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SOIL ATTENUATION OF LEACHATES FROM LOW-RANK COAL COMBUSTION WASTES: A LITERATURE SURVEY

By
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January 1984

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Grand Forks, North Dakota
By
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Department of Civil Engineering
College Station, Texas

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ABSTRACT

In parallel with pursuing the goal of increased utilization of low-rank solid fuels, the U.S. Department of Energy is investigating various aspects associated with the disposal of coal-combustion solid wastes. Concern has been expressed relative to the potential hazards presented by leachates from fly ash, bottom ash and scrubber wastes. This is of particular interest in some regions where disposal areas overlap aquifer recharge regions.

The western regions of the United States are characterized by relatively dry alkaline soils which may effect substantial attenuation of contaminants in the leachates thereby reducing the pollution potential.

A project has been initiated to study the contaminant uptake of western soils. This effort consists of two phases: 1) Preparation of a state-of-the-art document on soil attenuation; and 2) Laboratory experimental studies to characterize attenuation of a western soil. The state-of-the-art document, represented herein, presents the results of studies on the characteristics of selected wastes, reviews the suggested models which account for the uptake, discusses the specialized columnar laboratory studies on the interaction of leachates and soils, and gives an overview of characteristics of Texas and Wyoming soils.

SECTION 1

INTRODUCTION

As a consequence of the well-known problems associated with the availability of liquid and gaseous hydrocarbons, the U.S. Department of Energy is promoting the utilization of low-rank Western coals. Typically, these solid fuels are of modest heat content, of a relatively high ash fraction and of moderate sulfur percentage. When combusted on the scale currently envisioned, the resulting solid waste disposal problem could be substantial. Leachates from both the ash and the scrubber sludge may have the potential for contaminating groundwater which could lead to the necessity for expensive disposal methods; however, the question of the fate of the contaminants in the soils has not been adequately addressed. It may be that these migrations of contaminant materials into the water reserves is not of consequence due to contaminant uptake by the soils.

Under contract from the Grand Forks Energy Technology Center of U.S. DOE, the Texas A&M Research Foundation has undertaken a two-phase program to investigate the phenomenon of soils uptake. The first phase, reported herein, is a summary of the literature on the waste disposal problem with particular emphasis on the characterization of the wastes, leachates, soils and uptake mechanisms. The second phase will involve experimentation to obtain representative data on soil uptake and to model the uptake processes.

SECTION 2

BACKGROUND INFORMATION

The locations of the principal lignite, subbituminous, and bituminous coal reserves of the U.S. are illustrated in Figure 2-1. It may be noted that there are substantial bands of lignite in Texas and the Northern Great Plains, and large areas of subbituminous coal in the region centered about Wyoming. These coal deposits are currently subject to large-scale development projects.

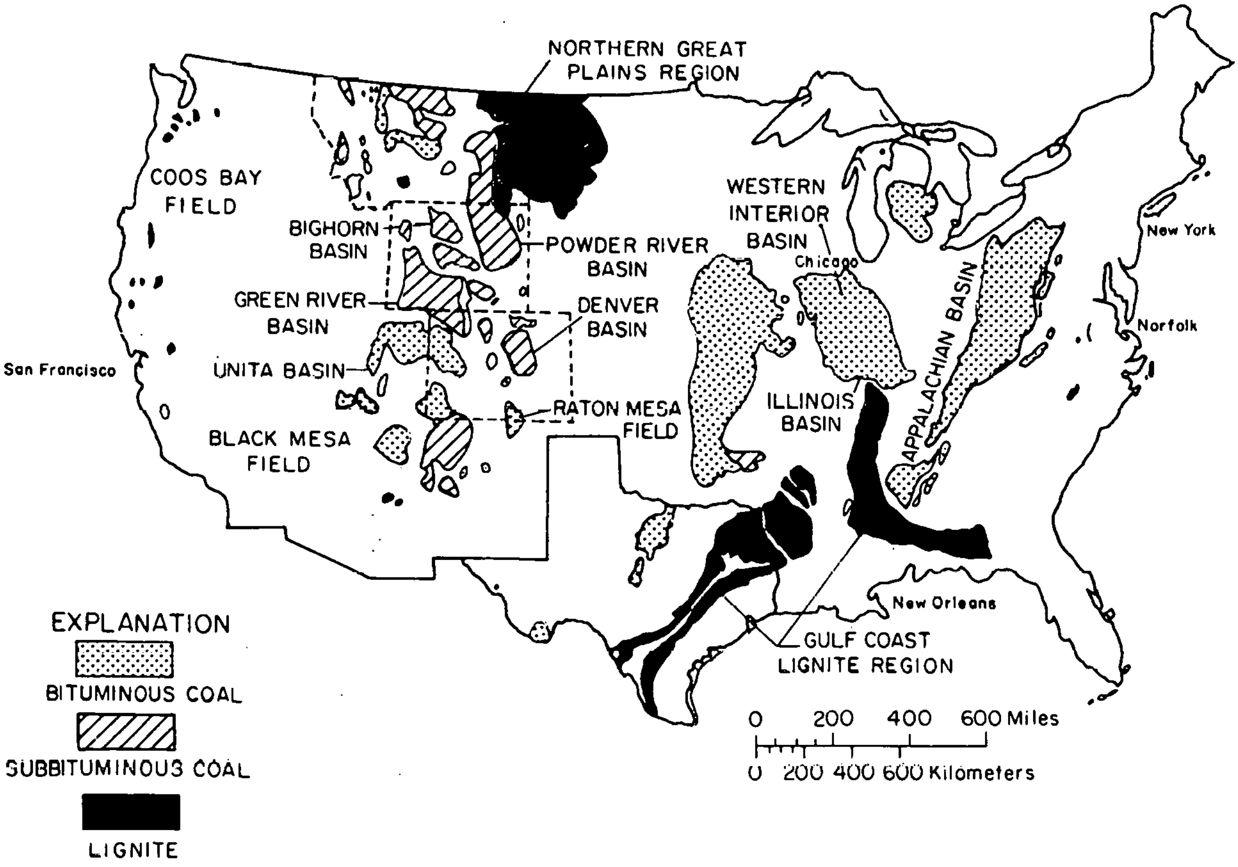


Figure 2-1. Lignite and Bituminous Coal Fields in the Contiguous United States. (Compiled From: Averitt, 1975; Arbingast, 1976; and Hoskins and Russell, 1982)

2.1 OVERVIEW OF WESTERN COAL DEVELOPMENT

There has been a recent revival of interest in coal, especially low rank coal, as an energy source. This has come about largely as a result of the 1973 OPEC oil embargo and the consequent perceived energy crisis. In actuality this re-emphasis was anticipated during the late 1950's and the 1960's as coal producers and electric utilities began to obtain coal leases for large tracts of western coal and Texas lignite (Friggens, 1974; Energy Resources Co., Inc., 1980). The increase in use of these low rank coals is reflected by the production statistics shown in Figure 2-2.

