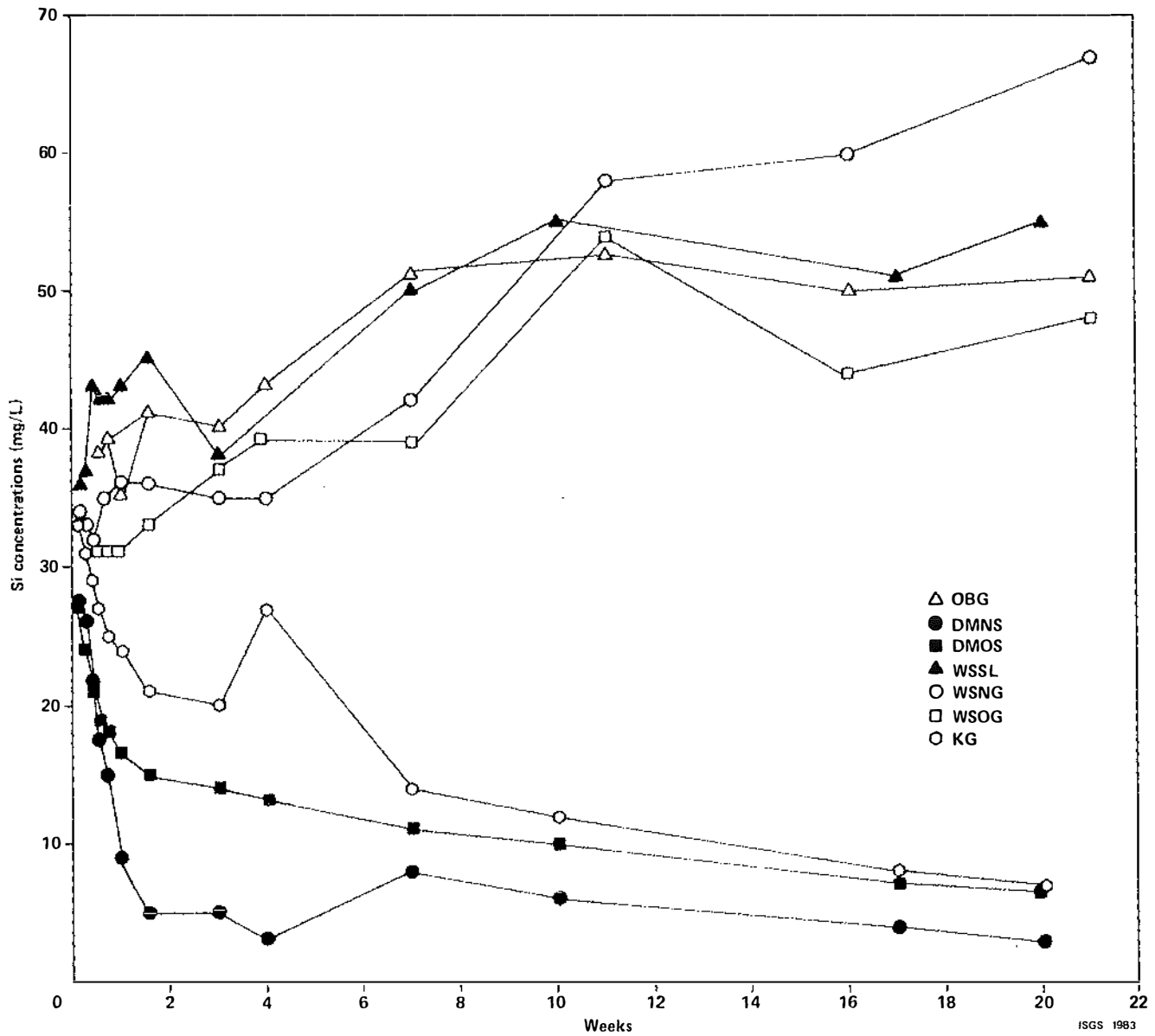


Figure 8. Changes in silica concentrations with time for all seven long-term equilibrations.

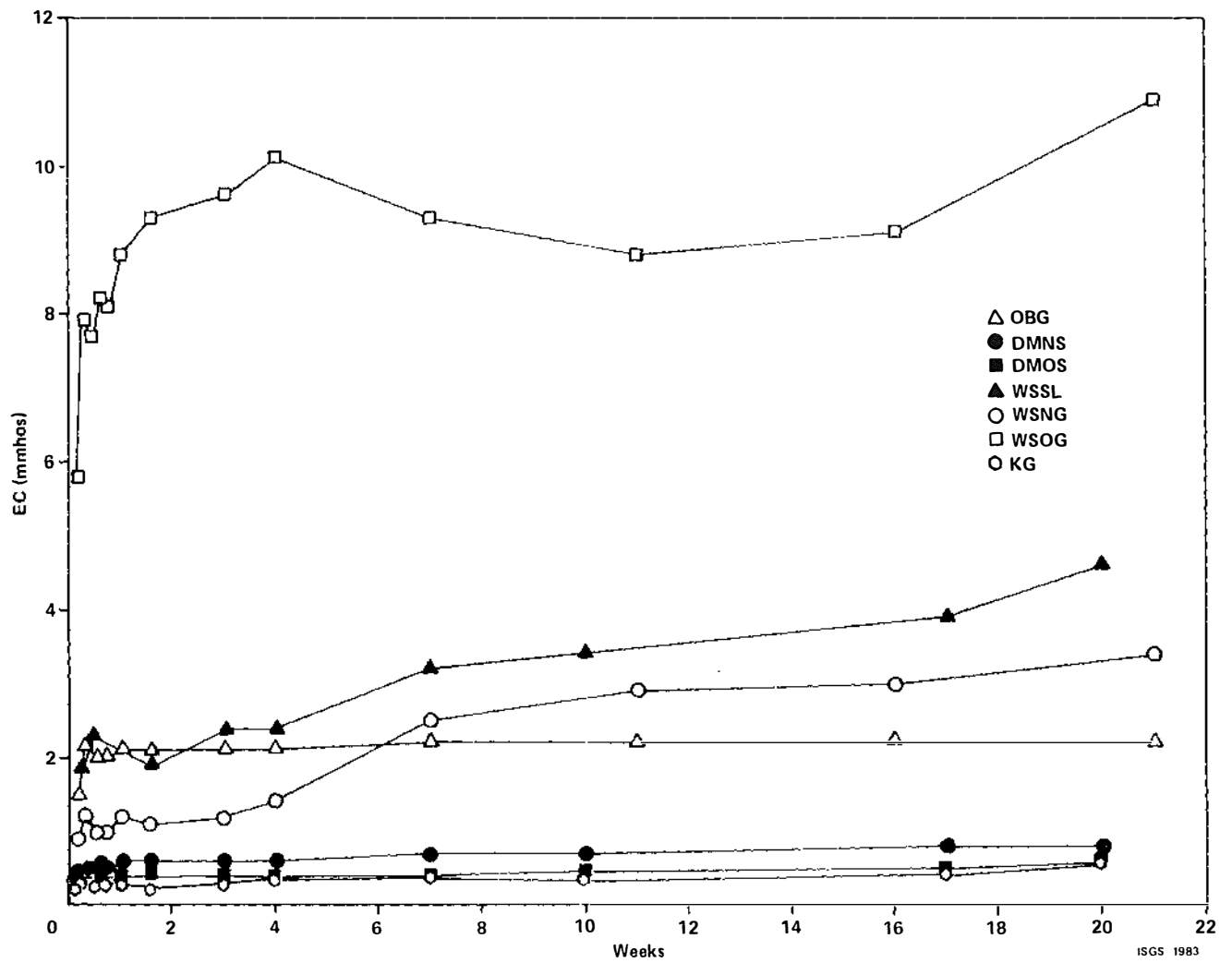


Figure 9. Changes in electrical conductance (EC) with time for all seven long-term equilibrations.

SECTION 8

ORGANIC CHARACTERIZATION OF THE SOLID WASTES AND LABORATORY EXTRACTS¹

The total organic carbon (TOC) content of the laboratory extracts generated by the ASTM-A, ASTM-B, carbonic acid procedure (CAP), 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.

The CAP extracts were generated using water saturated with carbon dioxide as previously discussed. In order to determine the TOC values for this set of solutions, it was necessary to first determine total carbon, then to remove the inorganic carbon by an acid sparge followed by 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 WSNG and OBG extracts since no acetic acid was added and for the KG extract, where a reasonable TOC was obtained. 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

¹Authors: D. R. Dickerson and R. A. Griffin

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

Sample	Method				
	ASTM-A ¹	ASTM-B ²	CAP ^a	EP ¹	LTE
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	

¹Values corrected for blank.

²Values not corrected for blank.

³Value for sample less than blank.

reasons, they are about an order of magnitude greater.

The ASTM-B extracts are 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. However, it was more likely due to microbial utilization of some of the acetate buffer, which is an excellent substrate for microbial growth.

8.1 METHYLENE CHLORIDE EXTRACTION OF LEACHATES

The results of the total chromatographable organics (TCO) and gravimetric analyses of the 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). This is in keeping with the low TOC content of the extracts.

The IR spectra obtained for the CH_2Cl_2 extracts were all very similar, even though 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), and 800 cm^{-1} (aromatic substi-

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

Sample	Extraction method	Extract Vol. (L)	CH ₂ Cl ₂ Vol. (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

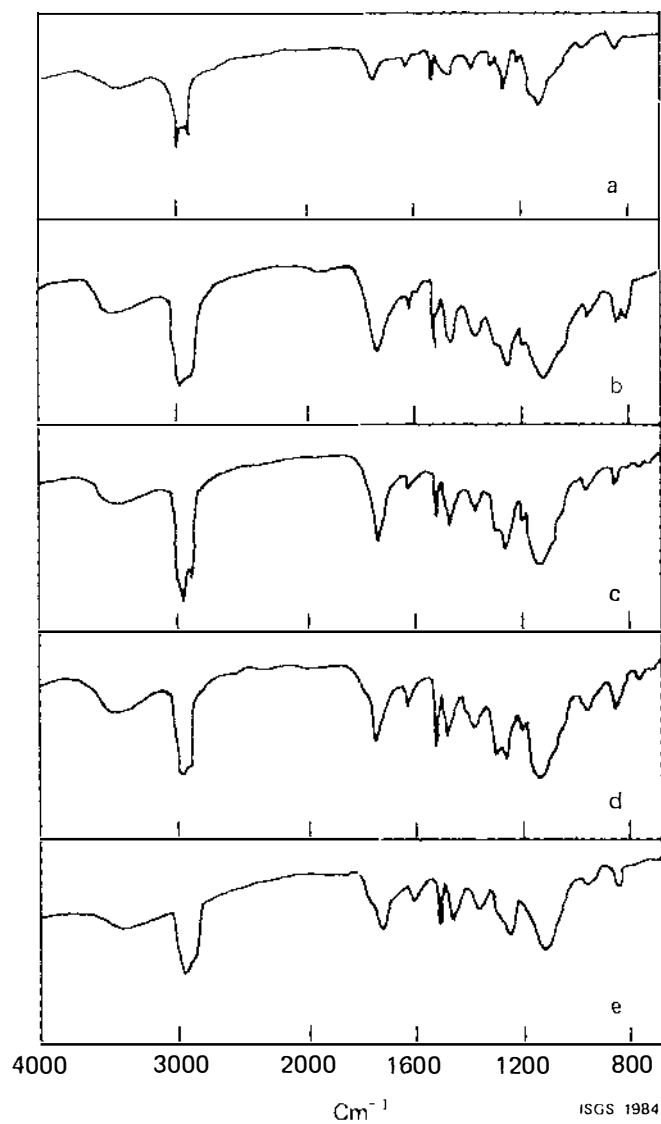


Figure 10. Infrared spectra of the organics extracted by CH_2Cl_2 from the extracts of WSSL generated by (a) LTE; (b) ASTM-A; (c) EP; (d) CAP; (e) ASTM-B methods.

tution). 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 and, if present, would 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 would be expected to be found in an aqueous extract. Since these organics are derived from coal solid wastes, it is likely that some of them may be included on the EPA priority pollutant list. They do not, however, appear to be in concentrations that would be considered to be hazardous other than by long-term accumulation.

