CONSIDERATIONS IN THE SELECTION OF MODEL SUBSTRATES FOR MICROBIOLOGICAL EFFECTS RESEARCH

A.J. Francis and A.W. Rose*

***Department of Geosciences
Pennsylvania State University
University Park, PA 16802**

January 1984

NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE.
It has been reproduced from the best
available copy to permit the broadest
possible availability.

**TERRESTRIAL AND AQUATIC ECOLOGY DIVISION
DEPARTMENT OF APPLIED SCIENCE
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.**

**UNDER CONTRACT NO. DE-AC02-76CH00016 WITH THE
UNITED STATES DEPARTMENT OF ENERGY**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency, contractor or subcontractor thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency, contractor or subcontractor thereof.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes:
Printed Copy: A03; Microfiche Copy: A01

PREFACE

The purpose of this paper is to select a representative or a model substrate for basic research on anaerobic microbiological transformation and transport of chemical substances (e.g., trace metals) in subsurface environments. This research is part of the "Subsurface Transport Program" in which geochemical, hydrological and biological cycling of energy residuals in subsurface environments are being studied (Wobber, 1983). This research is sponsored by the Ecological Research Division, Office of Health and Environmental Research, Department of Energy. This working paper was prepared at the request of Dr. Frank J. Wobber of the Department of Energy and is a result of the Geochemical and Biochemical Working Group meeting which met at Brookhaven National Laboratory (BNL), August 1983.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

The physical and chemical characteristics of several energy residues have been briefly reviewed in order to select a model or representative substrate of basic research to determine the significance of anaerobic microbial dissolution and mobilization or immobilization of toxic trace elements under subsurface environmental conditions. The major factors which influence the dissolution and mobilization of trace metals have been critically examined, e.g., (i) effects on pH of leachates (pyrite oxidation), soluble acid, and basic compounds; (ii) effects on oxidation state of leachates (oxidation state of Fe, presence of organics); (iii) concentration of toxic inorganic species, and chemical form; (iv) surface area of waste particles; and (v) physical strength and particle size, with resulting effects on permeability of the substrate. Several major physical and chemical characteristics are common to energy-related residues yet each of these materials has a unique set of physical and chemical properties. The pros and cons of selecting a single model substrate for microbiological research were discussed at the Geochemical and Biochemical Working Group Meeting and use of the end-member concept was suggested. From the abundance, distribution, forms of trace metals present, and volume of these metal-containing residues disposed of in the subsurface environments, microbiological studies can be performed with coal beneficiation and coal gasification residues under a variety of subsurface environmental conditions, and results can be validated in the field. The basic scientific information obtained from this research can be applied to other materials of similar composition.

ACKNOWLEDGMENTS

Valuable suggestions in the preparation of this document were provided by the members of the Geochemical and Biochemical Working group which met at BNL in August 1983. We thank Dr. F.J. Wobber, OHER, Department of Energy; Dr. R. Turner, Oak Ridge National Laboratory; Dr. J. Rogers, Pacific Northwest Laboratory; and Dr. P.J. Sullivan, Ball State University, Indiana, for their help.

CONTENTS

	<u>Page</u>
Preface.....	iii
Abstract.....	v
Acknowledgment.....	vi
I. Introduction.....	1
II. General Characteristics of Energy Residues.....	2
Characteristics of Waste from Coal Mining and Coal Conversion.....	2
Coal Preparation Waste.....	4
Coal Combustion Waste.....	4
Coal Conversion Waste.....	5
Uranium Mill Tailings.....	6
III. Important Characteristics of Model Substrate.....	6
Major Element Concentration and pH of Aqueous Solution.....	7
Acid pH.....	7
Alkaline pH.....	8
Neutral pH.....	8
Oxidation State of Leachates.....	9
Surface Properties of Particles in Substrate.....	13
Abundance and Chemical-Mineralogical Form of Trace Elements...	14
Particle Size, Shape, and Strength.....	14
IV. Selection of a Representative Substrate for Microbiological Research.....	15
V. Summary.....	23
VI. References.....	24

I. INTRODUCTION

A major national concern in the terrestrial disposal of complex mixtures of chemical substances is the contamination of ground and surface waters by leachate containing trace metals and organic compounds. Although much is known about microbial transformation of chemical substances under aerobic conditions, scientific information on the role of anaerobic microbial processes in the mobilization and immobilization of toxic metals in subsurface environments is unavailable. Trace element behavior is affected in a major way by bacteria, but little is known of the processes and mechanisms involved, in particular, of the range and nature of bacterial effects in environments that are anoxic or transitional between oxygenated and anoxic. The influence of environmental factors (pH, Eh, temperature, moisture) and the mechanisms involved in the microbial dissolution of toxic metals in anaerobic or transitional environments need further study, as does the interaction of aerobic and anaerobic environments. The form of the trace metal (elemental, oxide, or sulfide), the availability or presence of nutrients (carbon and nitrogen source), and the presence of alternate electron acceptors (Fe^{3+} , MnO_2 , NO_3^- , SO_4^{2-} , organic compounds) will affect microbial activity and microbial transformation of trace metals in subsurface environments.

Energy residuals contain a wide variety of minerals in their natural state (coal beneficiation residues, mill-tailings, etc.) or toxic trace metals converted to various other forms (elemental, oxides, etc.), depending on the specific process employed (coal combustion, coal conversion, nuclear, etc.). Considerable amounts of these energy wastes are presently being produced at sites like coal-cleanup plants and uranium mines, but with coal gasification, liquification and oil shales processing the volume of wastes will be enormous and the consequences of their improper disposal would be severe. Microorganisms will play a major role in the dissolution and fixation of toxic trace elements from energy residuals disposed of in the terrestrial environment and microbial mobilization of toxic metals could be critical, especially when these wastes are codisposed. The emphasis of this paper is, therefore, an identification of the key characteristics of energy residuals that are relevant to microbial processes and the selection of a limited number of materials for experimentation. The basic results of experimentation should be applicable to a wide variety of man-made and natural environments, including energy residues.

The objectives of this research are to determine (i) the ability of microbial processes to mobilize and immobilize toxic trace elements such as As, Cd, Cr, Cu, Hg, Mn, Ni, Se, Pb, and Zn under subsurface environmental conditions, (ii) the biochemical mechanisms involved in the dissolution and mobilization of selected trace metals in anaerobic environments, (iii) the environmental parameters affecting anaerobic microbial dissolution and mobilization of trace metals, and (iv) the effects of specific anaerobic microbial processes such as sulfate-reducing, denitrifying, iron-reducing, fermentative (biodegradation products and metabolites), and methanogenic conditions on dissolution of selected trace metals under anaerobic conditions.