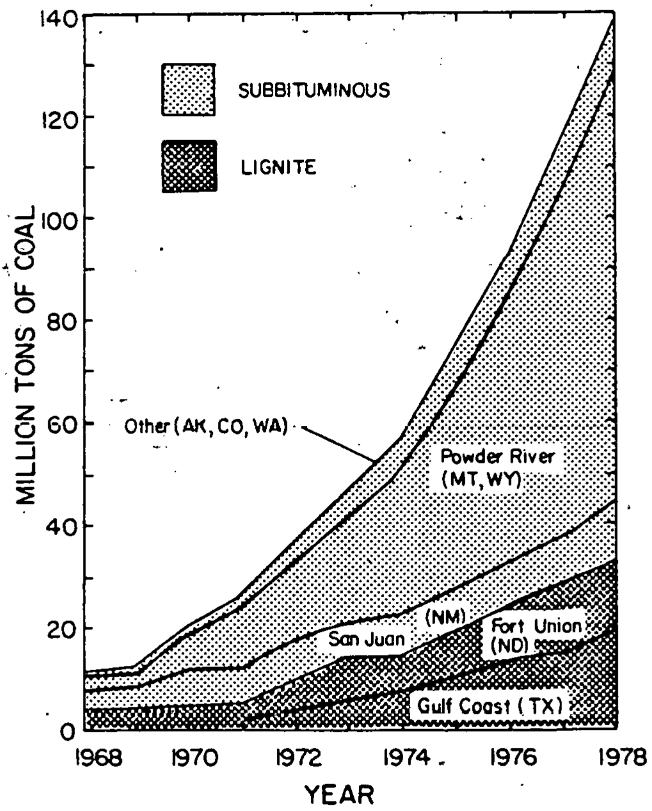


Figure 2-2. Low-Rank Coal Production (Energy Resources Co., Inc., 1980).

The U.S. reserves of these low rank coals are roughly equivalent to the reserves for higher rank coals. Estimates of identified resources of low rank coals are on the order of 1 trillion tons with an economically recoverable strippable reserve base of 100 billion tons. An additional 108 billion tons of subbituminous coal is classified as economically recoverable reserve base by underground mining. This may be compared with estimates for bituminous coal which are 75 billion tons of identified resources, 47 billion tons of strippable reserve base, and 182 billion tons reserve base recoverable by underground mining. On a Btu basis recoverable bituminous coal reserves exceed those of low rank coals by about twenty percent but low rank coal reserves exceed reserves of oil, natural gas, and shale oil combined by almost 200 percent (Energy Resources Co., Inc., 1980).

These coals have a lower heat potential than the more traditionally used bituminous coal. Lignite is classified as coal with a heat value less than 8300 Btu/lb on a moist, mineral-matter-free (m,mmf) basis while subbituminous coal is that with heat values between 8300 and 11,500 Btu/lb (m,mmf) (Energy Resources Co., Inc., 1980). The western subbituminous coals do have the attraction of significantly lower sulfur content than the midwestern bituminous coals. Table 2-1 provides data for comparison of various coals. The moisture content and oxygen content decrease with increasing rank, the heating value increases with increasing rank as does the carbon content. The heating values for both the Fort Union and Texas lignites are near the national average, and the values for the Powder River Basin subbituminous coals are likewise.

Because of the lower heat value, economics often dictate that the

Table 2-1. Selected Properties of U.S. Coals
(Energy Resources Co., Inc., 1980)

	Lignite				Subbituminous				Bituminous
		Gulf Region							
Property	U.S.	Average	Texas	Fort Union	U.S.	Powder River	Green River	San Juan	U.S.
Proximate Analysis (As Received Basis)									
Heating Value, $\frac{Btu}{lb}$	[a]6700	5800	[b]6700	6820	[a]9000	8820	11,200	10,200	[a]12,500
Moisture, weight percent	[a]35	30.8	[c]25.5 [d]17.9	37.2	[a]25	25.4	8.0	12.8	[a]<10
Ash Content, weight percent	-	13.5	[c]10.6 [d]22.0	6.2	-	6.3	5.-10.	13.5	-
Dry, Mineral-Matter-Free Basis (d,mmf)									
Carbon, weight percent	69	62.1	-	71.9	74.6	75.6	-	77.6	83
Hydrogen, weight percent	5.0	6.1	-	4.9	5.1	5.1	-	5.5	5.5
Oxygen, weight percent	24	28.8	-	21.0	18.5	17.3	-	14.3	10
Sulfur, weight percent	-	1.9	[e]1.-2.	1.1	-	0.8	-	1.2	2.-5.
Nitrogen, weight percent	-	1.1	-	1.1	-	1.2	-	1.4	-

[a] Moist, Mineral-Matter-Free Basis (m,mmf)

[b] Texas Railroad Commission: Information and Statistical Facts on Coal and Uranium Mining in Texas

[c] Texas Wilcox formation

[d] Texas Yegua-Jackson formation

[e] From Kaiser (1974)

coal must be used near the mine as is done with "minemouth" electric utility operations. In such cases combustion waste products, such as bottom and fly ash and sludge materials from flue gas desulfurization (FGD) processes, will be disposed of at the mine site.

The amount of these combustion by-products varies with the type of pollution control and with coal properties such as heat value, and sulfur and ash content. Lacy et al. (1979) have estimated that a 1500 MW plant will generate from 300,000 to 500,000 dry tons of FGD sludge per year, and two to three times as much fly ash. As can be seen, disposal of these wastes will require considerable land usage; the projection for Texas in the year 2020 is 32,400 acres (Radian Corp., 1978). This will of course be incorporated into the reclamation plan, a consideration in the development of which should be the areal extent of groundwater exposure.

2.1.1 The Powder River Region Subbituminous Coal

The Powder River Basin of northeast Wyoming and southeast Montana has the largest concentration of coal resources of any comparably-sized area in the United States. In 1974 the projection for 1990 production was 793 million tons (Averitt, 1975) while 1978 production was over 80 million tons (Energy Resources Co., Inc., 1980). Within this region the D-Wyodak-Anderson bed is the best known and thickest with deposits ranging from a minimum of 25 feet to a maximum of 150 feet (both local occurences only) with the usual range more on the order of 50 to 100 feet. It is estimated that of over 100 billion tons of coal in the formation, 15 billion tons lie within the region bounded by the outcrop to the line defined by the depth of overburden reaching 200 feet and are recoverable by strip mining methods (Averitt, 1975). The resources of the region appear in Table 2.2. In both Wyoming and Montana, the minimum seam thickness for stripping is taken as five feet. Identified resources total 238 billion tons with almost a quarter of that being considered the demonstrated coal reserve base. To put this in perspective, the total economically recoverable reserve base for low rank coals in the United States is 208 billion tons (Energy Resources Co., Inc., 1980). Figure 2-3 portrays the subbituminous resource area, shows the strippable deposits, and indicates subbituminous mine locations.