8.2 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 >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" semi-solid. 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.

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 percent organic C), but less well for the WSSL waste (57 percent organic C). This fact would indicate a need for a greater dilution (with an inert material) for wastes with a high organic carbon content. Three waste:

(KG, DMOS, and DMNS), contained less than 5 percent organic carbon (Table 12) presented none of the above extraction problems.

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 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 filtration, where deemed necessary, analyses were continued as specified in the IERL-RTP Procedures Manual: Level I Environmental Assessment (2nd Edition). 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 gave better resolution with the chromatograph used than did either a 10 percent loading of SP 2100, or 10 percent loading of OV-101 as recommended in the Level I procedures.

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. Total chromatographable organics and gravimetric analysis of the methylene chloride extraction of coal solid wastes.

Solid	Sample (g)	CH ₂ Cl ₂ Vol. (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

Note: Values expressed for TCO are based on duplicate runs and computed from a standard curve. Error is estimated as $\pm 10\%$.

¹Not analyzed.

²Less than detectable limit.

³Mixed with equal weight of organic free silica before extraction.

Table 13: Elemental sulfur content of the methylene chloride extracts of the coal solid wastes.

Sample	Sulfur (percent weight)	
WSOG	34.3	(elemental analysis)
WSNG	4.2	(elemental analysis)
OBG	<u><50</u>	(calculated by difference)
WSSL	Not determined	
DMOS	<u><20</u>	(calculated by difference)
DMNS	<u><17</u>	(calculated by difference)
KG	<u><91</u>	(calculated by difference)

Table 12).

The Infrared spectra of the CH_2Cl_2 extracts of the coal solid wastes did not, in general, 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 was found for the spectra of the other wastes. Discernible in this spectrum are peaks at 3350 cm^{-1} (H-bonded OH and/or NH_2), $3040\text{--}3020\text{ cm}^{-1}$ (naphthalene-type aromatic C-H) 2950 , 2925 and 2860 cm^{-1} (aliphatic C-H stretching), $1800\text{--}1700\text{ cm}^{-1}$ (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 with peaks that were less well resolved.

8.3 LIQUID CHROMATOGRAPHY OF THE CH_2Cl_2 EXTRACTS OF THE COAL SOLID WASTES

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

The LC analyses were run on samples WSNG and WSOG prior to discovering that the extract was contaminated with large quantities of "free" sulfur. Some unforeseen effects of this sulfur may in part account for the greater than 100% recovery from the LC columns for these two samples. For these two samples the TCO quantity was below the detectable limits of the method

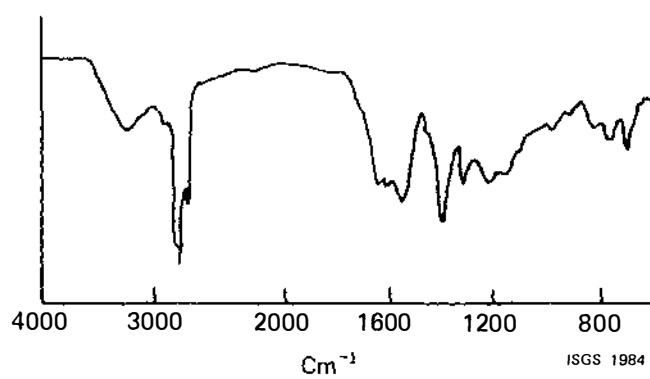


Figure 11. Infrared spectrum of the methylene chloride extraction of the OBG solid waste.

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 portion of 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 used. 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 contains the paraffins, fraction 3, the large aromatics and fraction 6 the polar compounds. These organic classes are in keeping with the the type of solid waste being extracted.

Since for all practical purposes, the organics found in the wastes studied originated from coal, and therefore were found to be quite similar, the LC analyses of only two of the wastes (OBG and KG) will be discussed. It can be assumed that the majority of the compounds found in one waste will be found in each of the remaining wastes although they may vary in concentration. This was borne out by the IR spectra of the CH_2Cl_2 extracts of the solid wastes of which the spectrum of the CH_2Cl_2 extract of the OBG solid waste (Fig. 11) was typical. The extracts contained numerous compounds with a variety of functional groups. A gross interpretation of

Table 14: Gravimetric (GRAV) analysis of liquid chromatography fractions from CH₂Cl₂ extracts of the solid wastes

Fraction	Sample	WSNG	WSOG	OBG	WSSL	DMNS	DMOS	KG
Total LC	mg	92.7	100.2	102.9	100.0	112.0	90.4	41.2
LC 1	mg	22.5	48.7	1.7	9.1	9.6	17.0	24.7
LC 2	mg	4.4	13.6	1.0	5.5	1.8	2.4	3.6
LC 3	mg	15.4	14.4	14.7	16.0	22.9	15.3	5.3
LC 4	mg	16.4	7.8	8.6	7.9	15.8	5.1	2.2
LC 5	mg	16.4	10.0	9.4	10.2	1.8	4.3	
LC 6	mg	25.4	16.8	34.4	24.1	26.5	17.5	
LC 7	mg	1.8	1.2	11.4	4.9	14.0	10.4	1.0
Recovered	mg	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 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 infrared 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. However, no nitrogen compounds were identified by GC/MS in the CH_2Cl_2 extract of the Kilngas residue.

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 $-(\text{CH})_n-$ 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 (see Fig. 12). Approximately 40% 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 Gas Chromatography/Mass Spectrometry (GS/MS).

An HPLC analysis of the total extractable organics from KG was obtained with toluene as an internal marker. There were two prominent peaks, one prior to and the other following toluene. The former is due to polar compounds such as phenols and the latter to di- and poly-aromatic hydrocarbons. The HPLC analysis of LC-2 showed essentially all the compounds eluting later than toluene in the range expected for naphthalene and alkyl

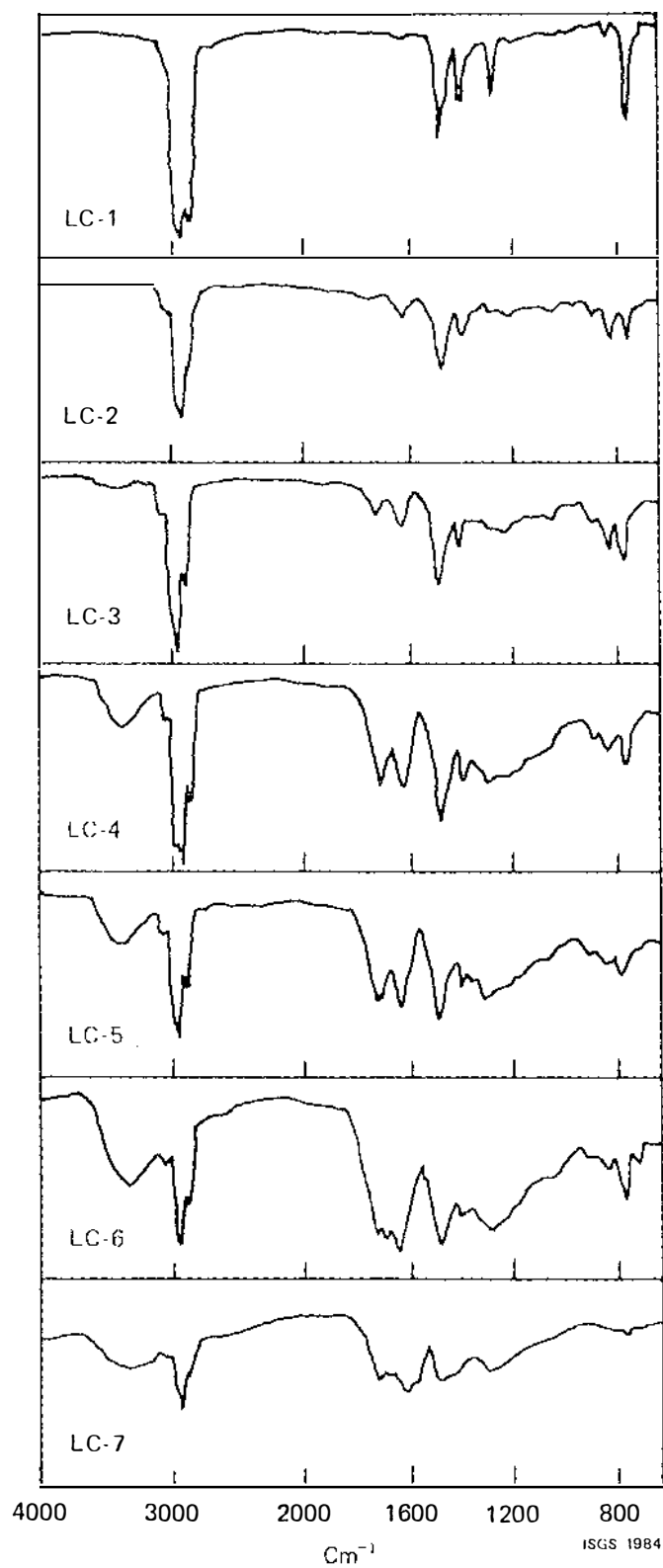


Figure 12. Infrared spectra of the liquid chromatography fractionation of the methylene chloride extraction of OBG.

substituted naphthalenes. The HPLC analysis of LC-3 showed two small peaks eluting ahead of toluene, which indicated little or no polar compounds in this fraction. The larger concentration of peaks were in the elution range of naphthalenes 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 (>200) and to aryl esters, as well as polyaromatics. The HPLC analysis of LC-6 shows a large envelope of early eluting peaks, as would be expected for highly polar compounds in this analysis method.

The chromatogram from the GC/MS analysis of LC-1 (KG) shows a large envelope of unresolved peaks as well as a number of well resolved peaks eluting in the C_{15} to C_{21} range. The identification of the major compounds, mostly n-paraffins, are listed in Table 15. Thirty-six peaks in the GC/MS chromatogram of LC-2 were analyzed. Of these, 19 were identified as alkyl substituted benzenes and biphenyls, or acenaphthene. Fourteen major peaks were identified by the GC/MS analysis of fraction LC-3 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. A listing by fraction of all the compounds tentatively identified by GC/MS is given in Table 15.

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

Table 15: Compounds identified by GC/MS in the LC fractions of the CH₂Cl₂ extract of KG.