Initially, experiments will be performed to provide optimal conditions for anaerobic microbial growth (nutrient amendments, pH, temperature, etc.) in order to show that trace metals from a model substrate are being solubilized by anaerobic microbial action. Subsequent laboratory experiments will address the effect of various environmental conditions (nutrients, pH, Eh, temperature, moisture) that exists in subsurface environments and determine the rate and extent of dissolution of selected metals.

Laboratory evaluation of the accelerated weathering and release of toxic constituents from energy residuals will be simplified if experiments can be performed on a representative substrate in great detail under a variety of conditions. In order to carry out experiments under conditions more similar to natural environments, it is desirable to select one or more typical materials to serve as a substrate. The intent of this paper is to discuss the characteristics of such a material and the range of natural conditions under which experimentation might be relevant to obtain basic scientific information which can be applied to many types of natural materials and man-made wastes.

II. GENERAL CHARACTERISTICS OF ENERGY RESIDUES

The wastes from coal mining, coal combustion, gasification, and liquefaction, as well as oil shale and uranium mining, are similar in that the major mineralogical components are derived from sedimentary rocks and minerals existing within or in proximity to the coal or other energy material. Accompanying these inorganic materials are residual coal and other organic reaction products.

A. Characteristics of Waste from Coal Mining and Coal Conversion

The most abundant minerals in coal and its overburden are various types of clays (Ca-K-Na-Mg-Fe aluminosilicates), quartz (SiO_2), Ca, Mg, and Fe carbonates, pyrite and marcasite (FeS_2), and Fe oxides (Mackowski, 1968; O'Gorman, and Walker, 1972; Griffin et al., 1980). Many other minerals are present locally or in trace amounts (Table 1). The bulk composition is usually dominated by quartz and aluminosilicates containing varying proportions of Fe, Ca and Mg and lesser amounts of K and Na. The Eastern and Midwestern coals tend to have higher pyrite (and therefore Fe) contents, and the Western coals tend to contain higher than average Ca and Mg carbonates. The minerals occur in the coal as isolated small grains, as thin layers and nodules enclosed by coal, as fracture fillings, and as separate beds of shale, sandstone, and sometimes limestone within and overlying the coal.

During burning, gasification, and liquefaction, the mineral composition is commonly modified. Silicates and oxides stable at higher temperatures are formed (feldspar, Fe-bearing silicate, magnetite, wollastonite, mullite). The pyrite breaks down to Fe oxides (hematite, Fe_2O_3 , or goethite, FeOOH), FeS (pyrrhotite or troilite) or Fe sulfate, and the Ca, Mg and Fe carbonates decompose to oxides and sulfates. In some processes, the material partly melts to form glassy material or slag. Some constituents (e.g., Hg, As) are lost in volatile form, and other nonvolatile constituents

Table 1
Important Minerals Occurring in Coal
(modified after A. Davis, Penn. State Univ., personal communication)

Clays

Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
 Illite $\text{K}_{1-1.5}\text{Al}_4(\text{Si}_{6.6-7}\text{Al}_{1-1.5})\text{O}_{20}(\text{OH})_4$
 Smectite (including montmorillonite)
 $\text{X}^*\text{O}_{.33}(\text{Al}, \text{Mg}, \text{Fe})_{2-3}(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$
 (*=exchangeable Na^+ , K^+ , Ca^{2+} , etc.)
 Mixed layer illite-montmorillonite
 Chlorite (Mg-Fe-Al silicate)

Sulfides

Pyrite FeS_2
 Marcasite FeS_2
 Sphalerite $(\text{Zn}, \text{Fe})\text{S}$
 Galena PbS
 Chalcopyrite CuFeS_2

Silica

Quartz SiO_2
 Chalcedony SiO_2

Carbonates

Calcite CaCO_3
 Dolomite $\text{CaMg}(\text{CO}_3)_2$
 Siderite FeCO_3
 Ankerite $\text{Ca}(\text{Mg}, \text{Fe})(\text{CO}_3)_2$

Sulfates

Barite BaSO_4
 Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
 Jarosite $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$

Oxides

Hematite Fe_2O_3
 Goethite $\text{FeO}(\text{OH})$

Phosphates

Apatite $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$

Others (usually minor to trace)

Feldspar $\text{KAlSi}_3\text{O}_8, \text{NaAlSi}_3\text{O}_8, \text{CaAl}_2\text{Si}_2\text{O}_8$
 Mica $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2, \text{K}(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$
 Rutile TiO_2
 Anatase TiO_2
 Zircon ZrSiO_4
 Tourmaline $\text{Na}(\text{Mg}, \text{Fe}, \text{Al})_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO})_3(\text{OH}, \text{F})_4$
 Chlorides
 Nitrates

formerly occurring in organic form in the coal are liberated as oxides and other compounds.

Physically, the wastes vary from microscopic fly ash particles through slag to large boulder-size pieces of overburden at a strip mine. The strength also varies from soft plastic clays and shales to hard brittle sandstone or slag.

Coal Preparation Waste. Over three billion tons of coal cleaning wastes have accumulated in the U.S. and the current levels have exceeded 100 million tons per year. Nearly one third of the mined coal is discarded as refuse after physical cleaning. The refuse generally contains waste coal, slate, carbonaceous and pyritic shales, pyrite, clay, and other impurities associated with a coal seam. Currently, most of the preparation plants dewater the fine refuse and dispose of it along with coarse refuse in landfills or disposal ponds.

The types of contaminants generated from coal cleaning waste at the landfill are suspended solids, dissolved solids, metal ions, acidity, and organic compounds. Leachates from coal preparation refuse are variable, in composition and volume, depending on the raw coal from which they are derived as well as the amount of infiltrating rainfall and other environmental factors. Because of the enrichment of many heavy metals in coals and the fact that many of the highly toxic metals such as mercury and lead are generally associated with the mineral fraction, leachate from the refuse is commonly high in metal ions. In particular, acid leachates tend to have high contents of heavy metals because most of these elements are relatively soluble in acid. The less common neutral-to-alkaline leachates may be enriched in Si, As, B, and other elements forming oxyanions.

Coal Combustion Waste. Fly ash and bottom ash are residues generated from conventional coal-fired power plants. Ash (inorganic materials) present in the initial coal feedstock remains as a solid waste. Chemically, this material may vary on a regional basis depending on the coal feedstock that is used.