Table 2-2. Subbituminous Coal Reserves
of the Powder River Region
(Energy Resources Co., Inc., 1980)

State	[a]Identified Resources (billion tons)	Demonstrated Coal Reserve Base (billion tons)	[b]Stripping Ratio	Maximum Overburden Depth (feet)
Montana	127.9	34.5	8:1	125
Wyoming	110.2	23.0	10:1	120
Total	238.1	57.5		

[a] Identified resources include demonstrated and inferred measures 2½ feet or more thick to an overburden depth of 3000 feet.

[b] Refers to maximum feet of overburden thickness at the highwall per foot of coalbed thickness.

2.1.2 Fort Union Region Lignite

The Fort Union Region, Figure 2-4, which contains lignite reserves has been called the largest coal basin on earth. The region is characterized by moderately thick seams and very favorable stripping ratios. The minimum economically recoverable seam thickness is considered to be five feet. A conservative estimate of

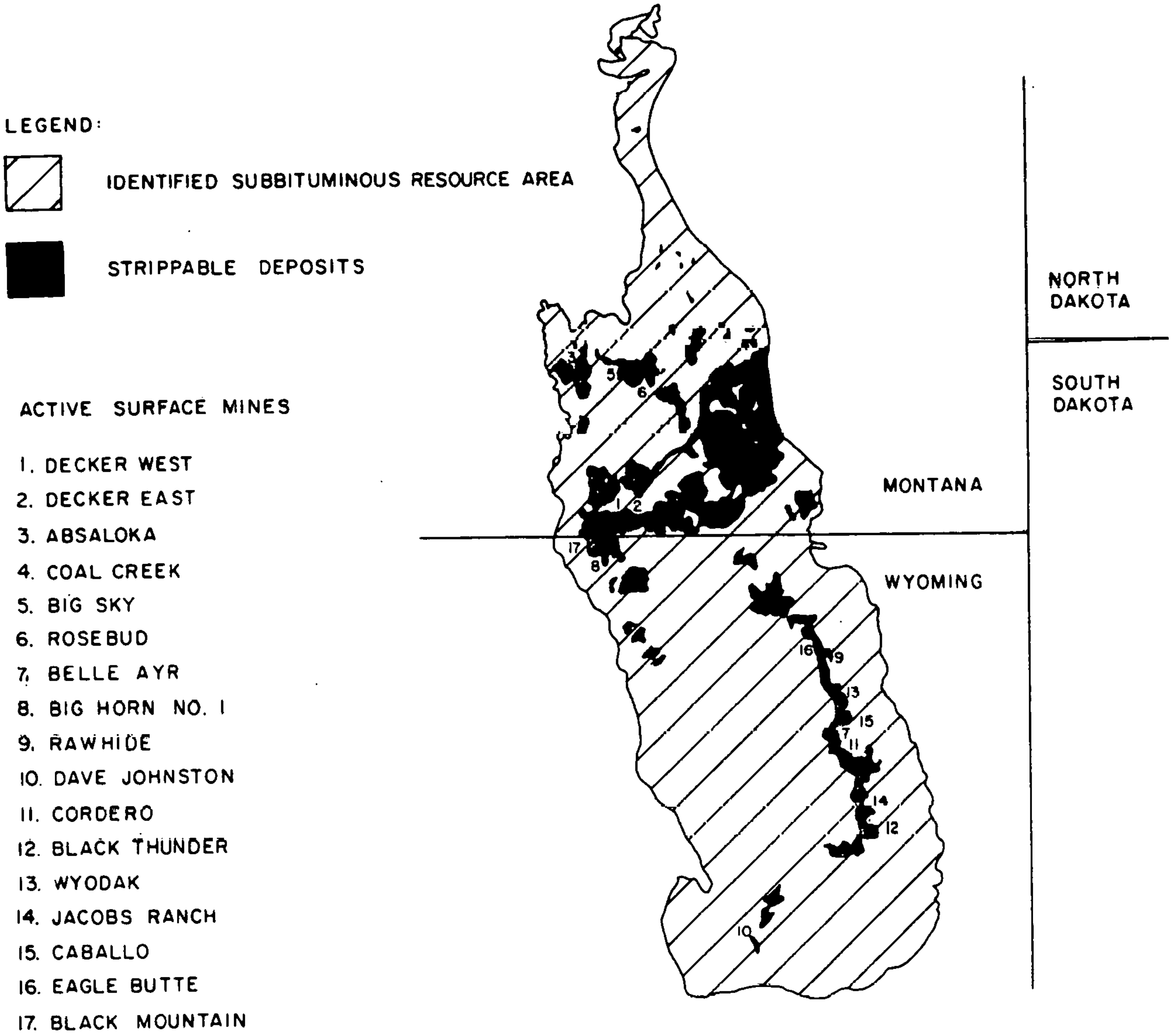
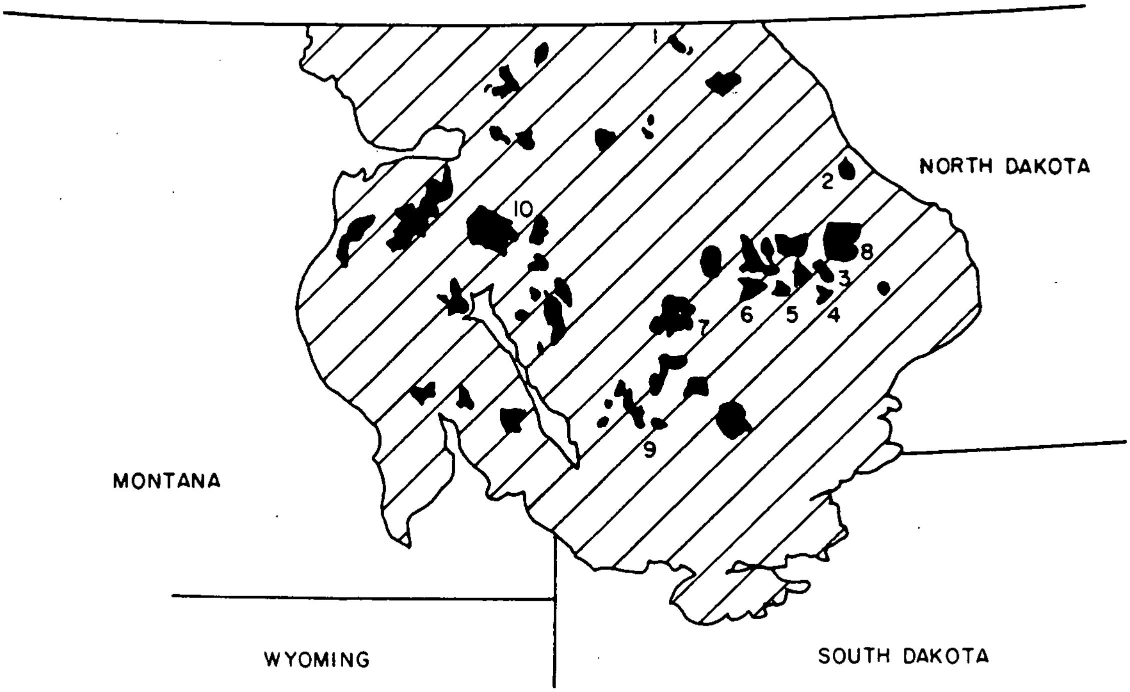