<u>Fraction LC-1</u>	<u>Fraction LC-3</u>
C ₈ -Cyclohexane	2 C ₂ -Naphthalenes
C ₁₆ -Branched Alkane	3 C ₃ -Naphthalenes
n-Hexadecane	3 C ₄ -Naphthalenes
C ₁₀ -Cyclohexane	Phenathrene
n-Heptadecane	C ₂ -Phenanthrene
Pristane (branched C ₁₉ H ₄₀)	C ₃ -Phenanthrene
n-Octadecane	Acenaphthene or C ₄ -Biphenyl
n-Nondecane	C ₁ -Phenanthrene
n-Eicosane	C ₄ -Phenanthrene
n-Heneicosane	<u>Fraction LC-6</u>
n-Docosane	2,6-Di-t-butyl benzoquinone
n-Tricosane	C ₅ -Thiophenol
n-Tetracosane	C ₆ -Thiophenol
n-Pentacosane	Diethyl phthalate
n-Hexacosane	Methoxyanthracene
<u>Fraction LC-2</u>	Substituted Cychohexane
2 C ₁ -Naphthalenes	2,4-bis-(1-Methyl butyl) phenol
5 C ₂ -Naphthalenes	Phthalate (di-isobutyl?)
C ₄ -tetrahydronaphthalene	Phthalate (di-butyl?)
5 C ₃ -Naphthalenes	Phthalate (diethyl hexyl?)
8 C ₄ -Naphthalenes	Phthalate
C ₇ -Benzene	
2 Acenaphthenes or C ₂ -Biphenyls	
2 C ₃ -Acenaphthenes or C ₃ -Biphenyls	
Acenaphthene or C ₄ -Biphenyl	

directly in the organics extracted from the aqueous extract. However, they were identified in the organics extracted from the solid spoil and waste by an organic solvent and 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 from the aqueous extracts and since the TOC was also of that order, it seems doubtful that any single priority pollutant would be present in the extracts in a quantity that would be hazardous.

SECTION 9

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

The application of chemical equilibrium models can lead to useful insights into the chemistry of aqueous systems such as coal waste extracts or acid mine drainage. However, the results of such modeling must be interpreted cautiously. Discrepancies in reported values for solubility constants for some mineral phases resulting from a lack of uniform experimental procedures can make the determination of equilibrium controls difficult. Moreover, pure mineral compounds in distilled water are often used for determining thermodynamic parameters which might not be representative of these compounds when they are associated with complex multi-component 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 predict the theoretical activities of aqueous species and calculates the saturation indices 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 laboratory 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

¹Authors: W. R. Roy and R. A. Griffin

addition to the LTEs, the chemical composition of the ASTM-A extracts were 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 including a sample of an acid mine drainage stream flowing from the base of one of the refuse piles. This small stream was flowing into a man-made basin at the time of sampling and a sample of the ponded effluent was also taken. The chemical composition 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 from the aforementioned pile in the proximity of the two field samples.

Three field samples were taken at the Will Scarlett mine. One sample was of effluent emanating 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 Fe and SO_4^{2-} concentration (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 and 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

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).

Constituent	OBG pond	OBG AMD	WSOG AMD	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

¹relative to a standard hydrogen electrode

laboratory extracts (WSSL) as that particular basin was dry at the time of sampling. All three slurry deposits are in close proximity to one another.

While the samples are suggestive as to 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 in an attempt 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 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, whereas a fly ash sample (an acidic 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 (1983) 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 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

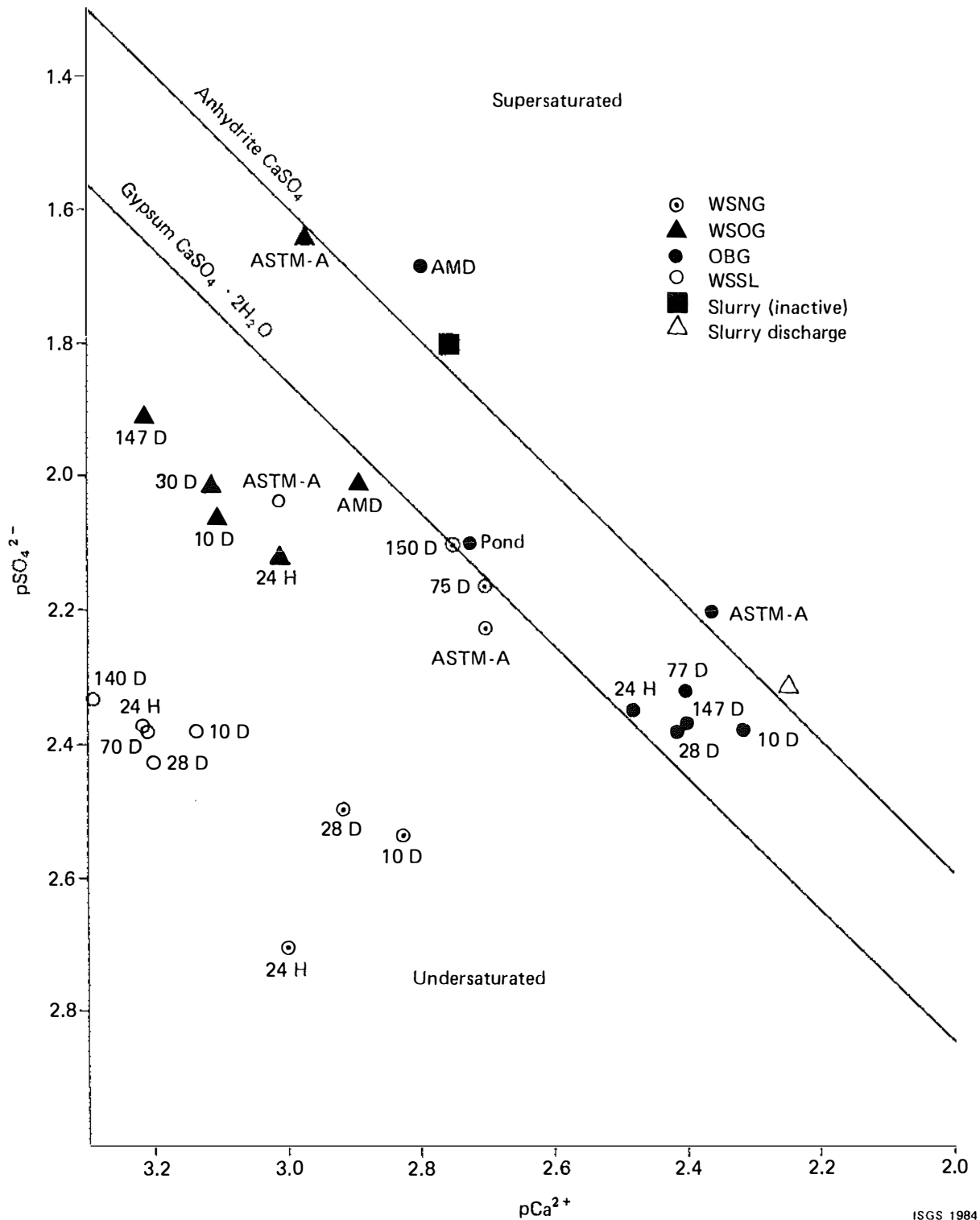


Figure 13. Calcium sulfate equilibria of the acidic laboratory extracts (ASTM-A and the long-term equilibration) and field leachate samples.

interpreted in three different ways;

- (1) The solution had not reached thermodynamic equilibrium and 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 some 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, a more reliable equation, the Extended Debye-Hückel (eq. 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, eqs. 5 and 6) can be used to calculate individual activity coefficients in solutions having an ionic strength up to 0.5M. The WATEQ2 program uses both the Debye-Hückel equations and a Davies-Extended Debye-Hückel equation (eq. 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 by the program since WATEQ2 was written primarily for natural surface waters. Since several of the acidic, high salt extracts and leachates have ionic strengths in excess of 0.1, solubility interpretations involving Ca^{2+} and SO_4^{2-} must be made with extreme caution.

Table 17: The Debye-Hückel Limiting Law and Variants

Debye-Hückel Limiting Law (1923)	$\log \gamma_i = -A z_i^2 \sqrt{I}$	(1)
Extended Debye-Hückel (1923-1934)	$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B a \sqrt{I}}$	(2)
Güntelberg (1926)	$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + \sqrt{I}} + b I$	(3)
Guggenheim and Schindler (1934)	$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + \sqrt{I}}$	(4)
Davies (1938)	$\log \gamma_i = -A z_i^2 \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 I$	(5)
Davies (1962)	$\log \gamma_i = -A z_i^2 \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30 I$	(6)
Robinson and Stokes (1959)	$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B a \sqrt{I}} + b I$	(7)

γ_i = activity coefficient of ion i

I = ionic strength

Z_i = charge of ion i

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

a = radius of hydrated ion

$B = \frac{50.2916 \times 10^8 d^{1/2}}{(\epsilon T)^{3/2} \text{ moles}^{1/2}} (10^3 \text{ g H}_2\text{O})^{1/2}$ (d = density of water)

b = empirical constant

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 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 during the extraction interval which 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 super-saturated with respect to both CaSO_4 phases but again, the high ionic strength (0.3866) rendered the calculated activities of 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 but were in equilibrium with anhydrite as were both the field slurry samples. However, 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)