Fly ash, the dominant waste material from many coal-fired electric power plants, varies widely in trace and major element content and in pH of leachates; these are a function of the coal source and the specific combustion temperature. However, typical fly ash is highly enriched (10x average soils) in B, Hg, Se, Sr, and Te and significantly enriched (3x average soils) in Ag, As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, Zn, and, in some cases, U (Furr et al., 1976; Dudas, 1981, unpublished data). Generally, fly ashes produced from combustion of Western subbituminous and lignitic coals have higher than average boron content and produce leachates of alkaline pH. Ashes from combustion of Eastern and Midwestern bituminous and subbituminous coals are generally higher in S, more enriched in trace elements such as As, Cd, Co, Cr, Pb, Sb, and Zn, and produce acidic leachates. Mineralogically, fly ash consists of glassy spheres of ferro- and aluminosilicate composition (~60-90 wt. %) with lesser quantities of quartz (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), hematite (Fe_2O_3), and magnetite (Fe_2O_4) (Adriano et al., 1980; Wangen and Wewerka, DOE, ER-0131). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and

anhydrite (CaSO_4) are also commonly found, but mostly in fly ashes from Western U.S. coals. The ash and slag residues remaining in the fire box, collectively referred to as bottom ash, are the other residues generated in a coal-fired power plant; these are generally less enriched in trace elements. Residual organic carbon may also exist and fused aromatic compounds have been detected. When contacted with subsurface water, fly ash may produce leachates with high pH, elevated levels of soluble salts, and some trace elements, including B, Mo, Se, and Pb (Straughan et al., 1978; Dudas, 1981).

Coal Conversion Waste. The primary wastes produced by coal conversion processes include coal cleaning residues and a mineral ash or slag remaining after direct gasification of coal, or, in the case of liquefaction, from the gasification of the mineral residue or vacuum bottoms. As with coal combustion, these wastes are subject to significant variability in chemical composition reflecting coal feedstock. Additional wastes produced in limited quantities in coal conversion include coal gasification char (residual carbon remaining after incomplete conversion), wastewater treatment sludge, spent catalysts, and still bottom and tar sludges.

Gasification wastes can vary significantly with the specific processes utilized and are generally termed ashes or slag depending on the temperature reached during processing. Ashes, produced mainly by fluidized- and fixed-bed gasifiers, contain a secondary mineral assemblage consisting of high temperature crystalline silicates (mullite, Fe^{2+} -silicate), quartz, feldspars, and a variety of iron oxides such as hematite, goethite, and magnetite (Griffin et al., 1980). These materials may be fine-grained ashes or partially klinkered aggregates. Slag is produced at higher temperatures by entrained-bed and some fluidized- and fixed-bed gasifiers and arises from the melting of coal minerals and their subsequent solidification upon cooling. Slags are composed mainly of amorphous and some partially crystalline Fe^{2+} -Al silicates, with the proportions of glass vs crystals and size of crystals depending upon the cooling rate (Griffin et al., 1980). The particle size distribution of slags is usually sand size, but may vary significantly depending on the extent of mechanical crushing and specific waste handling procedures used in disposal.

The major elements found in gasification residues are Si, Al, and Fe (each comprising greater than 10% of the residue), and with lesser amounts of K, Ca, Mg, and Na. The concentrations of some minor elements (B, Ba, and V), as well as those of Cu, Ni, Cr, Pb, and Zn, can be quite high and exceed levels found in most soil materials (Griffin et al., 1980). The concentration and chemical form of S may be quite variable in gasifier slag (0.5 to 1%) depending upon S content in the coal feedstock as well as the conversion process. Reduced S forms have been detected in the gasification residues. A wide range of aromatic and aliphatic hydrocarbons in low concentration have been detected in gasification wastes (Francis and Wobber, 1982).

Laboratory leaching studies with selected gasifier ashes and slags produced mildly basic (pH 8.0-9.0) or acidic (<4.0-6.5) leachates with varying quantities of soluble salts (Ca, SO_4). Some minor elements (e.g., B) trace metals (e.g., Cd, Pb, Al, Fe, As, Mn, Mo, Sb), and macroions (K, NH_4),

occasionally exceed water quality criteria (Griffin et al., 1980). Those wastes producing acid leachates generally contain higher levels of metals and sulfate (Francis and Wobber, 1982), possibly resulting from the formation of soluble ferric sulfates or the oxidation of residual reduced sulfur remaining after conversion.

B. Uranium Mill Tailings

The particle size of uranium mill tailings is typically 60 to 70% sand (50-200 μ m), 15 to 20% silt (2-50 μ m), and 15 to 20% clay (<2 μ m). The mineralogy is strongly dependent on the parent ore body, but quartz, feldspar, and phyllosilicates are ubiquitous in tailings from sandstone uranium ore deposits, the predominant ore type currently being mined in the United States. Chemically, the mill tailings are composed of major elements Si, Al, Fe, Mg, Ca, Na, K, and Mn accompanied by varying amounts of Zn, Ni, Mo, Cr, V, and Se and other trace elements. In particular, Se, Mo, V, and U may be found in elevated levels over average sandstone and soil concentrations. Approximately 10% of the original uranium and almost all members of the uranium decay series in the original ore (^{238}U , ^{234}U , ^{230}Th , ^{226}Ra and ^{210}Pb) are retained in the tailings in amounts much higher than in normal soils. In addition to these enriched ore constituents, high levels of inorganic species are present in spent leach solutions discharged from mills: SO_4^{2-} from acid leach solutions, Na^+ from carbonate leach solutions, Cl^- from sodium chlorate oxidant, and NH_4^+ used in yellowcake precipitation. Further, many major and minor elements, for example, Fe and Mn, are dissolved during acid leaching of uranium ore. Organic chemicals such as tertiary amines, alkylphosphoric acids, isodecanol, and kerosene (as a carrier) used in solvent extraction circuits are also found in mill liquors disposed of in tailing ponds.

III. IMPORTANT CHARACTERISTICS OF MODEL SUBSTRATE

In selecting a substrate material for experiments, it is important to consider that it meets the objectives of the study, the kinds of effects this material might have on the outcome of experiments, and the range of characteristics that might be found in nature. The characteristics of the substrate that are expected to be important to microbial processes in the mobilization of trace metals are summarized as follows:

- a. Characteristics influencing pH and major element content of aqueous solutions in contact with the substrate.
- b. Characteristics influencing the oxidation state of aqueous solutions.
- c. Surface area and other surface properties of particles comprising the waste or substrate, and the resulting adsorption and catalysis of reactions.
- d. Abundance and form of toxic elements.
- e. Size, shape, and strength of particles comprising the substrate.