Figure 2-3. Powder River Region Strippable Subbituminous Deposits and Mine Locations. (Energy Resources Co., Inc., 1980)



LEGEND:

▨ IDENTIFIED LIGNITE RESOURCE AREA

■ STRIPPABLE LIGNITE DEPOSITS

ACTIVE SURFACE MINES

1. BAUKOL-NOONAN, INC.
2. VFIVA MINE
3. GLENHAROLD MINE
4. BAUKOL-NOONAN, INC.
5. BEULAH MINE
6. INDIAN HEAD MINE
7. LEHIGH MINE
8. FALKIRK MINE
9. GASCOYNE (PEERLESS) MINE
10. SAVAGE MINE

Figure 2-4. Fort Union Region Strippable Lignite Deposits and Mine Locations. (Energy Resources Co., Inc., 1980)

26.3 billion tons of demonstrated coal reserve base appears in Table 2.3; however, some estimates for North Dakota alone range as high as 40 billion tons. Figure 2-4 identifies the lignite resource area, the strippable deposits, and active lignite mine locations. All identified reserves are within 1000 feet of the surface.

Table 2-3. Lignite Coal Reserves of the Fort Union Region (Energy Resources Co., Inc., 1980)

State	[a]Identified Resources (billion tons)	Demonstrated Coal Reserve Base (billion tons)	[b]Stripping Ratio	Maximum Overburden Depth (feet)
North Dakota	350.6	10.1	10:1	100
Montana	112.5	15.8	8:1	125
South Dakota	2.2	0.4	12:1	100
Total	465.3	26.3		

[a] Identified resources include demonstrated and inferred resources 2½ feet thick to an overburden depth of 3000 feet.

[b] Refers to maximum feet of overburden thickness at the highwall per foot of coalbed thickness.

The lignite has an ash content on the order of 5 to 10 percent which is low for lignite (Texas lignite averages 15 percent). The sulfur content is also low at less than 1 percent on an "as-received" basis These figures of course must be tempered by the realization that on a Btu basis, the content of ash and sulfur will be less favorable than for more efficient, higher rank coals. The figures are nonetheless favorable.

2.1.3 Green River Region

Located in southwestern Wyoming and northwestern Colorado, the Green River Region has estimated original subbituminous coal resources of 25.3 billion tons, viz. Table 2-4. The region has even more substantial bituminous resources and some anthracite which are not considered here. There are three subbituminous mines in the region (Figure 2-5) and some additional mines which contain both bituminous and subbitiminous coals (not shown). When considering both underground and strippable reserves the demonstrated reserve base for the Colorado portion of the region is estimated as 6.68 billion tons. The strippable portion is about 1.0 billion tons in Colorado and 1.9 billion tons in Wyoming.

Table 2-4. Subbituminous Coal Resources
of the Green River Region
(Energy Resources Co., Inc., 1980)

State	[a]Identified Subbituminous Coal Resources (billion tons)	[b]Strippable Tonnages (billion tons)	Maximum Seam Thickness (feet)	Maximum Overburden Thickness (feet)	Maximum Stripping Ratio
Wyoming	6.051	1.9	5	120	10:1
Colorado	19.3	1.0	2	150	-
Total	25.3	2.9			

[a] Identified resources include demonstrated (measured and indicated) and inferred resources 2½ feet or more thick to an overburden depth of 3000 feet. Colorado resources include coals to 6000 feet, which by definition are considered estimated resources.

[b] Colorado estimates are for strippable resources; Wyoming estimates are for reserves.

There is a minimal amount of data on the thickness and depth of the coal seams, and the ash and sulfur content are not well defined. The bed thicknesses usually are on the order of 2½ to 10 feet. The sulfur content can be as high as 5 percent, but usually is much lower. Ash contents as high as 25 percent have been recorded, but a range of

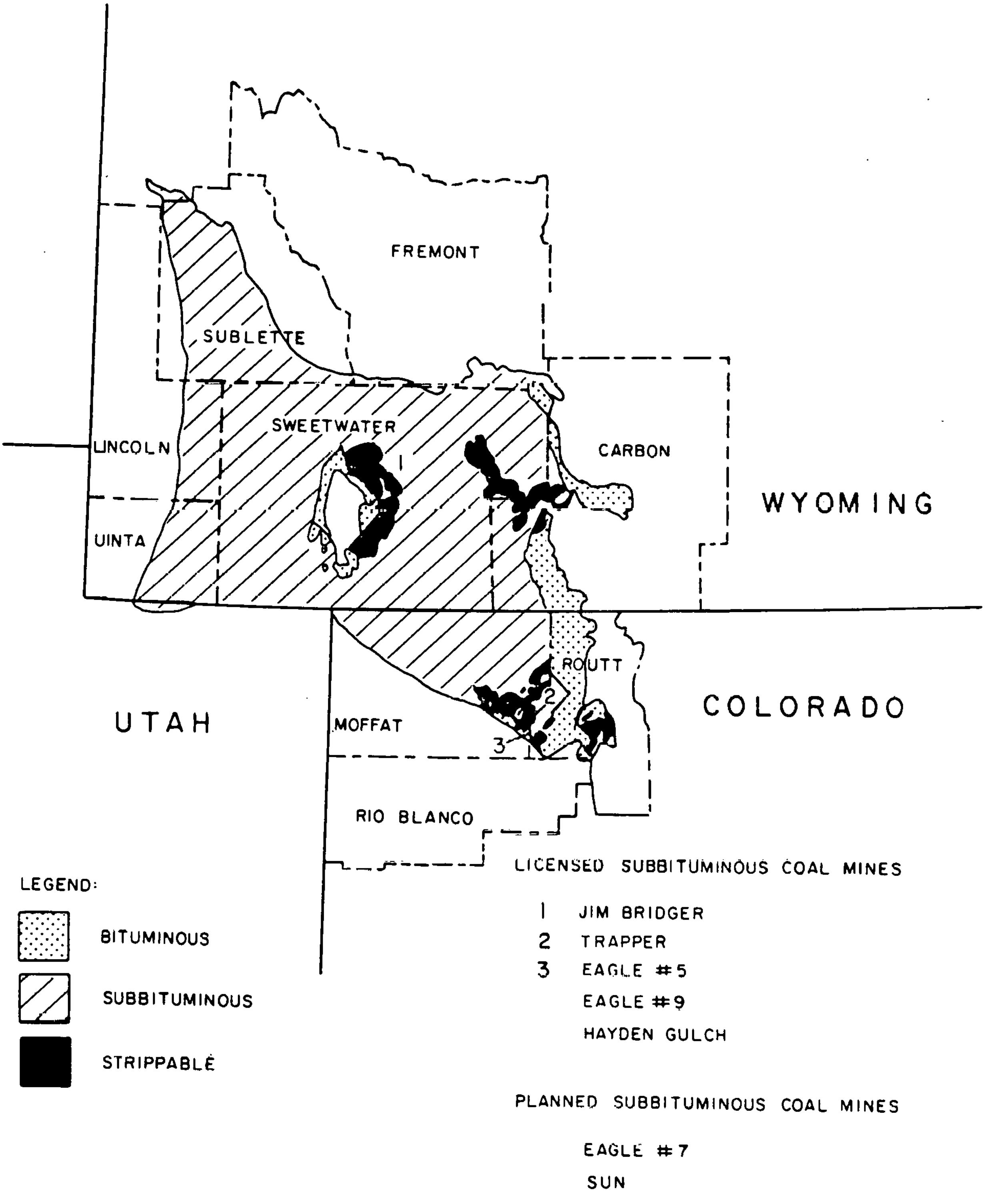


Figure 2-5. Green River Region Strippable Subbituminous Deposits and Mine Locations. (Energy Resources Co., Inc., 1980)

from 5 to 10 percent is more usual.