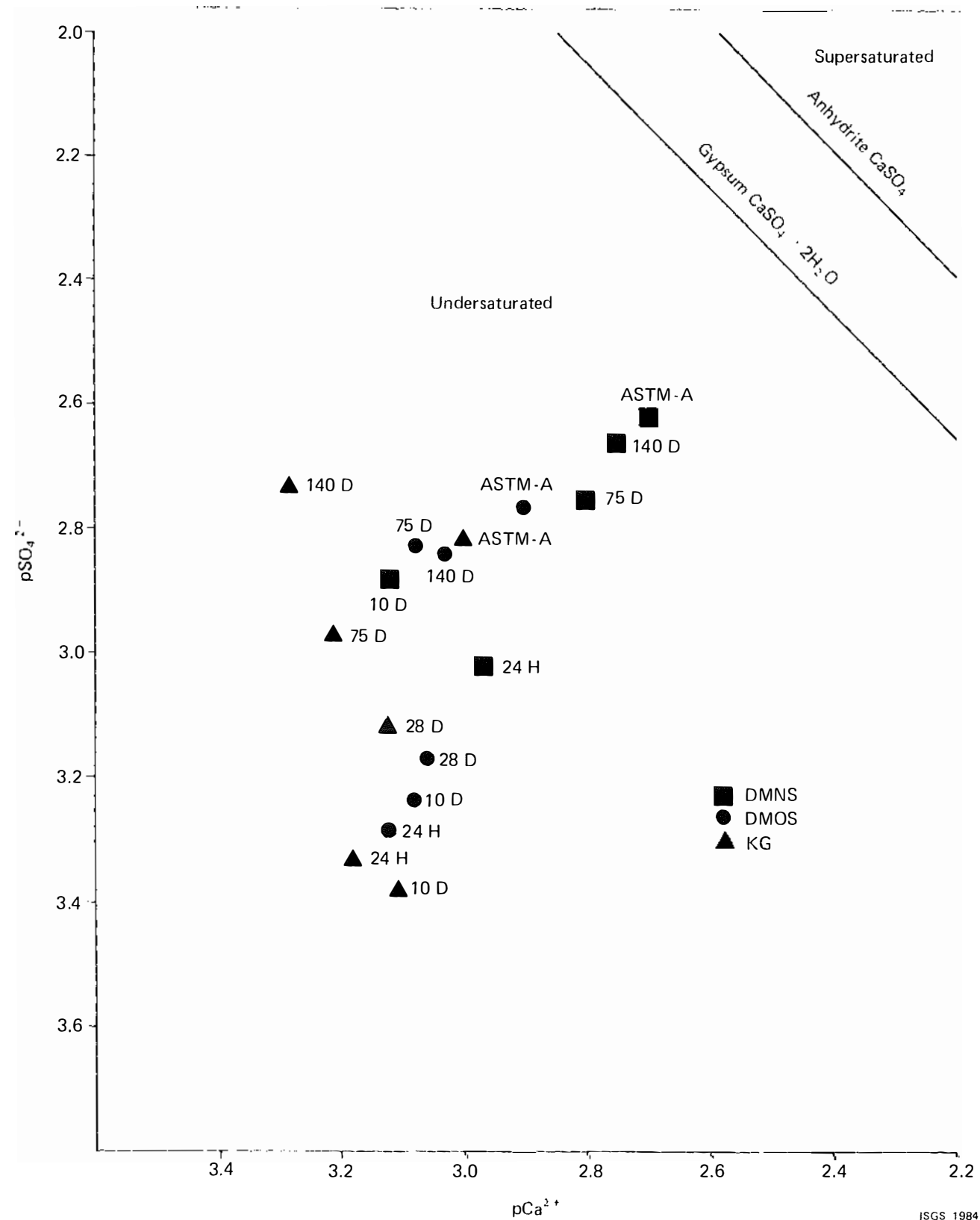
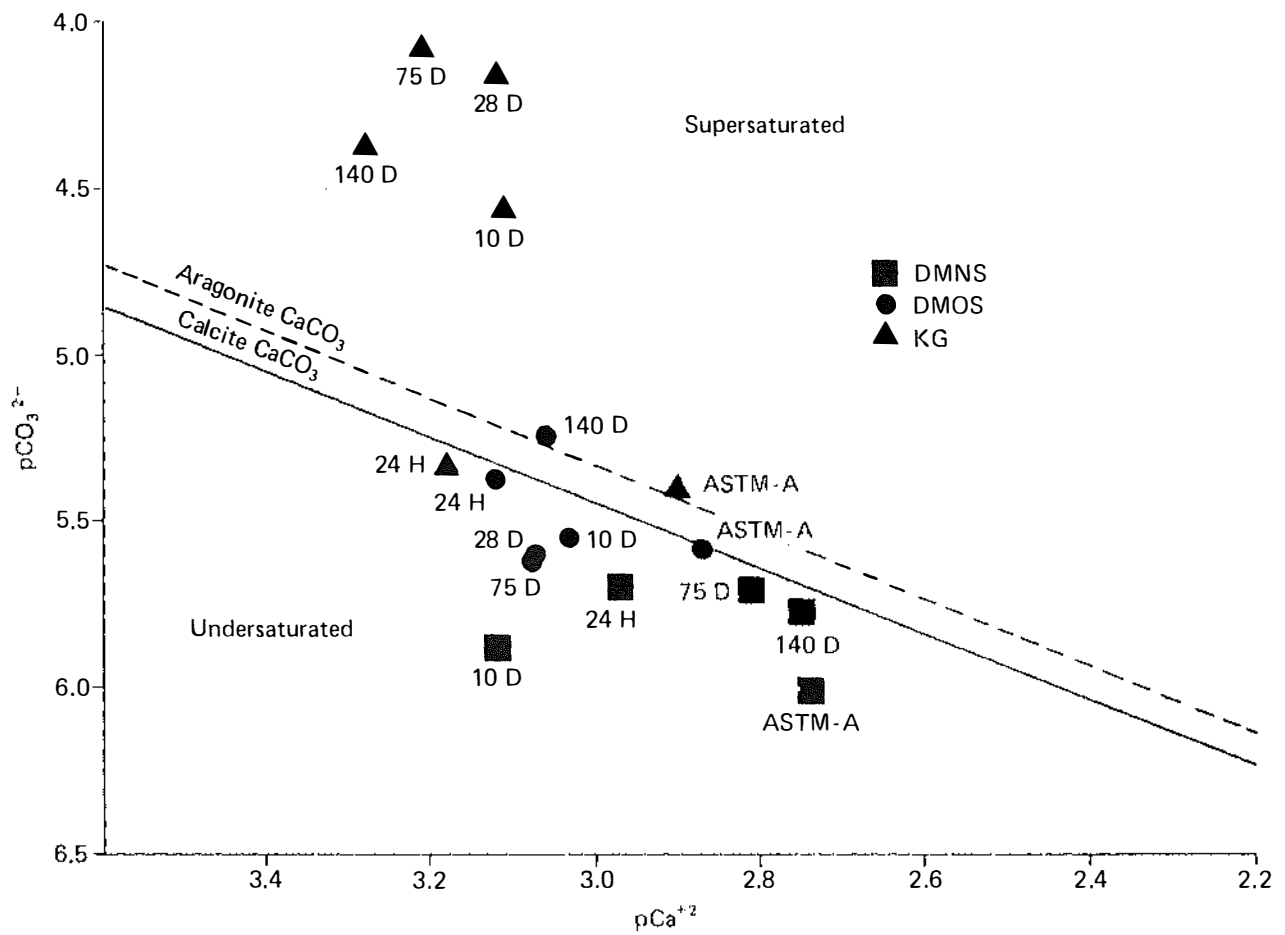


Figure 14. Calcium sulfate equilibria of the non-acidic laboratory extracts (ASTM-A and the long-term equilibrations).



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

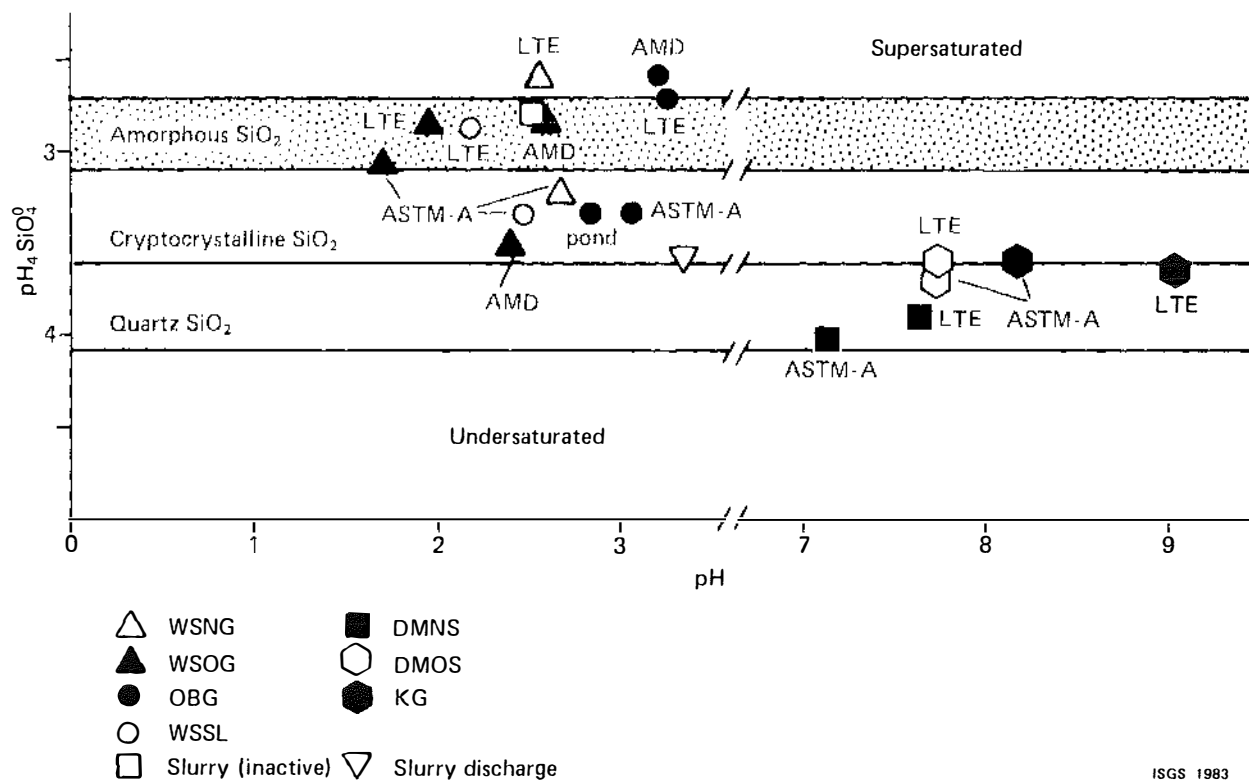
as was the ASTM-A extract but later appeared to approach equilibrium. The LTE of DMOS was initially near equilibrium with calcite but later equilibrated with aragonite, a meta-stable phase of calcite, some time after 75 days of equilibration. The aragonite could have formed as a precipitate at the expense of the dissolution of calcite and 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 super-saturated 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 Ca-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 Si and Al in the laboratory extracts and field leachates include the feldspars and clay minerals detected by x-ray diffraction (Table 2). However, all of the acidic LTE, ASTM-A, and field samples were all undersaturated with respect to albite ($\text{Na}\{\text{AlSi}_3\text{O}_8\}$), anorthite ($\text{Ca}\{\text{Al}_2\text{Si}_2\text{O}_8\}$), adularia ($\text{K}\{\text{AlSi}_3\text{O}_8\}$), analcime ($\text{Na}\{\text{AlSi}_2\text{O}_6\}$), halloysite ($\text{Al}_4\{\text{Si}_4\text{O}_{10}\}\{\text{OH}\}_8$), illite ($\approx \text{K,Mg}$, aluminosilicate hydroxide), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5\{\text{OH}\}_4$), and montmorillonite ($\approx \text{Ca,Na,K,Mg,Fe}$, aluminosilicate hydroxide) LTEs and ASTM-A extracts of alkaline materials, DMNS, DMDS, and KG were also undersaturated with all the feldspar minerals considered by WATEQ2. The LTEs of the alkaline samples were initially

super-saturated with respect to illite, montmorillonite and kaolinite then became either slightly super-saturated or undersaturated with respect to these clay minerals during the latter part of the equilibration period. Figure 16 shows the silicon dioxide equilibria. All of the samples fell within the range of Si solubilities that are expected from either quartz, cryptocrystalline SiO_2 , or amorphous SiO_2 . Only the final subsamples of the LTEs are shown to simplify the illustration. 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_4^0 . This relationship may have been partially obscured in that glass containers were used in all of the extraction studies shifting the Si equilibria towards the less stable, amorphous SiO_2 boundaries. However, all of the field leachate samples also fell along the amorphous SiO_2 boundaries.