A. Major Element Concentration and pH of Aqueous Solutions

The mobility of most cations is affected by pH and in many situations by other dissolved constituents that form insoluble compounds or soluble complexes with contaminants. In general, cations are most mobile in acid solutions and anions tend to be more mobile in basic solution.

Acid pH: The major waste constituent causing acid pH values is pyrite (or marcasite) and its oxidation products. In the presence of oxygenated water, pyrite and marcasite oxidize in the following sequence of reactions:

If Fe^{3+} concentration is significant (pH below about 4.5), Fe^{3+} acts as the oxidant of pyrite rather than O_2 :

The Fe^{3+} is regenerated by catalysis of Reaction (2) by Thiobacillus ferro-oxidans, greatly accelerating the reaction. In addition to production of SO_4^{2-} by Reaction (1), less oxidized sulfur species may be formed (SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, S^0 , polysulfides, etc.). These species eventually transform to SO_4^{2-} , but may be involved in catalyzing or inhibiting the reactions.

The pH commonly reaches 2 to 3 during oxidation of pyritic material and occasionally goes to 1.5. Values of pH between 3 and 6 are observed in less pyritic materials in oxygen-depleted Fe^{2+} -rich solutions which have not yet undergone Reaction (3), or in solutions neutralized by reaction with other minerals. Under some conditions, ferric sulfate or jarosite (Table 1) may precipitate. These species are most stable at pH of 2 to 3. The $\text{Fe}(\text{OH})_3$ gradually dehydrates and recrystallizes to hematite or goethite.

The acid produced in Reactions (1), (3), and (4) may be neutralized by reactions with carbonates and other minerals to form solutions enriched in Ca, Mg, K, Na, etc.:

Relatively high concentrations of various cations may be achieved in this manner. Reaction (5) is rapid, but reactions like (6) with aluminosilicates tend to be much slower. The breakdown of most minerals by the acid solutions liberates many trace elements (Rb, Sr, Ba, V, Cr, Mn, Ni, Cu, Zn, Ga, Ge, As, Se, Mo, Ag, Cd, Sb, Hg, Tl, U, and others) as well as the major constituents (K, Na, Ca, Mg, Al, Si, Fe, S). Under some conditions, sulfates and oxides, such as gypsum, barite, or rutile, may precipitate.

In liquefaction wastes pyrrhotite is commonly present rather than pyrite. The initial breakdown of pyrrhotite produces no acid:

However, this reaction is followed by (2) and (3), which do produce acid.

Other sulfides containing Fe behave like pyrrhotite, but nearly all other common sulfides oxidize without forming acid.

If highly acid conditions are produced by pyrite oxidation or similar processes, some Al may be dissolved from aluminosilicates. This Al can later precipitate as $\text{Al}(\text{OH})_3$ or similar phases, releasing acid in a reaction analogous to (3). However, the initial acid was produced by pyrite oxidation, and the dissolved Al [or soluble Al minerals such as $\text{Al}_2(\text{SO}_4)_3$] may be considered stored acidity.

Alkaline pH: At the other extreme of high pH, the most common control is probably the formation of alkaline-earth oxides and hydroxides by decomposition of carbonates during gasification or liquefaction

This reaction and the analogous one for Mg can produce pH values as high as 11 to 12. As an apparent example of this process, a liquefaction waste and a Lurgi ash tested by Griffin et al. (1980) produced pH values of 11.31 and 11.05 when slurried with water. Another possible cause of high pH might be the presence of soluble ammonia compounds formed in liquefaction or gasification.

Neutral pH: In the intermediate pH region, carbonate minerals in combination with dissolved carbonate or gaseous CO_2 are the most important pH controls. This system has been discussed by Garrels and Christ (1965). In a solution exposed to a fixed P_{CO_2} , such as $10^{-3.5}$ atm in open air, the dissolution reaction for calcite is

where a indicates chemical activity of the solute and K is an equilibrium constant. The system must also satisfy the various carbonate equilibria so that

If Ca^{2+} is derived only by dissolution of calcite, the equations can be solved to give $\text{pH} = 8.4$. At higher values of P_{CO_2} , as might be found in the subsurface, pH values are lower. If calcite or other carbonates are not present, Eq. (11) defines a pH near 5.5 for atmospheric P_{CO_2} . In general,

these reactions are relatively rapid for calcite, and slower for other carbonates.

Other minerals in the energy waste may affect pH values at a much slower rate than the reactions discussed above. For example, for aluminosilicate materials, reactions like (6) may tend to buffer pH. Such reactants could include glass formed on melting of the ash materials. In general, it appears that Al-rich residues will tend to form slightly acid solutions on breakdown, and Ca-, Mg-, and Na-rich residues will have an alkaline reaction.

In summary, wastes with soluble ferric minerals will tend to produce acid leachates, wastes with high temperature decomposition products of carbonates will produce alkaline leachates, Fe-sulfides exposed to oxygenated environments will produce acid leachates, and other mineralogies will generally produce leachates of intermediate pH. Some of the last will react only very slowly and their pH effects may be overwhelmed by more rapid reactions if waters percolate through the waste at a significant rate.

B. Oxidation State of Leachates

The main reducing constituents in wastes include sulfides, ferrous iron compounds, and organic matter. As previously described, the oxidation of sulfides consumes oxygen and can lead to reducing conditions, commonly on the stability boundary of Fe^{2+} with Fe-oxide (Kleinmann et al., 1981), or perhaps in some cases on the Fe^{2+} -pyrite boundary (or Fe^{2+} -pyrrhotite boundary, if it is the sulfide present) (Figures 1-3). The Fe^{2+} may be complexed as FeSO_4 , $\text{Fe}(\text{HSO}_4)^+$, or a similar species, if SO_4^{2-} is moderately concentrated. Attainment of these low redox values usually involves the activity of Thiobacillus or other bacteria that catalyze pyrite dissolution.

Organic compounds in bituminous and anthracite coal probably oxidize only very slowly in oxygenated environments, because the more reactive components have been consumed or lost in the original process of forming the coal. Some organic matter in lignite might oxidize rapidly enough to consume O_2 . However, experiments on the reactivity of these materials are needed to confirm whether these materials can be utilized by heterotrophic bacteria. In general, coal is probably not a very potent reductant because most of the rapidly reacting functional groups were probably consumed or destroyed by bacteria active during coal formation and subsequent elevated temperatures in the geologic past.