Data for eight samples from the Yampa Field, which has about 3/4 of Colorado's strippable resources show an average moisture content of 8.0 percent with a high of 10.9 percent and a low of 5.7 percent. The ash content ranged from 3.0 to 17.8 percent with an average of 8.8 percent. Heat content was very good averaging over 11,000 Btu/lb with a high and low respectively of 12,440 Btu/lb and 10,400 Btu/lb. All of the above data were determined for an "as-received basis".

2.1.4 Gulf Coast and Texas Lignite

The Gulf Coast has 68.3 billion tons of total reserves of lignite, of which 52.2 billion tons are in Texas. As shown in Table 2-5 the demonstrable reserve base for the region is 11.6 billion tons while the portion in Texas is 7.9 billion tons (Energy Resources Co., Inc., 1980).

Table 2-5. Lignite Coal Reserves
of the Gulf Coast Region
(Energy Resources Co., Inc., 1980)

State	[a]Identified Lignite Resources (billion tons)	Strippable Reserve Base (billion tons)	Minimum Seam Thickness (feet)	Maximum Overburden Depth (feet)	Maximum Stripping Ratio
Texas	52.2	7.9	4	200	15:1
Louisiana	0.6	0.6	-	-	15:1
Arkansas	13.5	2.0	-	150	-
Mississippi	-	-	-	150	10:1
Alabama	2.0	1.1	-	250	-
Total	68.3	11.6			

[a] Identified resources include Demonstrated (Measured and Indicated) and Inferred resources 2½ feet or more thick to an overburden depth of 3000 feet.

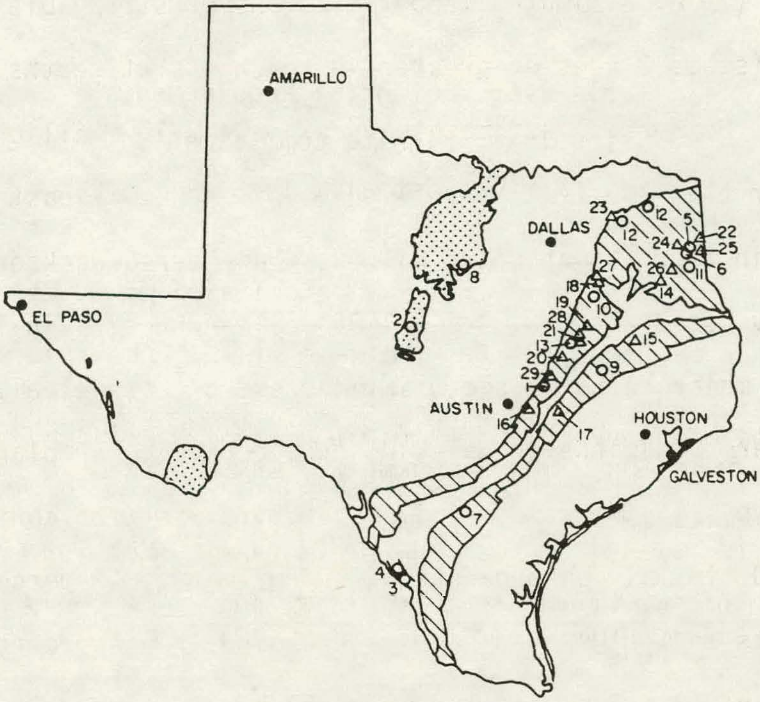
Kaiser (1978) estimates 12 billion tons of strippable lignite for Texas alone (seams 3 feet or greater in thickness at depths of less than 200 feet). He further estimates approximately 100 billion tons at depths greater than 200 feet. The lignite of the Gulf Coast Region is located in four formations: Wilcox, Clairborne, Jackson, and Yegua (Energy Resources Co., Inc., 1980). The deposits in Texas are located in two major belts as shown in Figure 2-6 (Lacy et al., 1979); also shown are locations of existing or proposed power plants.

Typical properties of Texas lignite are heat contents on the order of 7000 Btu/lb, ash contents of approximately 15 percent (although some deposits in South Texas have values of over 40 percent) and sulfur levels of 1 to 2 percent (Kaiser, 1974).

Energy forecasts for Texas call for a major dependence upon lignite resources to meet the projected energy demands of industry and the utilities. In a study of lignite development (Radian Corp., 1978, and Lacy et al., 1979), researchers noted that lignite is anticipated to provide approximately sixty percent of the solid fossil fuel in 1987, with the remaining forty percent provided by coal. These trends are expected to persist until about the year 2000, at which time the Texas lignite resources will be significantly diminished. Table 2-6 indicates the anticipated lignite demands over this time period.

2.2 LEGAL CONSIDERATIONS

As the nation has become more aware of environmental issues, additional procedures for the combustion of fossil fuels have been mandated which require substantial cleaning of stack emissions and waste effluents. A consequence of these regulations has been that large amounts of ash



o PERMITTED

1 Aluminum Company of America (Sandow)
2 Amistad Fuel Company (Little Bull Creek)
3 FARCO Mining Company (Palafox)
4 FARCO Mining Company (Rachal)
5 ICI Americas, Inc. (Darco)
6 Sabine Mining Company (South Hallsville)
7 San Miguel Electric Cooperative, Inc. (San Miguel)
8 Thurber Coal Company (Thurber)
9 Texas Municipal Power Agency (Gibbons Creek)
10 Texas Utilities Generating Company (Big Brown)
11 Texas Utilities Generating Company (Martin Lake)
12 Texas Utilities Generating Company (Monticello)
13 Texas Utilities Generating Company (Twin Oaks)

△ PROPOSED

14 Exxon Coal Company (Troup)
15 Gulf States Utilities
16 Lower Colorado River Authority (Powell Bend)
17 Lower Colorado River Authority (Cummins Creek)
18 North American Coal Company (Malakoff - Cayuga)
19 Northwestern Resources Company (Jewett)
20 Phillips Coal Company (Calvert)
21 Phillips Coal Company (Cole Creek)
22 Phillips Coal Company (North Marshall)
23 Phillips Coal Company (Yantis)
24 Texas Lignite Products Corporation
25 Texas Lignite Products Corporation
26 Texas Utilities Generating Company (Martin Lake "D")
27 Texas Utilities Generating Company (Forest Grove)
28 Texas Utilities Generating Company (Oak Knolle)
29 Shell Oil Company (Milam)