Griffin et al. (1980) found that Al^{3+} activities in their long-term extracts of coal solid wastes were dominated by meta-stable Al phases (amorphous $\text{Al}(\text{OH})_3$ and AlOOH) rather than aluminum containing minerals known to be present in the solid wastes. In this study, all of the acidic systems were undersaturated with respect to these particular meta-stable phases. In general, it appeared that most of the laboratory extracts and field samples were not in equilibrium with any known meta-stable phases of aluminum. Two of the field leachate samples (WSOG-AMD and WSSL-discharge) were near equilibrium with a meta-stable 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



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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.

and sulfide stability fields when $\text{Fe}^{2+} \text{ aq} = 10^{-6} \text{ M}$ and total sulfur = 10^{-3} M . Solution Fe concentrations in this study varied from 0.21 mg/L Fe to 5625 mg/L Fe and thus, the classical Fe 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, most of the laboratory extracts and field leachates tended to plot near the maghemite boundary, a meta-stable phase of hematite (Fig. 17). Consequently, all of the aqueous samples were undersaturated with respect to amorphous ferric hydroxide. This is in disagreement 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 Fe equilibrium was influenced by $\text{Fe}(\text{OH})_3$. Griffin et al. (1980) concluded that amorphous $\text{Fe}(\text{OH})_3$ was probably a control on iron concentrations in some extracts while 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 $\text{pFe}^{2+} = 7.35$, the pFe^{2+} activity after 147 days, since the equilibria of magnetite is Eh dependent. The LTE of WSNB was near equilibria with $\text{Fe}(\text{OH})_3$ after 28 days of equilibration then equilibrated with maghemite.

However, the kinetic hypothesis is obscured by the fact that all of

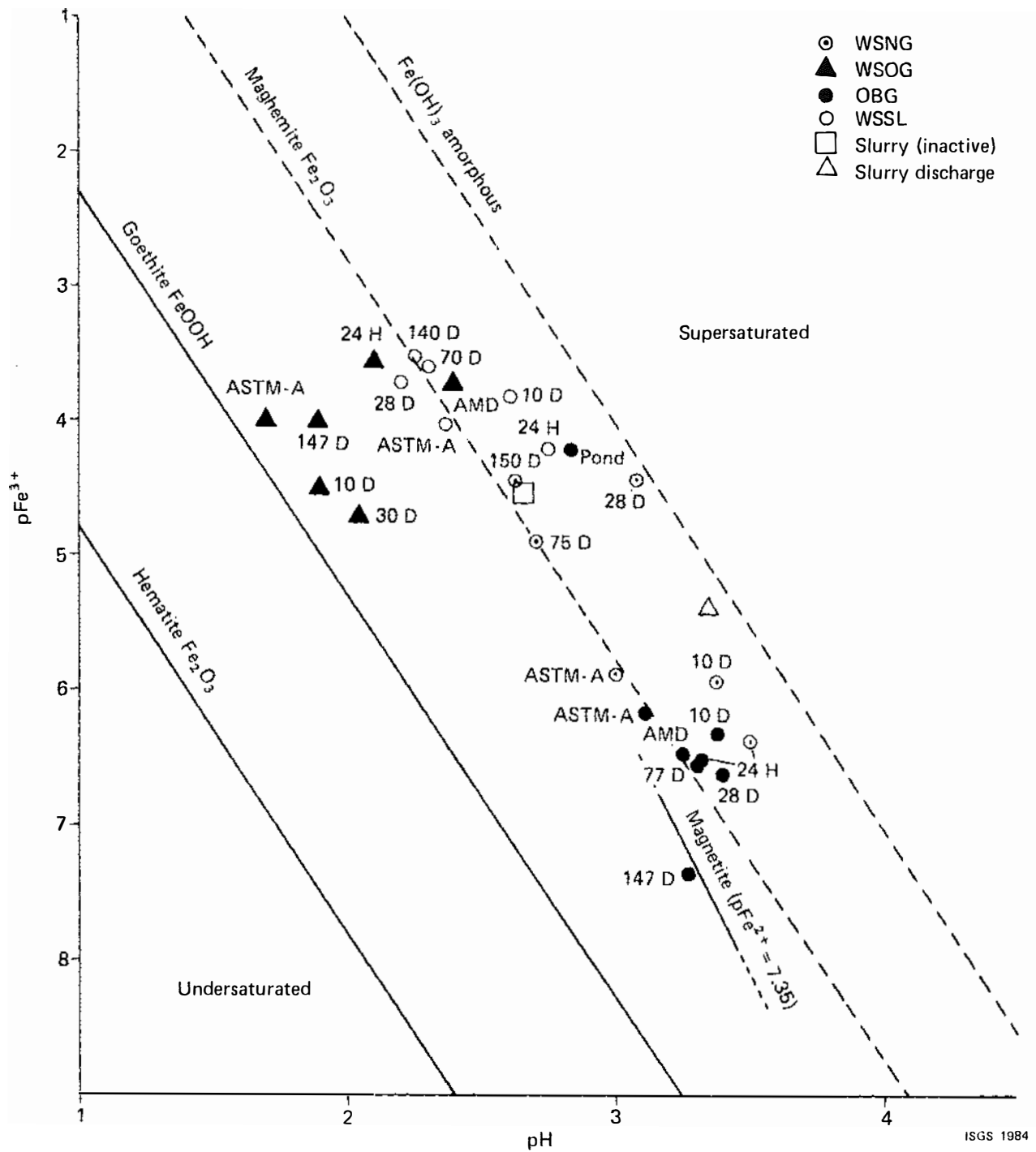


Figure 17. Fe^{3+} solubility equilibria as a function of pH for the acidic laboratory extracts (ASTM-A and the long-term equilibrations) and the field leachate samples.

the short-term ASTM-A extracts were in near equilibrium with maghemite in only 48 hours while the LTEs took months to reach the same phase boundary. Moreover, it would be expected that the higher slurry concentrations of the ASTM-A systems would "force" the data point towards the amorphous $\text{Fe}(\text{OH})_3$ boundary and not towards the maghemite boundary. The $\text{Fe}(\text{OH})_3$ - 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, $\text{NaFe}(\text{SO}_4)_2(\text{OH})_6$ was identified in OBG by x-ray diffraction (Table 2) and the LTE of OBG may have also equilibrated with natrojarosite ($\text{S.I.} = -0.221$)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 AMD field samples were supersaturated with respect to natrojarosite. Coquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) was detected by Mössbauer in WSNG and WSOG but there are no thermodynamic data available on this iron sulfate phase which precludes solubility analysis.

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

SECTION 10

ACUTE STATIC BIOASSAYS OF EXTRACTS GENERATED FROM SAMPLES OF COAL SOLID WASTES¹

10.1 INTRODUCTION

The major objectives of the biological investigations were to determine:

1) if 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, 2) the relative toxicities of the extracts which were shown to be acutely toxic, 3) the relative sensitivities of the four test organisms to the toxic extracts and 4) if there were any significant correlations between the acute toxicity of a solution and its physicochemical composition.

10.2 METHODS AND MATERIALS

The LTE extracts, upon attaining steady state concentrations (Section 7) were decanted from the carboys and filtered through 0.45 micron pore-sized 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) a screening procedure and b) the LC-50 determination. During the screening procedure, the test organisms were exposed to undiluted extracts; in the LC-50 determinations, 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.

¹Authors: T. M. Skelly and J. J. Suloway

One-to-two-day-old Daphnia, one-to-six-day-old fathead minnow fry, juvenile snails (shell length = 5.0 ± 0.5 mm) and yoke sac green sunfish fry were exposed to the extracts in bioassay tests at a constant temperature ($20 \pm 1^{\circ}\text{C}$) with a constant photoperiod (16L-8D) in an environmental chamber. For each bioassay, ten 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 test organisms. During the bioassays pH, temperature, and dissolved oxygen concentrations were monitored. Mortality data were collected at 24, 48, 72, and 96 hours after the bioassays were begun except during the Daphnia tests which were terminated after 48 hours. In addition, after 96 hours snails scored as dead were placed in reconstituted water and checked within 24 hours to more accurately assess mortality. 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 ten test organisms, were tested for each set of bioassays.

Regression analysis was used to test for 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.

10.3 RESULTS

10.3.1 Acute toxicity of extracts

The screening procedures were conducted in order 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 = 7.69-8.85) and the mean final pH was 7.72 ± 0.14 (range = 7.30-7.91). The mean initial

dissolved oxygen was 7.94 ± 0.37 mg/L (range = 6.93-8.86 mg/L) and the mean final dissolved oxygen concentration was 8.56 ± 0.64 mg/L (range = 6.67-9.90 mg/L). The mean hardness, as determined by titration, was 29.6 ± 5.37 mg/L = CaCO_3 (range = 15-35 mg/L). The mean survival of the test organisms exposed to the control solutions was 95.0%, 97.0%, 98.2% and 98.1% for Daphnia, Physa, Lepomis and Pimephales, respectively.

To test only the effects of pH on mortality, static bioassays were conducted of 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 caused total mortality in Pimephales, Daphnia, Lepomis and Physa bioassays if the pH's were below 6.0, 5.6, 5.4 and 3.5, respectively. Undiluted extracts generated from the spoil bank (DMNS and DMOS) and Kilngas (KG) samples were not acutely toxic (mortality $\leq 5\%$) to Daphnia, Pimephales, Lepomis and Physa (Figure 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 of the extracts caused 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 gob pile samples (WSNG, WSOG and OBG) and the slurry sample (WSSL) were evaluated as to their relative acute toxicities in the LC-50 determinations. In addition, results from these bioassays were used to estimate 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% mortality.

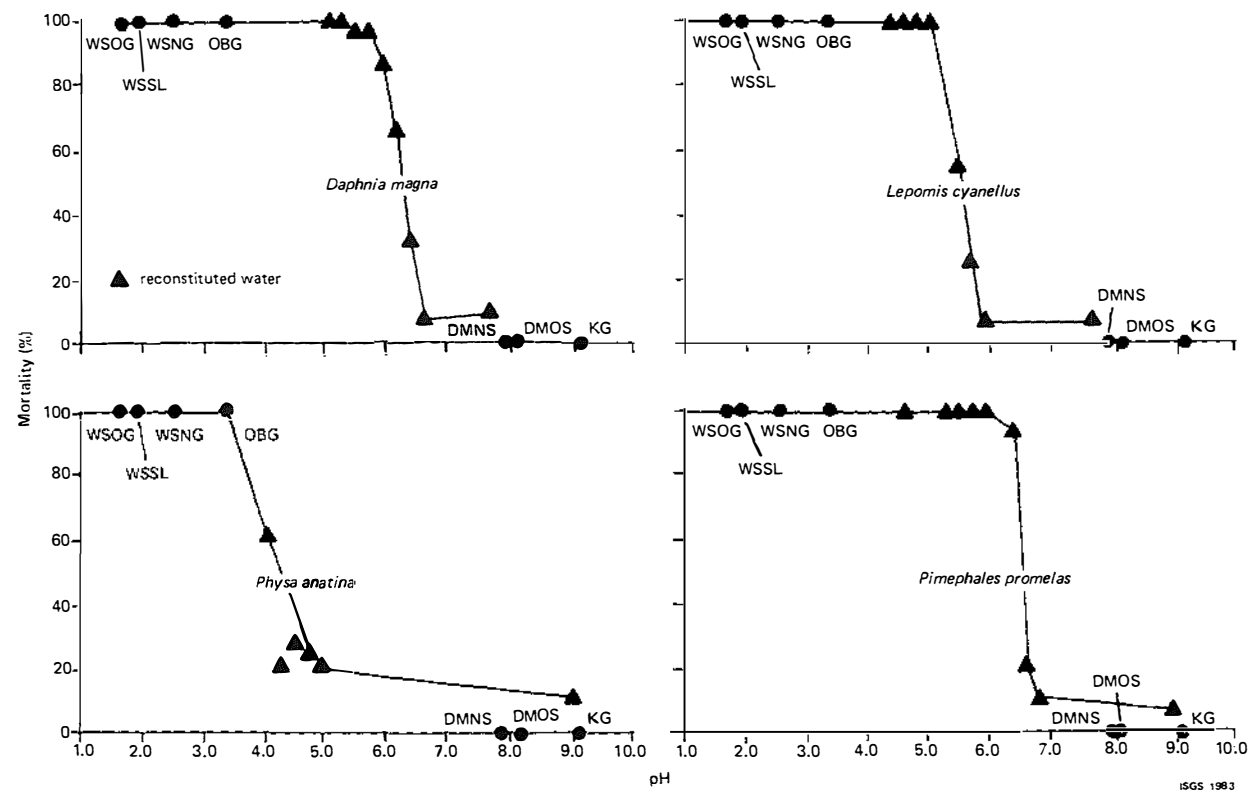


Figure 18. Percent of mortality of *Daphnia magna*, *Lepomis cyanellus*, *Physa anatina* and *Pimephales promelas* resulting from exposure to undiluted extracts generated from seven coal solid wastes and buffered solutions of reconstituted water.