The organic compounds formed during liquefaction and possibly during gasification may oxidize relatively rapidly, either by themselves or through bacterial action, to consume O_2 and other oxidants and thereby create a reducing environment.

Ferrous compounds such as ferrous sulfates, ferrous silicates (clays, chlorite, pyroxene, glasses), and ferrous oxides (magnetite) may be soluble and reactive enough to create a reducing environment. The sulfates are readily soluble (though an acid solution would dissolve them more rapidly).

Figure 1. Eh-pH diagram for the system Fe-S-O-H. Species written in vertical letters are solids, and species written in slanted letters are aqueous species. Fe_2O_3 is hematite, Fe_3O_4 is magnetite, FeS_2 is pyrite, and Fe_7S_8 is pyrrhotite. Data largely from Parker et al. (1976) and Langmuir (1969), compiled by H. L. Barnes, D. Langmuir, and co-workers.

Figure 2. Eh-pH diagram for the system Fe-S-OH with hematite, goethite, and magnetite suppressed so that amorphous Fe(OH)₃ is the stable phase. Symbols same as in Figure 1. Note the increased extent of the field of Fe(II) soluble as FeSO₄.

Figure 3. Eh-pH diagram for the system Fe-S-OH with hematite, goethite, magnetite and pyrite suppressed so that pyrrhotite is the major reduced sulfur phase. Symbols same as in Figure 1.

Possible oxidizing agents in the wastes include ferric oxides [hematite, goethite, $\text{Fe}(\text{OH})_3$], ferric sulfate, and possibly manganese oxides (MnO_2 , Mn_2O_3), and any ferric iron in silicates and glasses. The $\text{Fe}(\text{III})$ and Mn oxides would react relatively rapidly, especially if fine grained. Oxidation states along or near the $\text{Fe}(\text{OH})_3$ - Fe^{2+} boundary would be expected if Fe^{3+} compounds are present (Figures 2 and 3). The silicates and glasses would react slowly, in the absence of acid, and probably would generally include both $\text{Fe}(\text{III})$ and $\text{Fe}(\text{II})$ so highly oxidizing conditions would not be likely.

In summary, the most likely phases controlling the oxidation state include Fe-sulfides, ferric oxides, and non-coal organic compounds.

C. Surface Properties of Particles in Substrate

The reaction of solids with leachates is enhanced by a large surface area, and the adsorption of dissolved constituents and the catalysis of reactions are strongly dependent on the surface area of the solid material. For example, hematite (Fe_2O_3) with a grain size of 1 mm would adsorb negligible amounts of trace elements like Pb, but fine-grained hematite in particles of 1 μm or less might immobilize all lead from solution by adsorption on its surface, which has 10^9 times the area of a similar mass of 1 mm grains (Jenne, 1968). For these reasons, the physical state (particle and crystal size) of energy waste materials is crucial in determining the character of leachates.

Fe-oxides are very good adsorbents for a wide variety of cations and anions (Jenne, 1968). Experiments show that colloidal and fine-grained Fe-oxides strongly adsorb transition metal cations (Cu, Pb, Zn, Cd, Ni, Co, Ag) at pH values greater than about 5 to 6 (Benjamin and Leckie, 1981; Balestrieri and Murray, 1982). High concentrations of competing adsorbents may inhibit adsorption, as can strong complexing, but the presence of fine-grained Fe-oxides will generally minimize the content of transition metal cations in leachates. The Fe-oxides also bind strongly to AsO_4^{2-} , SeO_4^{2-} , SeO_3^{2-} , MoO_4^{2-} , VO_2^{2+} , and similar species, especially under acid conditions (Harrison and Berkheiser, 1982). If the Fe-oxides are coarse grained, and well-crystalline, this adsorption will be decreased. Typically, the Fe-oxides coat other particles, for example, clays, and the area of the Fe-oxide surface is therefore maximized by fine particle size of the overall material. Freshly precipitated Fe oxides are generally far more reactive than aged precipitates.

Mn-oxides are generally even more effective adsorbents than Fe-oxides, in part, because they can strongly adsorb cations to more acid pH values than Fe oxides. In addition, the Mn-oxides are effective in catalyzing some oxidation-reduction reactions.

Similar effects are known for ion exchange on clays, and for adsorption on partly decayed organic matter of soils and peats. Anthracite and bituminous coals generally do not have surface areas large enough to be significantly adsorbent, but lignites may. The chars and similar materials formed in gasification and liquefaction could have large surface areas and

reactivities. Glasses and vapor condensates of the type found in fly ash are expected to have large surface areas and may be relatively reactive.

In summary, finely divided Fe-oxides, organic matter, glasses, and fine grain size, in general, will tend to enhance reactivity and adsorption, and must be controlled in a model waste form.

D. Abundance and Chemical-Mineralogical Form of Trace Elements

For study of the mobilization and dispersion of toxic trace elements from wastes, the abundance of these elements in the waste is obviously critical, as is the chemical form in which the elements occur. For example, in a study of 56 coal ashes from various coal fields of the U.S., Pb ranged from 20 to 1500 ppm, and Hg in 10 coals ranged from 0.11 to 13.3 ppm (O'Gorman and Walker, 1972). Many other transition metal trace elements have concentration ranges of several orders of magnitude. Regional differences in coals are also documented (Gluskoter et al., 1977). A waste with low concentrations of an element is likely to produce only minor environmental problems for this element, and wastes with high concentrations have a high potential for contamination.

The chemical-mineralogical form of the element can be at least as important as the total concentration. As noted previously, wastes contain some very soluble minerals and others that react slowly. Trace elements incorporated in or co-precipitated with soluble minerals will be rapidly released to solution, whereas trace elements in relatively stable minerals will generally be released very slowly, as the host mineral breaks down. For example, it seems likely that As and Se in oxidized wastes may occur as arsenate, arsenite, selenate, and selenite anions incorporated in Fe or Ca sulfates and be readily released to solution. Most of the Zn, Cd, and Pb in coals containing high amounts of these elements probably occur in readily oxidized and soluble ZnS and PbS. In fly ash, a considerable proportion of many trace elements is apparently loosely bonded to particle surfaces, and is thereby readily available. In contrast, high concentrations of Cr might occur in relatively stable minerals such as magnetite or pyroxene $[(Fe,Mg)SiO_3]$. The readily soluble constituents are much more reactive and potentially toxic in both short-term experiments and large-scale waste disposal.