Figure 2-6. Location of Permitted and Proposed Coal Mines for Power Plants Associated with Texas Lignite and Bituminous Coal Deposits. (Texas Railroad Commission, 1982)

Table 2-6. Potential Requirements
for Texas Lignite Committment.
(Lacy et al., 1979)

		1978	1985	2000
Total Energy Required (10^{15} Btu's)	Utilities	1.8	2.6	4.8
	Industry	2.4	3.1	5.2
Solid Fuel Demand (10^{15} Btu's)	Utilities	0.50	1.0	3.1
	Industry	0.05	0.2	1.2
Lignite Demand (10^{15} Btu's)	Utilities	0.30	0.6	1.9
	Industry	0.05	0.1	0.7
Lignite Reserve Commitment Required (Billions of Tons @ 6500 Btu/lb	Utilities	0.70	1.4	4.4
	Industry	0.10	0.2	1.6
	Total	0.80	1.6	6.0

and other waste products are now collected at the combustion site. At present, utility solid wastes are not considered hazardous by definition (CFR, Title 40, §261.4, (b), (4)), and this is likely to be the case in the foreseeable future. EPA was required to conduct a study (to be completed in late 1982) on the potential hazard, if any, presented by the "disposal and utilization of fly ash waste, bottom ash waste, slag waste, flue gas emission control waste, and other by-product materials generated primarily from the combustion of coal or other fossil fuels" (PL 94-580, Section 8002, (n) as amended by the Solid Waste Disposal Act Amendments of 1980). The final report of this study has not yet been published.

If, after additional study, utility combustion wastes are considered to be hazardous, there are several provisions pursuant to the Resource Conservation and Recovery Act (RCRA) which will be of relevance. First is the definition of hazardous waste:

> 1004 (5) The term 'hazardous waste' means a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may . . .
>
> (A) cause, or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or
>
> (B) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.

The current EPA regulations concerning hazardous wastes provide a definition worth consideration in regard to combustion wastes (Code of Federal Regulations (CFR), Title 40 - Protection of Environment, July 1, 1982).

> §261.24 Characteristic of EP Toxicity
>
> (a) A solid waste exhibits the characteristic of EP toxicity if, . . . the extract from a representative sample of the waste contains any of the contaminants listed in Table 1 at a concentration equal to or greater than the respective value given in that table.

Table 1. Maximum Concentration of Contaminants for Characteristic of EP Toxicity

EPA hazardous waste number	Contaminant	Maximum concentration (milligrams per liter)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0

Also, a substance is designated as hazardous if it demonstrates specified characteristics of toxicity, corrosivity, reactivity, or ignitability, or if it is listed in §261.30, Title 40 CFR.

Currently, all waste displaying radioactive properties is classified as either high or low level. There is no threshold below which a waste, if even slightly radioactive, can be classified as anything other than radioactive. Although the RCRA contains no definition of radioactive waste, Hart and Delaney (1978) discuss the problem in light of an interim regulation (FR, Dec. 18, 1978) and provide the definition:

> Radioactive . . . a waste is radioactive if it is not source, special nuclear or by-product material as defined by the Atomic Energy Act of 1954, as amended, and if a representative sample has either of the following properties:
>
> 1. The average radium-226 concentration exceeds 5 picocuries per gram for solid wastes or 50 picocuries (radium-226 and radium-228 combined) per liter for liquid wastes, as determined using either the precipitation method or the radon emanation method described in Interim Radio-chemical Methodology for Drinking Water (CEPA)-600/4-74-008 Revised).
>
> 2. The total radium-226 activity equals or exceeds 10 microcuries for any single discrete source.

2.3 PROPERTIES OF ASH AND ASH-SLUDGE LEACHATES

Coal ash is known to contain a number of oxide elements including those of silicon, iron, aluminum and calcium in addition to a variety of trace metals and elements. Numerous studies have documented measurements of the soluble and insoluble constituents in fly ash and bottom ash of coal and lignite. The sludges arising from the flue gas desulfurization process also contain a large number of trace metals in addition to significant quantities of sulfate and calcium in the forms of calcium sulfate and unreacted limestone. Tables 2-7 and 2-8 show information concerning the relative abundance of the major constituents of FGD sludge,

Table 2-7. Composition of Typical Limestone Sludge Solids from Flue Gas Desulfurization Equipment (Radian Corp., 1978)

Component	Percent by Weight
Gypsum ($CaSO_4 - 2H_2O$)	56
Coprecipitate ($.84\ CaSO_3 \cdot .16CaSO_4 \cdot \frac{1}{2}H_2O$)	34
Unreacted Limestone	6
Limestone Inerts & Fly Ash	4
TOTAL	100

Table 2-8. Typical Chemical Analysis of Fly Ash. (Williams, Smith and Raba, 1981; Energy Resources Co., Inc., 1980)

Constituent	Subbituminous				Lignite			
	Limits			Powder River	Limits			Texas
	Low	High	Average	Basin	Low	High	Average	
Silica Dioxide (SiO_2), %	15.2	52.8	38.2	38.4	6.3	39.4	19.7	44.4
Aluminum Oxide (Al_2O_3). %	9.0	27.6	20.6	19.0	4.2	26.1	11.1	18.4
Iron Oxide (Fe_2O_3), %	3.3	31.5	9.8	4.5	0.9	34.3	9.1	5.4
Magnesium Oxide (MgO), %	1.4	9.0	5.4	4.0	2.8	13.6	6.9	4.2
Sulfur Trioxide (SO_3), %	12.9	20.5	15.9	1.6	8.3	32.0	19.5	1.6
Calcium Oxide (CaO), %	10.5	52.6	19.5	24.1	12.4	52.0	24.6	18.2

and subbituminous and lignite ash. Table 2-9 provides similar information on U.S. bituminous and anthracite coals. A comparison of Tables 2-8 and 2-9 indicates that western subbituminous and Gulf Coast lignite ashes have higher calcium and magnesium oxide values than does typical U.S. bituminous coal ash. Since a scrubber is used principally to effect the removal of SO_2 from flue gas, the quality of FGD wastes from lignite plants should be comparable to those from other coal plants using similar limestones.