The LC-50 values, their 95% confidence intervals and dilutions necessary to eliminate mortality are listed in Table 18. The pH values listed are the pH's of the undiluted extracts prior to dilution with soft reconstituted water. There is an inverse relationship between toxicity and the LC-50 value. With an increase in the toxicity, there is a decrease in the LC-50 value. Thus, 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 for each of the organisms tested. The extracts produced from WSNG, WSOG, and WSSL were very toxic to all four test organisms with LC-50 values less than 3.0 mL/100 mL.

Generally, all extracts or leachates were acutely toxic when acidic ($\text{pH} < 5.0$); and 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 of the acutely toxic extracts required a relatively large amount of dilution ($> 1:20$) to eliminate mortality with the exception of 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 sensitive to the toxic effects of the extracts (Figure 19). As the concentration of the extract was increased, there was an increase in mortality for all species. The mortality curve for Physa anatina 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 in Table 19, the difference between the toxicity data sets were highly significantly different ($P < 0.001$ or 0.0001).

Table 18. The LC-50 values, their 95% 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
<u>WSOG</u>			
<u>Daphnia magna</u>	1.67	0.36 ± .02	1:1000
<u>Pimephales promelas</u>	1.71	0.42 ± .004	1:263
<u>Lepomis cyanellus</u>	1.68	0.60 ± .02	1:200
<u>Physa anatina</u>	1.65	0.98 ± .05	1:154
<u>WSSL</u>			
<u>Daphnia magna</u>	2.09	0.77 ± .02	1:143
<u>Pimephales promelas</u>	2.21	0.84 ± .02	1:143
<u>Lepomis cyanellus</u>	2.06	0.96 ± .05	1:118
<u>Physa anatina</u>	2.05	1.65 ± .05	1:91
<u>WSNG</u>			
<u>Daphnia magna</u>	2.44	1.70 ± .02	1:57
<u>Pimephales promelas</u>	2.30	1.69 ± .02	1:65
<u>Lepomis cyanellus</u>	2.52	1.95 ± .08	1:57
<u>Physa anatina</u>	2.51	2.90 ± .09	1:44
<u>OBG</u>			
<u>Daphnia magna</u>	3.34	7.4 ± 0.1	>1:50
<u>Pimephales promelas</u>	3.33	6.8 ± 0.3	1:20
<u>Lepomis cyanellus</u>	3.36	9.5 ± 2.9	1:33
<u>Physa anatina</u>	3.37	14.2 ± 0.3	1:9

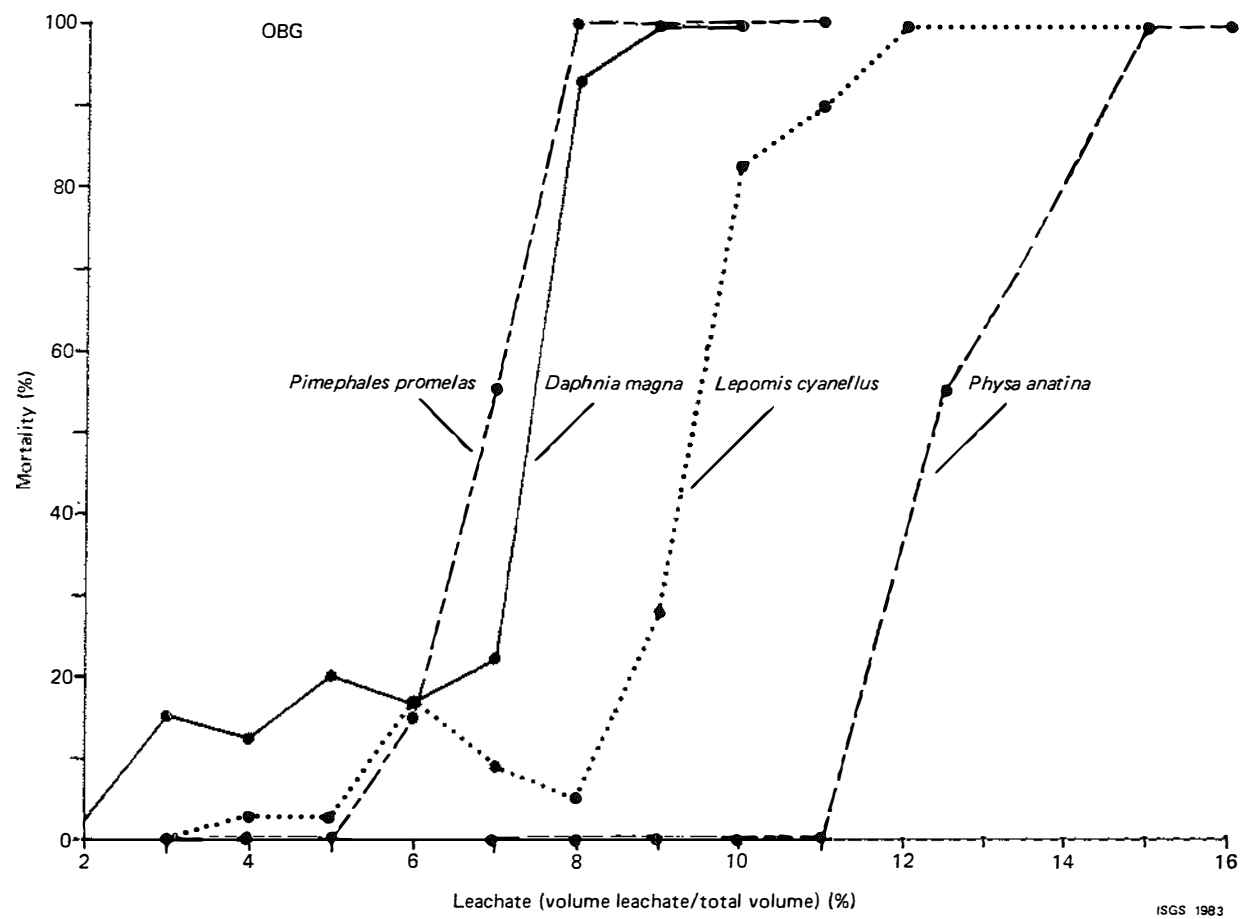


Figure 19. Relationships between the OBG extract and mortality for Pimephales promelas, Daphnia magna, Lepomis cyaneus, and Physa anatina.

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
<u>Pimephales</u>	0.0001	0.0001	0.0001	0.01	0.01	0.001
<u>Daphnia</u>	0.0001	0.0001	0.001	0.0001	0.0001	0.0001
<u>Physa</u>	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
<u>Lepomis</u>	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

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% confidence intervals for the LC-50 values (Table 18). For example, the 95% confidence intervals for the LC-50 of OBG to Daphnia (7.3-7.5) overlaps that for Lepomis (7.2-12.4). Physa, the most tolerant test organism, was very highly significantly different in its tolerance in 7 of 12 comparisons (Table 20).

10.32 Chemical characterization of the diluted extracts

After the acute static bioassays were completed, subsamples of all test solutions were filtered, and preserved with nitric acid and stored for analysis. The appropriate samples (those in which partial mortality occurred, the lowest concentration at which total mortality occurred, and the highest concentration at which no mortality occurred) were analyzed for the constituents which were present in sufficient concentrations to be potential hazards. 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.

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

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.

Extract	Test Organism			
	<u>Daphnia magna</u>	<u>Pimephales promelas</u>	<u>Lepomis cyanellus</u>	<u>Physa anatina</u>
OBG	pH	pH	pH	pH
	Mn	Mn	Al	Al
	Ni	Ni	Mn	Mn
	Zn	Zn	Ni	Ni
			SO ₄	Zn
WSNG	pH	pH	pH	pH
		Mn	Al	Al
		Zn	Fe	Fe
			Mn	Mn
			Ni	Ni
WSOG	pH	pH	pH	pH
	Fe		Fe	Al
			Pb	Fe
WSSL	pH	pH	pH	pH
	Cd		Fe	Al
	Ni			Fe
				Mn
				Ni

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 ($\text{pH} < 6.5$). Only eight physicochemical parameters other than pH are listed in Table 21. Aluminum, Fe, Mn, and Ni appear to be significantly correlative to mortality. Zinc is highly correlated with mortality in test solutions of OBG.

More physicochemical parameters were found correlated to mortality in the bioassays using Lepomis cyanellus and Physa anatina than those using Daphnia magna and Pimephales promelas. This difference was probably due to the fact that the test solutions used in the Lepomis and Physa bioassays were more concentrated because of the relatively higher levels of tolerance exhibited by Lepomis and Physa.

10.4 DISCUSSION

10.41 Non-toxic leachates

Several authors (Beyer and Hulnik, 1969; Barnhisel and Rotromel, 1974; Hood et al., 1979; Klimstra and Jewell, 1973; Mason, 1978; and many others) have cited spoil banks as sources of problematic leachates. The laboratory extracts generated from the spoil bank samples (DMNS and DMOS) in this study were essentially neutral in pH, contained relatively low concentrations of accessory elements and were not acutely toxic (mortality $\leq 5\%$).

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).

10.42 Toxic Leachates

The extracts generated from the coal cleaning refuse samples (WSNG, WSOG and OBG) 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 that were 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% mortality in Physa bioassays. Also the concentration of Zn in some OBG test solutions exceeded the LC-50 values established by Biesinger and Christensen (1972), Benoit and Holcombe (1978), and Patrick (1968) for Daphnia, Pimephales, and Physa, respectively. Relatively high concentrations of Al were measured in the OBG test solutions; however, LC-50 values for Al 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.

Relative Tolerances of Test Organisms

Daphnia and Pimephales were the most sensitive species to the toxic effects of the extracts. Lepomis cyanellus were less tolerant than Physa; however, they are more tolerant than Daphnia or Pimephales promelas. Daphnia have been shown to be more sensitive to cations than fish (Anderson, 1948).

There was a distinct threshold where the buffering capacity of the re-constituted water used as dilution water 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 extract using snail shells (the animals were removed from the shells) 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.

SECTION 11

CHRONIC BIOASSAYS OF LEACHATES GENERATED FROM COAL CLEANING REFUSE SAMPLES¹

11.1 INTRODUCTION

The major objectives of these biological investigations were to determine:

- 1) at what concentrations 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 (growth, reproduction, mortality, etc.) during the bioassays, and 4) if there were any significant correlations between the chronic toxicity of a leachate and its physicochemical composition.