E. Particle Size, Shape, and Strength

These characteristics are related to the surface area, but seem distinctive enough to justify separation in considering a model waste medium. The porosity and permeability of the waste are dependent on particle size and strength. A coarse (>1 mm) waste composed of fragments strong enough to support overlying material will pack with a relatively high proportion of open space with large openings, and consequently will tend to drain readily and be air-filled if above the water table. In contrast, a fine-grained material like fly ash, especially if it contains a wide range of grain sizes, will have very small pore spaces, and water will tend to be held in the pores by capillary forces. Flow through this waste will be slow, and air will probably not have easy access by convection.

Similarly, if the fragments or particles are weak or plastic, the fragments in the bottom of the waste pile will crumble or deform to decrease or eliminate the pore space. Also, silt- and clay-size particles will tend to expose more surface to solution attack.

IV. SELECTION OF A REPRESENTATIVE SUBSTRATE FOR MICROBIOLOGICAL RESEARCH

A model or a representative medium should possess the major physical and chemical properties common to all energy residues and contain trace metals in their natural and modified (after combustion, conversion, etc.) forms. Microbial transformations of metals in such a medium can be studied under controlled conditions. If necessary, appropriate addition of organic and/or inorganic compounds can be achieved to study the effect on microbial dissolution of trace metals.

The major types of residues from current or projected utilization of coal are coal cleaning waste, fly ash, and coal gasification ash and wastes from uranium mining and milling. Although there are several major physical and chemical characteristics common to energy-related solid wastes (Table 2), each of these waste materials has a unique set of physical and chemical characteristics which seem to represent absolute opposites. For example, high organic matter content versus low organic matter content, dominance of iron sulfides and sulfates as opposed to a dominance of iron oxides, fine grained with high surface area versus low surface area, acid versus alkaline pH, and a high content of glasses as opposed to low glass content.

The analyses of Griffin et al. (1980) suggest that ash from gasification tends to be partly oxidized (Table 3, presence of goethite and hematite, as well as some magnetite), whereas liquefaction wastes tend to be more reducing (pyrrhotite, pyrite present, no goethite or hematite). The use of a gasification waste would thus allow research on reducing conditions brought about by the activities of anaerobic bacteria. The oxidized forms of metals present in gasification waste under appropriate conditions (temperature, pH, moisture, carbon source, alternate electron acceptors, etc.) would undergo reduction due to anaerobic microbial activity. In contrast, the reduced components present in the liquefaction waste may be oxidized by microorganisms under aerobic conditions, and the oxidized components in the leachate may be reduced by the anaerobic microbial action in subsurface environments. The mobility of the metal under these conditions is dependent upon the metal form (speciation) and solubility.

The very fine particle size and large surface area of fly ash probably make this material less suitable for use as a model substrate than other materials. Some fly ashes apparently contain relatively high concentrations of adsorbed elements or soluble condensates.

Given all these variables, it does not seem that a single material can be used as a model substrate for microbiological experimentation. Alternatively, it might be desirable to mix different kinds of waste materials in combination so that they reflect all the characteristics listed above. Once this model substrate is created and characterized physically and chemically,

Table 2
Physical/Chemical Characteristics Common to Energy-Related Solid Wastes (Zachara et al., 1982)

	Coal				Oil Shale			Nuclear	
	Combustion	Liquefaction	Gasification		Western		Eastern	Uranium	Mill Tailings
		Mineral	Bottom		Low T	High T		Acid	Carbonate
	Fly Ash	Residue	Ash or Slag	Fly Ash	Retorted Shale	Retorted Shale		Leach	Leach
Solid Characteristics									
Organic Residues	+	X	+	+	X	0	X	0	0
Sulfides		X	+	+	X		X	+	0
Carbonates	x ^b				X	x ^b		+	
Amorphous Oxides	X		X		X	X			
High Temperature Silicates	X		X			X			
Trace Elements	X	X	X	+	X	X	X	X	X
Fine Texture	X	X	+ ^c	+	X	X	X	X	X
Coarse Texture (50% > 2 mm)			X		X	X	X	X	X
Leachate Characteristics									
High Salts (TDS > 2000) mg/l	X	+	+		X	0	+	X	X
Alkalinity	X	+	+		X				X
Trace Elements	X	+	+	+	X	0	X	X	X
Reduced S		0 ^d		0	X	0	0		
High pH (>9)	X	+	+		X	0	+		X
Low pH (<4)	+	0 ^d	+	0 ^d		X	X		
Organics		X			X	0	0	0	
Other									X

X = Observed in most analyses.

+ = Occasionally observed.

0 = Data not available in open literature.

a. Coal and liquefaction residues.

b. Secondary formation after pyrolysis.

c. Depends on waste handling procedures.

d. With time.

Table 3
Mineral Composition of Coals and Coal Solid Wastes (Griffin et al., 1980)

	Rose- bud	No. 6 (washed)	No. 5 (washed)	Fines (slurry)	Refuse (high-S gob)	Refuse (low-S gob)	Medium- temper- ature char	High temper- ature char	H- Coal ^R	Lurgi ash (No. 6 coal)	Lurgi ash (No. 5 coal)	Lurgi ash (Rose- bud)	Fly ash	SRG residue	Water quenched slag
Nonferro minerals															
Sphalerite	-	X	X	-	-	X	-	-	-	-	-	-	-	-	-
Quartz	X*	X	X	X	X	X	X	X	X	X	X	X	X	X	-
Calcite	X	X	X	X	X	X	X	-	X	-	-	-	-	-	-
Dolomite	X	X	X	-	-	-	-	-	-	-	-	X	-	-	-
Anhydrite	X	X	X	X	-	-	X	-	-	-	-	-	X	-	-
Bassinite	X	-	-	X	-	-	-	-	-	-	-	-	-	-	-
Gypsum	X	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Kaolinite	X	X	X	X	X	X	-	-	X	-	-	-	-	X	-
Expandable clay	X	X	X	-	-	-	-	-	X	-	-	-	-	X	-
Feldspar	-	-	-	X	X	X	X	-	-	X	X	X	-	-	-
Wollastonite	-	-	-	-	-	-	-	-	SEM**	-	-	-	-	-	-
Ferro minerals															
Pyrite	X*	MK†	MK	M†	MK	X	MK	MK	-	-	-	-	-	-	-
Pyrrhotite	-	-	-	-	-	-	MK	MK	MK	-	-	-	-	MK	-
Illite†	X	X	MK	MK	MK	MK	MK	MK†	-	-	-	-	-	-	-
Mullite†	-	-	-	-	-	-	-	-	-	MK	MK	MK	-	-	-
Melanterite	X	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe ⁺² silicate	-	-	-	-	-	-	-	#	-	M	M	M	M	-	M
Hematite	-	-	-	-	-	-	-	-	-	MK	MK	MK	MK	-	-
Goethite	X	-	-	-	-	-	-	-	-	M	M	M	M	-	-
Magnetite	-	-	-	-	-	-	-	#	-	M	M	M	M	-	-
Hydrated ferrous sulfate	-	-	MK§	-	MK§	-	MK	MK	MK	-	-	-	-	MK	-
Ferrous carbonate	-	-	-	-	-	M	-	-	-	-	-	-	-	-	-

* X-ray analyses.