Table 2-9. Ash Compositions for U.S. Bituminous and Anthracite Coals. (Energy Resources Co., Inc., 1980)

	Bituminous			Anthracite		
Constituent (percent of ash)	Low	High	Average	Low	High	Average
Silica Dioxide (SiO_2)	9.3	69.6	48.2	47.7	67.7	55.2
Aluminum Oxide (Al_2O_3)	5.6	41.7	24.9	24.7	43.5	34.0
Iron Oxide (Fe_2O_3)	3.8	84.2	14.9	2.1	10.2	6.3
Magnesium Oxide (MgO)	0.4	6.3	1.7	0.0	1.2	0.6
Sulfur Trioxide (SO_3)	-	-	-	0.0	2.0	0.7
Calcium Oxide (CaO)	0.2	36.7	6.6	0.2	3.7	1.0

2.4 Studies of Ash and Ash-Sludge Leachates

Shannon and Fine (1974) have determined the solubility in water of the basic cation constituents of four lignite ashes from coals of three Northern Great Plains mines. The water:ash ratios were varied from 5 to 100 by adding the appropriate weight of ash to 25 grams of deionized water. Apparently no pH control was exercised. Substantial amounts of calcium, sodium, magnesium and iron were dissolved, yielding supernatent pH values of 9 to 11. These results, which are presented in Table 2-10 not only show the leachability of several cations, but also show that in the laboratory, considerable washing may be required to note the full effect. A practical consequence of this in disposal is that it may take a long time for all the cations to be released. Further, the field water to ash ratios may be much less than 5:1 which suggests runoff would have high salt concentrations and the rate at which cations are released could be even slower.

Data obtained by Dreesen et al. (1977) demonstrate a dependence of heavy metal solubility upon leachate pH value. Precipitator ash from a power plant at Fruitland, New Mexico was washed with aqueous solutions which had initial pH values ranging from acid (pH = 0.5) to basic (pH = 11.3). The trace metals eluted from an ash-extractant mixture (1:4 by weight) were quantified, Tables 2-11 and 2-12. At high pH values, certain trace elements, particularly molybdenum, fluoride and selenium, were found to exist in solution at significant concentrations. This would be anticipated for an anion such as fluoride, and it would be suspected that selenium is behaving also as an anion in this situation. There also appears to be a slight dip in the amount of selenium leached, but it is only slight and its behavior otherwise is consistent with its chemical nature. A similar study conducted by Theis and Wirth (1977) complements the pH-metal concentration relationships observed by Dreesen et al. With the notable exception of arsenic at a pH of 12, their results for coal ash, Table 2-13, show substantial reductions in element concentration with increasing pH. The authors discuss the behavior of arsenic and suggest that it is behaving as an anion. They suggest that

Table 2-10. Results of Batch Leachate Tests on Lignite Ash. (Shannon and Fine, 1974)

		Cations Solubilized from Four Fly Ash Samples									From Composite of Five Washings			
		After One Washing, mg/kg				After Five Washings, mg/kg					Total Cations		SO_4	
Fly Ash Number	Water:Ash Ratio	Ca	Na	Mg	Fe	Ca	Na	Mg	Fe	pH supernatant	meq/L	Equiv. Ca^{2+} mg/L	meq/L	mg/L
1	5	2,360	834	6	1.1	11,000	1,790	125	5.3	11.8	25.70	515.0	1.25	66.0
	50	11,200	955	36	11.7	28,000	1,820	461	54	10.5	6.16	124.0	0.64	31.0
	100	14,000	1,184	47	23.2	36,000	2,970	916	124	9.7	4.08	82.0	0.48	23.0
2	5	4,760	9,550	8	1.5	15,800	16,900	88	4.9	11.6	61.61	1,235.0	30.0	1,441.0
	50	14,800	10,300	71	17.4	38,000	12,400	369	65	10.7	10.02	201.0	4.3	207.0
	100	22,800	10,350	135	33.3	54,000	10,800	582	76	10.3	6.66	134.0	2.5	120.0
3	5	5,960	11,040	0	1.5	10,200	7,580	0	17.4	11.6	50.97	1,021.0	31.6	1,518.0
	50	11,800	11,720	30	11.7	32,000	9,350	56	9.3	11.1	8.98	180.0	4.5	216.0
	100	17,600	12,880	36	30.0	44,000	8,640	374	18.4	10.8	5.87	118.0	2.2	106.0
4	5	2,480	6.030	2	1.8	6,200	9,660	4	6.9	11.6	29.41	589.0	16.4	788.0
	50	7,000	6.490	36	16.7	18,000	8.420	126	42.1	11.0	5.26	105.0	1.6	77.0
	100	8,800	6,850	72	35.0	26,000	8.640	285	111	9.2	3.79	76.0	0.9	43.0

Table 2-11. Percentage of Trace Element Content of Ash Extracted by Each Solution and Trace Element Content of Precipitator Ash. (Dreesen et al., 1977)

Molarity	1.0 M	1.0 M	0.1 M	0.1 M	0.01 M	0.001 M		0.1 M	
Solution	HNO_3	HCl	Citric acid	HNO_3	HNO_3	HNO_3	H_2O	NH_4OH	
Initial pH[a]	0.5	0.5	2.2	1.4	2.2	3.1	7.4	11.3	Conc in precipitator ash, µg/g
Final pH[b]	0.5	0.6	3.6	4.1	11.7	11.9	11.9	11.9	
	Percent Leached								
As	64	78	59	0.65	0.31	0.17	0.10	0.51	12
B	78	24	94	55	3.9	1.4	1.5	<0.05	260
Be	8.6	12	6.1	1.7	<0.09	<0.09	<0.09	<0.09	4.7
Cd	48	32	33	35	3.8	0.28	<0.14	0.14	0.29
Cr	15	14	13	1.2	0.54	0.38	0.33	0.29	34
Cu	7.3	7.9	4.6	3.3	0.11	<0.01	<0.01	<0.01	58
F	75	63	86	83	11	8.1	7.2	8.7	120[c]
Mo	120	120	110	4.7	57	55	59	54	4.2
Se	78	35	46	5.1	11	5.9	5.1	4.5	8.0
V	20	28	16	0.04	0.02	<0.01	<0.01	<0.01	98
Zn	3.1	3.1	1.8	1.2	0.27	<0.03	<0.03	0.07	160

[a] pH determined before ash was added to the extractants. [b] pH determined after agitation of ash-extractant mixture. [c] The fluorine concentration given is the mean concentration reported by the Southwest Energy Study (6) and Woodward Envicon (7).

Table 2-12. Extractability Categories for Trace Elements in Extraction Experiment for Strongly Acidic and Basic Extractants. (Dreesen et al., 1977)

Extractability, %	Strongly acid extractant (1.0 M HNO_3) final pH = 0.5	Strongly basic extractant (H_2O) final pH = 11.9
>30	As, B, Cd, F, Mo, Se	Mo
10-30	Cr, V	...
1-10	Be, Cu, Zn	B, F, Se
0.1-1.0	...	As, Cr
<0.1	...	Be, Cd, Cu, V, Zn

Table 2-13. Metal Release at Various pH Values
(Theis and Wirth, 1977)

(All Values in μg/g of Fly Ash)

Metal	pH 3		pH 6		pH 9		pH 12	
	Range	Av	Range	Av	Range	Av	Range	Av
Arsenic	3-325	51.9	0.1-8.0	1.0	0.1-4.8	0.80	1.0-650	72.9
Cadmium	<0.1-5.5	1.1	<0.1-2.75	0.41	<0.1-0.9	0.15	<0.1-0.75	0.18
Chromium	1.5-23.5	9.4	<0.1-8	1.9	<0.1-7.5	2.0	0.5-10	2.4
Copper	5-52	15.6	<0.1-1.75	0.82	<0.1-1.0	0.36	0.5-1.5	0.59
Lead	0.5-60	9.1	<0.5-5.5	1.4	<0.5-3.0	0.73	<0.5-3.0	0.91
Nickel	1.8-35	11.7	0.1-6.5	3.6	<0.1-2.5	0.50	0.1-1.2	0.61
Zinc	5.8-112	25.7	0.1-75	8.3	<0.1-0.9	0.28	<0.1-10	1.7

at pH 12 there is an insufficiency of available metal ions to cause precipitation.