11.2 METHODS AND MATERIALS

The composition of the leachates generated from samples of OBG and WSNG by the large volume generation procedure (Section 7) were continuously monitored. The composition of the two leachates after times comparable to the LTE solutions is given in Appendix A. After about one year, the leachates were first assayed for acute toxicity with the four test organisms. This particular procedure was used to generate the leachate because of an anticipated need for large volumes of solution for the chronic bioassays. 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 described in Section 10.

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

¹Authors: T. M. Skelly and J. J. Suloway

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 was a blend of dechlorinated tap and deionized water. The dilution water was passed through an ultra-violet filter prior to use and was 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) % (by volume) of the undiluted OBG leachate, and 0.1, 0.05, 0.025, 0.0125, 0.00625 and 0.0 percent of the WSNL leachate.

Fathead minnows were tested for 32 days (4 days as embryos and 28 days post-hatch). Thirty eggs were placed in screened egg cups in each chamber to initiate these embryo-larval chronic bioassays. The egg cups were mechanically rocked slowly up and down to facilitate oxygen transfer, and cleaning of 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. Fish were killed with ice water at the termination of the test and measured for total length and weight.

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

Daphnia magna experiments for both OBG and WSNL were conducted for 28 days. Five individual Daphnia were maintained separately within stainless

steel cages in each exposure chamber. Tests were initiated with 2-26 hour-old Daphnia. Daphnia were fed a blended solution of trout chow and baker's yeast three times per day. When the Daphnia reproduced, 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 three times per day, three 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 was 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 during the week, 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 and 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 four hours and 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.

11.3 RESULTS

11.31 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, the screening procedures were conducted to determine if the undiluted leachates were acutely toxic (Table 22). Undiluted OBG leachate was not acutely toxic to any of the species of test organisms during acute bioassays conducted in the second year of the study. 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 all 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 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% was the highest concentration 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

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

Organism	PROCEDURE			
	LTE		LVG	
	pH	LC-50 mL/100 mL	pH	LC-50 mL/100 mL
<u>OBG</u>				
<u>Pimephales</u>	3.33	6.8 ± 0.3	5.74	>100 ¹
<u>Daphnia</u>	3.34	7.4 ± 0.1	5.62	>100
<u>Lepomis</u>	3.36	9.4 ± 2.9	6.04	>100
<u>Physa</u>	3.37	14.2 ± 0.3	5.70	>100
<u>WSNG</u>				
<u>Pimephales</u>	2.30	1.69 ± 0.02	3.56	0.240 ± 0.010
<u>Daphnia</u>	2.44	1.70 ± 0.02	3.49	0.335 ± 0.018
<u>Lepomis</u>	2.52	1.95 ± 0.08	3.51	- ²
<u>Physa</u>	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.

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 of limited amount of undiluted OBG that was generated during the second year.

11.32 Chronic toxicity of the leachates

The results of the chronic bioassays of WSNG using Pimephales promelas are summarized in Table 23. One-way 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 the control and concentration of 0.05%) to 20.7 mm in the highest concentration (0.1%). A similar trend was observed in the mean weights, with the lowest weight measured in the strongest concentration and the highest mean weight measured in the chambers with a concentration of 0.05% 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%. 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% leachate (hatchability = 84.0%, $P < 0.001$), 0.05% leachate (hatchability = 91.7%, $P < 0.025$), and 0.015% leachate (hatchability = 89.3%, $P < 0.005$).

The results of the chronic bioassays of WSNG using Lepomis cyanellus are summarized in Table 24. The same parameters were measured and same statistical

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	Total Length $\bar{X} \pm \text{S.D. (mm)}$	Weight (g) $\bar{X} \pm \text{S.D.}$	Percent Mortality	Percent Hatchability
0.10	54	20.7 $\pm$ 1.59	0.073 $\pm$ 0.017	8.3	84.0
0.05	47	21.6 $\pm$ 1.78	0.087 $\pm$ 0.023	8.3	91.7
0.025	57	21.2 $\pm$ 1.85	0.085 $\pm$ 0.022	4.8	98.3
0.0125	51	21.1 $\pm$ 1.86	0.085 $\pm$ 0.022	5.0	89.3
0.00625	49	21.4 $\pm$ 1.60	0.083 $\pm$ 0.018	11.5	95.7
0.00 (control)	56	21.6 $\pm$ 1.44	0.085 $\pm$ 0.018	5.0	99.2

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

Concentration of Leachate (%)	N	Total Length $\bar{X} \pm \text{S.D. (mm)}$	Weight (g) $\bar{X} \pm \text{S.D.}$	Percent Mortality	Percent Hatchability
0.10	24	16.9 $\pm$ 1.45	0.060 $\pm$ 0.016	45.0	56.0
0.05	43	16.5 $\pm$ 1.44	0.059 $\pm$ 0.012	21.7	74.5
0.025	40	16.2 $\pm$ 1.16	0.054 $\pm$ 0.012	26.7	78.1
0.0125	40	15.8 $\pm$ 1.80	0.049 $\pm$ 0.014	29.5	63.1
0.00625	44	16.2 $\pm$ 0.97	0.053 $\pm$ 0.010	21.7	76.0
0.00 (control)	43	16.4 $\pm$ 0.79	0.056 $\pm$ 0.009	23.3	80.7

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 WSN. There was a significant increase in the amount of mortality in the highest concentration over that found in the control ($X^2 = 9.58$, $P < 0.005$). The hatchability in the control (90.7%) was significantly higher than that measured in the test solutions of 0.10% leachate (hatchability = 56.0% $P < 0.005$) and 0.0125% leachate (hatchability = 63.1 %, $P < 0.005$).

The results of the chronic bioassays of WSN using Daphnia magna, are summarized in Table 25. The leachate had several detrimental dramatic effects on the Daphnia. The mortality observed in chambers exposed to 0.10% and 0.05% (75%) leachate was significantly higher than that observed in the controls (15%) as determined by chi-square contingency analysis. The mortality in the other treatments (30-50%) 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/adult, was significantly reduced in the three highest concentrations (0.10, 0.05 and 0.025% WSN) from that observed in the control. The reproduction at doses of 0.0125 and 0.00625% WSN 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 WSN ($F_{(4,47)} = 0.0014$, $P > 0.10$).

The results of the chronic bioassays of WSN 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

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

Concentration of Leachate (%)	Progeny/Adult $\bar{X} \pm \text{S.D.}$	First Day of Reproduction	Percent Mortality	Total Length $\bar{X} \pm \text{S.D. (mm)}$
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

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

Concentration of Leachate (%)	N	Shell Length $\bar{X} \pm \text{S.D. (mm)}$	Weight (g) $\bar{X} \pm \text{S.D.}$	Percent Mortality	Egg Mass Production $\bar{X} \pm \text{S.D.}$
0.10	33	5.4 $\pm$ 0.40	0.018 $\pm$.003	30.0	89.3 $\pm$ 27.0
0.05	49	5.4 $\pm$ 0.50	0.020 $\pm$.005	13.3	133.3 $\pm$ 12.7
0.025	49	5.7 $\pm$ 0.73	0.022 $\pm$.007	15.0	106.3 $\pm$ 17.3
0.0125	43	5.8 $\pm$ 0.48	0.023 $\pm$.005	18.3	108.5 $\pm$ 24.2
0.00625	45	5.9 $\pm$ 0.80	0.026 $\pm$.009	18.3	99.0 $\pm$ 14.1
0.00 (control)	46	5.9 $\pm$ 0.56	0.025 $\pm$.006	8.3	119.3 $\pm$ 22.1

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 an SNK 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% WSNG ($P < 0.001$), 0.05% WSNG ($P < 0.001$) and 0.025% 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% WSNG treatment ($\chi^2 = 8.08$, $df = 1$, $P < 0.005$). Reproduction as measured by egg mass production, was not significantly impacted 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 significantly 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 bioassays of OBG using Pimephales promelas. No significant differences in mortality or hatchability were observed between the various concentrations of OBG and the control.

The green sunfish chronic bioassays of OBG were terminated after 14 days because of an insufficient quantity of leachate. Only total length, mortality and hatchability were recorded. The results of these chronic bioassays are

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	Total Length $\bar{X} \pm \text{S.D. (mm)}$	Weight (g) $\bar{X} \pm \text{S.D.}$	Percent Mortality	Percent Hatchability
10.0	61	24.2 $\pm$ 1.63	0.133 $\pm$.031	0.0	93.2
5.0	49	23.5 $\pm$ 1.59	0.131 $\pm$.029	8.3	98.3
2.5	51	23.3 $\pm$ 1.98	0.013 $\pm$.037	6.7	93.9
1.25	57	23.7 $\pm$ 1.95	0.140 $\pm$.037	3.3	98.3
0.625	53	23.1 $\pm$ 2.28	0.127 $\pm$.037	10.0	98.3
0.00 (control)	49	23.1 $\pm$ 1.37	0.126 $\pm$.025	1.7	97.3

summarized in Table 28. Mean length did not differ significantly between treatments ($F_{(5,205)} = 0.5276$, $P > 0.10$). Observed mortality showed no discernible trend. The only significant difference for green sunfish was the higher mortality of those individuals exposed to a leachate concentration of 2.5% OBG than those in control solution ($X^2 = 6.17$, $df = 1$, $P < 0.025$). Hatchability for eggs in all treatments was nearly complete (>96.5%) during the bioassays of OBG using green sunfish; no significant differences among treatments were observed.

The results of the chronic bioassays of OBG using Daphnia magna are listed in Table 29. Reproduction, measured as number of progeny produced/adult, was greater in the controls and lowest concentration of OBG; however, due to the large variability in progeny production 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 (15-35%) in all treatments; there were no significant differences between mortality observed in the controls and the other treatments ($X^2 = 3.305$, $df = 5$, $P > 0.10$). 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 leachate concentration of 5.0% 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 impacted by the OBG leachate. Observed mortality ($X^2 = 1.03$, $df = 5$, $P > 0.10$) and egg mass production ($F_{(5,18)} = 0.9890$, $P > 0.10$) did not differ significantly among the treatments and control.