**Scanning electron microscope.

† X-ray diffraction cannot distinguish between valence states of iron.

‡ Mössbauer analysis.

§ Anhydrous.

Spinel group hercynite.

it might be utilized by several researchers and the results correlated. However, in practice the disposal of a combination of all these waste materials is very unlikely. Research on such a mixed medium would provide some general information on bacterial activities, but the elucidation of basic scientific information on the types of reactions and the controlling factors would be more difficult because of the mixture of waste properties. These deficiencies obviously make the use of a mixed model waste also undesirable.

A preferred approach to microbiological experimentation is to utilize several materials or substrates which reflect uniquely different characteristics of the range of expected environments. For example, a substrate with a high pH and low organic carbon and a substrate with a low pH and high organic carbon could be selected. Each end member material would be characterized individually and subjected to microbial research (Tables 4 to 6). In addition to experiments on end-members, various ratios of the different substrates could be mixed, duplicating the range of expected environments, and subjected to the same microbial studies as were previously conducted on the individual substrates. The data collected from the individual substrates could be used to formulate hypotheses on the microbial activity of unknown systems.

For initial studies, the following three substrates are selected, using the end-member concept to examine most of the problems in microbiological and related effects:

1. A coal-cleaning waste with high content of pyrite and trace elements;
2. A gasification waste that is at least partly oxidized; and
3. Peat with high organic carbon and low levels of trace elements.

These three substrates are chosen on the basis of physical and chemical characteristics as well as availability. The gasification waste represents an end-member in oxidation state and is available from pilot gasification plants.

The pyritic coal-cleaning waste, in addition to being a type of waste produced in significant amounts by some current and proposed processes, would be relatively reducing chemically and would produce considerable acid on oxidation, thereby providing a range of reducing-neutral to oxidizing acid conditions under appropriate physical conditions, as in a large low-permeability pile or column with slowly flowing oxidizing water. A large sample of such a waste was collected from a major coal-cleaning plant near Clearfield, Pennsylvania. This waste contains high concentration of the toxic elements As, Cd, Pb, Ni, and Hg (Table 7), as well as in pyrite. Because of natural oxidation of pyrite, the coal-cleaning waste and the mixture will be stored in sealed containers, possibly in an inert gas atmosphere, to avoid changes in character with time, i.e., development of various soluble sulfates by oxidation of the pyrite. Research is examining the behavior of these phases and the toxic elements in a range of conditions

Table 4
Microbial Dissolution of Toxic Metals in Anaerobic Environments

Trace Metal (As, Cd, Cr, Hg, Mn, Ni, Pb, Th, U) Source Terms

*Source: Daniel, P.B. 1981. The Occurrence and Distribution of Element in a Modern Coal-Forsing Environment on the Atlantic Coastal Plain in Dare County, North Carolina. M.S. Thesis, University of South Carolina. Also see Otte, L.J. and A.J. Francis. Anaerobic Microbial Transformations of Trace Metals and Organics in Peat: Field Site Characteristics.

Table 5
Metal Forms for Use in Laboratory Experiments*

Name	Formula	Relevance for Study
Arsenopyrite	(FeAs)S	1
Sphalerite	(ZnCd)S	
Greenochite	CdS	1
Cadmium Oxide	CdO	2
Cadmium	Cd ⁰	3
Galena	PbS	1
Lead Oxide	PbO	2
Lead	Pb ⁰	3
Millerite	NiS	1
Pentlandite	(NiFe)S	1
Nickel Oxide	NiO	2
Nickel	Ni ⁰	3

* Final choice will depend upon availability in form needed for experiment to examine microbial dissolution and mechanism involved.

1. Natural form of element - present in peat, coal beneficiation waste.
2. Oxidized form - present in coal combustion and conversion residues.
3. Reduced form - present in peat, coal conversion wastes, particularly coal liquefaction wastes.

Table 6
Effect of Environmental Variables on Selected Trace
Metal Dissolution from Representative Waste Medium

Temperature	12-15°C
Moisture	Saturated, unsaturated
pH	Neutral (~7), acidic (~2.0-5.0), and alkaline (~8)
Oxygen	Anaerobic, partially anaerobic, aerobic and aerobic/anaerobic/aerobic
Alternate electron acceptors under anaerobic conditions	(i) Nitrate (ii) Sulfate (iii) Ferric oxides (iv) Manganic oxides (v) Carbonate (vi) Fermentation (energy yielding) oxidation-reduction reaction in which organic compounds serve as the final electron acceptors)

Table 7
Physical, Chemical and Biological Characterization of Coal Beneficiation Residues (Francis, A.J., C. Dodge and H.L. Quinby, unpublished results).

	Fines Fraction	Filter Cake
Physical		
Moisture (%)	5.78±0.2	28.8±0.2
Ash (%)	55.8±0.7	26.6
Particle size (mm) % retained)		
1.98 "	44.8	
1.40 "	15.2	
0.71 "	23.5	
0.59 "	5.2	1.1
0.35 "	7.3	32.3
0.25 "	2.2	22.6
0.12 "	1.4	27.9
0.09 "	0.3	6.8
0.04 "	0.2	9.2
<0.04 "	0	0.1
Chemical		
Arsenic (µg/g dry wt)	344±27	40.4
Cadmium "	<10	<10
Chromium "	309±12	156±6
Copper "	60.4±0.9	42.4±.8
Lead "	155±48	38.6±1.4
Nickel "	79.7±1.7	31.3±1.2
Mercury "	0.092±.007	0.057±.026
Manganese "	33.9±11	106±6
Zinc "	240±30	150±13
Pyritic Iron (%)	12.05	2.43
Pyritic Sulfur (%)	13.83	2.79
Sulfate Sulfur (%)	0.16	0.20
Organic Sulfur (%)	1.43	1.10
Total Sulfur (%)	15.42	4.09
Carbon (%)	27.77	60.33
Nitrogen (%)	0.47	1.02
Biological		
Total Bacteria (AODC/g)	1.84x10 ⁷	4.73x10 ⁷
Total Aerobic Bacteria (CFU/g dry wt)	2.44x10 ⁶	5.96x10 ⁶
Anaerobic Bacteria (CFU/g dry wt)	1.30x10 ⁷	2.57x10 ⁷
Sulfur-oxidizing Bacteria (MPN/g dry wt)	2.5x10 ⁵	3.2x10 ⁶
Iron-oxidizing Bacteria (MPN/g dry wt)	9.9x10 ⁶	1.3x10 ⁶

AODC--Acridine Orange Direct Counts
 CFU --Colony Forming Units
 MPN --Most Probable Number

(Table 6), including variable particle size, which can be varied by grinding, to examine effects of permeability and surface area. The oxidation of the pyrite under aerobic conditions can produce ferric oxides that should be effective adsorbents for many trace elements which can also serve as a source of trace metals for anaerobic microbial dissolution under anoxic conditions.

A specific gasification waste has not yet been collected but represents an oxidized end-member. In its natural state, it might be either acid or basic, depending on whether the coal from which it was produced was rich in pyrite (oxidized to acid ferric salts) or in Ca and Mg carbonates (converted to basic Mg or a Ca hydroxides). A waste with little of either of these constituents will be sought and the pH will be adjusted by added acid or base during experiments. The toxic trace elements in this waste would probably be in readily soluble oxidized forms, in glassy or fine crystalline silicate material and adsorbed on surfaces. The silicates would break down gradually to release trace elements more slowly than the pyrite in the coal-cleaning waste. Fe-oxides in small amounts might be formed to act as adsorbents, but would be less abundant than in the coal waste. Organic carbon from coal gasification would constitute the main reductant, and would probably be relatively inert in the absence of bacterial activity. The surface area for reaction could again be varied by sieving or grinding. The physical strength of particles might remain higher than the coal-cleaning waste because no major phase would be rapidly decomposing as pyrite would in the coal-cleaning waste.

The coal-cleaning waste is readily available from many locations in the eastern U.S. Gasification waste appears to be available from a number of test sites.

V. SUMMARY

The key characteristics of several substrates generated due to energy-related activities were reviewed in order to select a model substrate for anaerobic microbiological research in subsurface environments. These include trace metal content, form (natural and modified), organic carbon content and pH. Model substrates high in trace metals and low in organic carbon (coal beneficiation and coal gasification residues); low in trace metals and high in organic carbon (peat); and several insoluble forms of pure metals and minerals were selected for microbiological research. These substrates will be used in experiments to determine the role and significance of anaerobic microbial processes in the dissolution and mobilization of trace metals under those conditions expected in subsurface environments. The basic information generated from this study should be useful to the transport of trace metals in subsurface and anoxic environments.

VI. REFERENCES

- Adriano, D.C., A.L. Page, A.A. Elseewi, A.C. Chang, and I. Straughan, 1980, Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: A review: *J. Environ. Qual.* 9, 333-42.
- Balestrieri, L.S. and Murray, J.W., 1982, The adsorption of Cu, Pb, Zn and Cd on goethite from major ion seawater: *Geochim. Cosmochim. Acta* 46, 1253-67.
- Benjamin, M.M. and Leckie, J.O., 1981, Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide: *J. Colloid Interface Sci.* 83, 410-17.
- Dudas, M.J., 1981, Long-term leachability of selected elements from fly ash: *Environ. Sci. Technol.* 15, 840-43.
- Francis, C.W. and F.J. Wobber, 1982, Status of Health and Environmental Research Relative to Solid Wastes from Coal Conversion: U.S. DOE/NBB-0008/1.
- Furr, A.K., T.F. Parkinson, W.H. Gutenmann, and D.J. List, 1976, Multielement uptake by vegetables and millet grown in pots on fly ash amended soil: *J. Agric. Food Chem.* 26, 357-59.
- Garrels, R.M., and Christ, C.L., 1965, Solutions, minerals and equilibria: Harper and Row, New York, p. 74-92.
- Gluskoter, H.J., Ruch, R.R., Miller, W.G., Cahill, R.A., Dreher, G.B. and Kuhn, J.K., 1977, Trace elements in coal: Occurrence and distribution: *Ill. State Geol. Surv. Circ.* 499, 154 pp.
- Griffin, R.A., Schuller, R.M., Suloway, J.J., Shimp, N.F., Childeres, W.F. and Shiley, R.H., 1980, Chemical and biological characterization of leachates from coal solid wastes: *Environ. Geol. Notes* 89, *Ill. State Geol. Surv.*, 99 pp.
- Harrison, J.B. and Berkheiser, V.E., 1982, Anion interactions with freshly prepared hydrous iron oxides: *Clays: Clay Miner.*, 30, 97-102.
- Jenne, E.A., 1968, Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: The significant role of Mn and Fe oxides: *Adv. Chem. Ser. No. 73*, p. 337-88.
- Kleinmann, R.R., Crerar, D.A., and Pacelli, R.R., 1981, Biogeochemistry of acid mine drainage and a method to control acid formation: *Min. Eng. (N.Y.)* 33, 300-304.
- Mackowski, M-Th., 1968, Mineral matter in coal: in *Coal and Coal-Bearing Strata*, edited by Murchison and Westoll, Oliver and Boyd, Edinburgh, p. 309-321.

- O'Gorman, J.V. and Walker, P.L. Jr., 1972, Mineral matter and trace elements in U.S. coals: Research and Dev. Rept 61, Interim Rept. 2, Office of Coal Research, U.S. Dept. of Interior 184 pp.
- Straughan, I., A.A. Elseewi and A.L. Page, 1978, Mobilization of selected trace elements in residues from coal combustion with special reference to fly ash in Trace Substances in Environmental Health - XII, edited by D.D. Hemphill, Univ. of Missouri, Columbia, MO, p. 389-402.
- Wangen, L.E., and E.M. Wewerke, Solid wastes from energy-producing technologies. Solid wastes from coal conversion and conventional coal combustion processes: DOE/ER-0131.
- Wobber, F.J., 1983, Subsurface transport program: Geochemical, hydrological and biological cycling of energy residuals: DOE/ER-0156/1.
- Zachara, J.M., R.E. Wildung, and F.J. Wobber, 1982, Subsurface transport with emphasis on hydrology: Research needs: DOE/ER-0177.