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	Total Length $\bar{X} \pm \text{S.D. (mm)}$	Weight (g) $\bar{X} \pm \text{S.D.}$	Percent Mortality	Percent Hatchability
10.0	33	8.4 $\pm$ 0.71	⁻¹	18.3	96.6
5.0	39	8.3 $\pm$ 0.87	⁻¹	8.3	98.3
2.5	30	8.4 $\pm$ 0.85	⁻¹	30.0	99.1
1.25	39	8.2 $\pm$ 0.84	⁻¹	13.3	98.3
0.625	39	8.2 $\pm$ 0.72	⁻¹	10.0	96.7
0.00 (control)	41	8.2 $\pm$ 0.97	⁻¹	10.0	99.2

¹ Not measured

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 $\bar{X} \pm \text{S.D.}$	First Day of Reproduction	Percent Mortality	Total Length $\bar{X} \pm \text{S.D. (mm)}$
10.0	56.6 $\pm$ 35.2	10	35.0	4.0 $\pm$ 0.38
5.0	66.3 $\pm$ 19.3	10	15.0	4.3 $\pm$ 0.17
2.5	56.5 $\pm$ 21.0	12	35.0	4.1 $\pm$ 0.27
1.25	52.5 $\pm$ 22.8	12	30.0	4.0 $\pm$ 0.20
0.625	71.5 $\pm$ 15.0	12	35.0	4.2 $\pm$ 0.06
0.00 (control)	70.0 $\pm$ 47.8	11	35.0	4.0 $\pm$ 0.32

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	Shell Length $\bar{X} \pm \text{S.D. (mm)}$	Weight (g) $\bar{X} \pm \text{S.D.}$	Percent Mortality	Egg Mass Production $\bar{X} \pm \text{S.D.}$
10.0	52	5.0 $\pm$ 0.56	0.012 .003	8.3	54.5 $\pm$ 5.7
5.0	55	5.2 $\pm$ 0.54	0.013 .003	6.7	62.5 $\pm$ 12.1
2.5	52	5.2 $\pm$ 0.58	0.014 .004	6.7	61.0 $\pm$ 7.7
1.25	51	5.2 $\pm$ 0.65	0.013 .005	5.0	75.5 $\pm$ 31.0
0.625	49	5.3 $\pm$ 0.62	0.014 .005	15.0	66.0 $\pm$ 5.5
0.00 (control)	55	5.2 $\pm$ 0.70	0.013 .005	5.0	55.8 $\pm$ 16.4

11.4 DISCUSSION

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

The WSNG leachate generated by the LVG procedure was quite toxic throughout the course of this investigation; however, 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 between the OBG solution (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 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 (Section 7) with a front-end loader in the same physical state as was collected 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 H₂SO₄ 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.

The OBG leachate was assayed as a ten percent solution for the highest concentration for chronic exposure to determine if any long-term effects might be associated with exposure to this acutely non-toxic leachate.

The organisms exposed to the OBG leachate were generally not detrimentally affected by dosages of this non-toxic solution. In fact, for 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 31-34) was quite innocuous which accounts for its relative lack of toxic effects.

Although the WSNG leachate generated change in chemical composition with time, its toxicity was still very great. Its low pH (3.49-3.98) was, in part, responsible for the toxicity during the screening procedures and LC-50 determinations; however, the pH during the chronic tests (pH 7.8-8.5) was not near the lethal limits for organisms, and yet mortality (Lepomis, Daphnia, Physa), lowered hatchability (Lepomis cyaneus, Pimephales promelas), reduced reproduction (Daphnia), and reduced weight gain (Physa) were all factors associated with chronic exposure to the WSNG leachate.

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

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

The lowered hatchability of both green sunfish and fathead minnow eggs was probably due to suffocation as the precipitate would attach to eggs

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

Parameter	Concentrations (% OBG)					
	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 (mg/L)	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*).

Parameter	Concentrations (% OBG)					
	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 (mg/L)	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.

Parameter	Concentration (% OBG)					
	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 (mg/L)	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 chemical parameter values (mg/L) for replicate concentrations of OBG during chronic bioassays for the snail, Physa anatina.

Parameter	Concentration (% OBG)					
	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 (mg/L)	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	0.426-0.638	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	9.5-9.7	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
Mn	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Zn	<0.14	<0.15	<0.15	<0.15	<0.15	<0.15
in	<0.07-0.21	<0.13	<0.08-0.17	<0.32	<0.33	<0.14-0.14

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

Parameter	Concentration (% WSNB)					
	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 (mg/L)	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 WSNB during chronic bioassays for green sunfish (*Leponis cyanellus*).

Parameter	Concentrations (% WSNB)					
	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 (mg/L)	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, Duphnia magna.

Parameter	Concentrations (% WSNG)					
	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 (mg/L)	7.72-8.42	7.72-8.66	7.83-8.20	7.82-8.70	7.83-8.51	7.96-8.68
Turdibity (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 chemical parameter values (mg/L) for replicate concentrations of WSNG during chronic bioassays for the snail, (Physa anatina).

Parameter	Concentrations (% WSNG)					
	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 (mg/L)	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

thereby blocking oxygen transfer. Small masses of ferric hydroxide suspensions are similar in size to the pore size in the chorion of fathead minnow eggs. Consequently, the clogging of these pores by ferric hydroxide particles would reduce oxygen diffusion across the chorion and hence 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 the eggs somewhat free of the precipitate, whereas if eggs had rested on the chamber bottoms, hatchability would have probably been further reduced.

The gills of fish that hatched and subsequently 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; however, high mortality was noted in the highest concentration of WSNG tested green sunfish. These results support previous evidence that different life stages and different 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 the consumption of 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 greater mortality in the highest WSNG concentrations for Physa. These snails often consumed the precipitate as was evident by their orange fecal material.

The 0.1%, 0.05%, and 0.025% WSNG concentrations were toxic in some form to all the organisms tested which corresponded to concentrations of 3.37-8.16 mg/L, 1.43-4.37 mg/L, and 0.79-1.40 mg/L total solution iron concentrations,

respectively. Significant differences in development were observed in both fish species in their exposure to 0.0125% WSNG vs. control solutions. These WSNG solutions were characterized by iron concentrations of 0.42-0.58 mg/L total solution iron. Concentration of total iron in solutions of 0.00625% WSNG (the "no effect" concentration) used in green sunfish and fathead minnow tests ranged from 0.26-0.29 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% solution of WSNG (an acutely 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 a variety of 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 has the potential of modifying an entire aquatic ecosystem. The toxicity shown here for the WSNG leachate is demonstrative of the potential effects of these types of wastes should they ever enter a receiving water in a natural setting.

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APPENDIX-A

COMPILATION OF CHEMICAL ANALYSES OF ALL
SHORT-TERM EXTRACTS (ASTM-A, ASTM-B,
carbonic acid, U.S. EPA Extraction
Procedure, and large volume generation
procedure) OF THE SEVEN COAL SOLID WASTES

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

Constituent	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

¹not determined

²average of three replicates

³sample taken after 147 days of equilibration

⁴sample taken after 133 days of leaching

⁵relative to normal hydrogen electrode

⁶concentration could not be determined due to spectral interferences (see Section B)

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

Constituent	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

¹not determined

²average of three replicates

³sample taken after 21 weeks of equilibration

⁴relative to normal hydrogen electrode

⁵could not be determined due to spectral interferences (see Section B)

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

Constituent	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

¹not determined

²average of three replicates

³sample taken after 147 days of equilibration

⁴sample taken after 150 days of leaching

⁵relative to normal hydrogen electrode

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

Constituent	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

¹not determined

²average of three replicates

³sample taken after 147 days of equilibration

⁴relative to normal hydrogen electrode

⁵could not be determined due to spectral interferences
(see Section B)

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

Constituent	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 ⁵	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

¹not determined

²average of three replicates

³sample taken after 147 days of equilibration

⁴relative to normal hydrogen electrode

⁵could not be determined due to spectral interferences
(see Section B)

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

Constituent	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 ⁵	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

¹not determined

²average of three replicates

³sample taken after 147 days of equilibration

⁴relative to normal hydrogen

⁵concentration could not be determined due to spectral interferences (see Section B)

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

Constituent	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 ⁵	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

¹not determined

²average of three replicates

³sample taken after 147 days of equilibration

⁴relative to normal hydrogen electrode

⁵concentration could not be determined due to spectral interferences (see Section B)

APPENDIX-B

INTERELEMENT INTERFERENCES IN INDUCTIVELY
COUPLED ARGON PLASMA (ICAP) AS APPLIED
TO HIGH-IRON SOLUTIONS¹

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 As or B which are not easily performed by conventional atomic absorption or emission techniques at trace levels.

However, complex solutions such as the high-iron laboratory extracts of the coal solid wastes yielded spectral interferences which 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 1-B. 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 that coming from the near-by iron lines as suggested by Figure 1-B. 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

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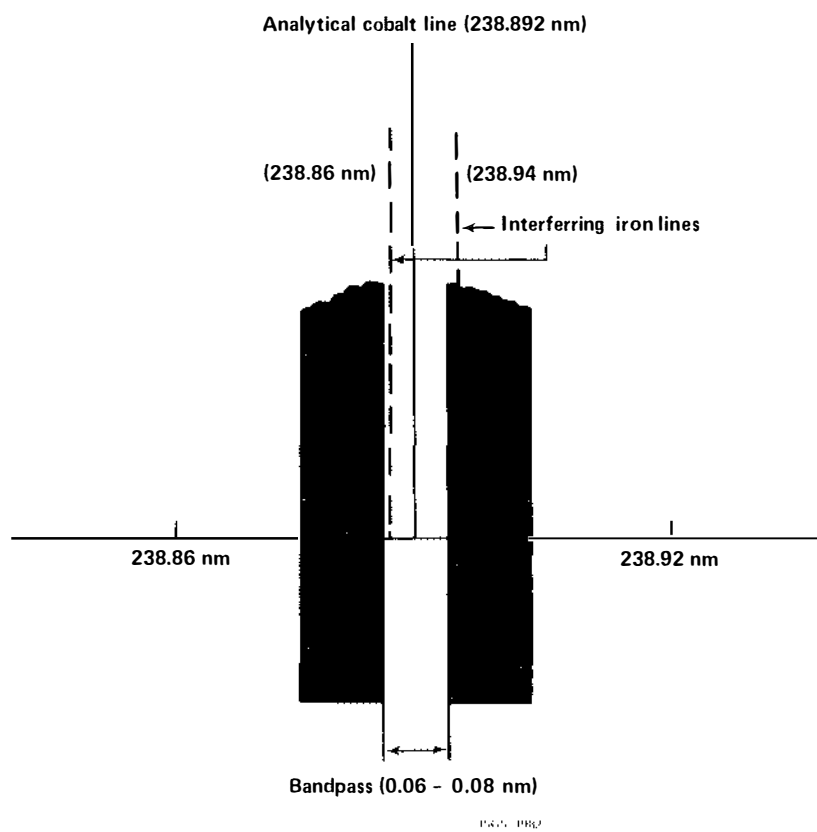


Figure 1-B. Relationship between the spectral bandpass, analytical cobalt emission line and two interfering iron lines.

interferences by iron, several other elements were also influenced by the presence of Fe (Table 1-B), Al, and Si. 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 which 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.

In the course of the project, correction factors were derived and tested. The apparent concentration of some elements 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. However, it was found 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 for reasons not well understood.

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

Element effected	wavelength (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

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

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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- Ediger, R. D., W. Stelzer, T. J. Hanson, and A. R. Knott, 1980, The selection of optimum ICP instrument parameters: Atomic Spectroscopy, ICP Application Study Number 8, 17 p.
- Marciello, L., and A. F. Ward, 1978, Technical Aid Note 3: Interelement corrections for spectral line interferences: Jarrell-Ash Plasma Newsletter, v. 1, n. 2, p. 12-13.

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.

Chemical Constituent	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)

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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)

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom Quality Criteria for Water. (U.S. EPA, 1976).

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

Chemical Constituent	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)

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom Quality Criteria for Water. (U.S. EPA, 1976).

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

Chemical Constituent	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

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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)

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom 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.

Chemical Constituent	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

^aMATE values cited from Cleland and Kingsbury (1977) unless otherwise indicated.

^bContribution to multiple regression of chemical composition on mortality.

^cLinear regression value (statistical significance).

^dFrom Quality Criteria for Water. (U.S. EPA, 1976).