James et al. (1976) performed 7-day batch leachate tests on Texas lignite, the results of which are summarized in Table 2-14. In this investigation, 250 grams of each material were batch-washed in one liter of deionized water. Raw lignite samples were obtained from three different plants and lignite ash from only one, the Texas Utilities Big Brown Plant near Fairfield, Texas. Both selenium and arsenic were present in measureable amounts in the coal and were found in moderate levels in the fly ash leachate (17 and 33 $\mu g/\ell$, respectively). It may be noted, Table 2-14, that the fly ash leachate had a pH of 12, and both these elements may exhibit anionic behavior at high pH.

Hart and Delaney (1978) provide an assay of the trace element content of typical FGD sludge. In their study of the impact on utility

Table 2-14. Seven-day Leachate Study of Texas Lignite Coal and Fly Ash, Metals. (James et al., 1976)

Sample	As µg/L	Be µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Fe mg/L	Hg µg/L	Mn mg/L	Ni µg/L	Pb µg/L	Se µg/L	Zn µg/L	SO_4 mg/L	pH
Lignite Coal														
Alcoa 1	5	<0.1	<1.0	<1	3	<0.1	0.7	<0.05	3	<1	8	14	<10	5.9
Alcoa 2	5	<0.1	<1.0	<1	3	<0.1	0.8	<0.05	4	<1	33	11	<10	5.8
Alcoa 3	11	<0.1	<1.0	<1	2	<0.1	0.2	<0.05	<2	<2	12	8	<10	—
Big Brown 1	8	0.3	<1.0	<1	3	<0.1	0.6	<0.05	3	<1	38	20	<10	6.6
Big Brown 2	11	0.1	<1.0	<1	1	<0.1	0.5	0.15	<2	<2	9	4	<10	5.8
Big Brown 3	2	<0.1	1.3	<1	3	<0.1	0.6	<0.05	3	<1	<2	42	<10	6.4
Darco 1	8	<0.1	1.0	<1	2	<0.1	0.9	<0.05	<2	<2	3	8	<10	5.9
$\bar{X}$	7.1	0.09	0.36	<1	2.4	<0.1	0.61	0.04	2.3	0.7	14.9	15.3	—	—
$\sigma_{\bar{x}}$	1.3	0.04	0.21	—	0.8	—	0.09	0.02	0.5	0.1	5.5	4.9	—	—
Fly ash (Big Brown)	17	0.2	<1.0	<1	<2	<0.1	0.5	<0.05	3	3	33	2	70	12.0

solid wastes by the Resource Conservation and Recovery Act, scrubber sludge trace metal concentrations are compared with the federal standards for drinking water. Both the FDG sludge, Table 2-15, and leachates from the sludge, Table 2-16, contain trace elements in relatively high concentrations. The concentrations of B, Hg and Se in the leachate all exceed drinking water standards by a factor of 10x or more, but do not exceed the current RCRA standard of 100x drinking water standards. All other listed elements are below 10x the drinking water standards.

A European study on the disposal of pulverized fuel ash (coal rank was not reported), reported on dissolved contaminant concentrations released from conditioned ash upon percolation of increments of 0.5 bed volumes of water through test columns (Brown et al., 1976). The resulting data, given in Table 2-17, show indications of washout of some of the

Table 2-15. Trace Elements in Sludge (Wet Limestone).

(Hart and Deleny, 1978)

Element	Concentration (ppm)	Drinking Water Standard (mg/L)
As	4.0-33.0	0.05
Ba	20.0-500.0	1.00
B	41.8-211.0	1.00
Cd	0.4-25.0	0.01
Cr	1.6-17.00	0.05
Cu	10.0-104.0	1.00
Pb	1.0-290.0	0.01
Mn	36.0-340.0	none
Hg	0.1-6.0	0.002
Ni	13.0-75.2	none
Se	2.1-60.00	0.01
V	50.0-100.0	
Zn	13.9-2050.0	

Table 2-16. Trace Elements in Scrubber Sludge Leachate.

(Hart and Delaney, 1978)

ELEMENT	STANDARD	MAX	MIN	STANDARD EXCEEDED		
		mg/L		100X	10X	1X
As	0.05	.13 .3	.001 .008	no	no	yes
Ba	1.0	2	.002	no	no	yes
B	1.0 0.75/irr.	40	.22	no	yes	yes
Cd	0.01	.047	.0005	no	no	yes
Cr	0.05	.011 .25	.001	no	no	yes
Cu	1.0	.56	.002	no	no	no
Pb	0.01	.04	.003	no	no	yes
Hg	0.002	.07 .003	.0004	no	yes	yes
Ni	0.5/irr.	.05	.015	no	no	no
Se	0.01	.54	.0005	no	yes	yes
V	-	.20	.10	-	-	-
Zn	5.0	4.2	.01	no	no	no

Table 2-17. Leachate Parameters Associated with Percolations of 0.5 Bed Volume Increments. (Brown et al., 1976)

Parameter	Total present mg/kg dry ash	Readily soluble by extraction mg/kg dry ash	Equivalent percolate concentrations by successive 0.5 bed increments as mg/L in solution				Units
			0 - 0.5	0.5 - 1.0	1.0 - 1.5	1.5 - 2.0	
pH			11.1	11.5	11.9	11.7	pH
Total dissolved solids		18,000	7900	3300	1800	1100	mg/L TDS
Total alkalinity		7,600	450	500	300	230	mg/L $CaCO_3$
Arsenic	90	10	0.5	0.4	0.15	0.06	mg/L As
Cadmium	10	<1	<0.01	<0.01	<0.01	<0.01	mg/L Cd
Calcium	31,000	4,400	60	10	20	40	mg/L Ca
Chromium	110	<2	9	4	2	0.9	mg/L Cr
Copper	160	<10	0.1	<0.1	<0.1	<0.1	mg/L Cu
Iron	54,000		<0.1	<0.1	<0.1	<0.1	mg/L Fe
Lead	280	<5	0.06	<0.05	<0.05	<0.05	mg/L Pb
Magnesium	9,000	<100	14	<10	<10	<10	mg/L Mg
Manganese	700	< 10	0.1	< 0.1	<0.1	<0.1	mg/L Mn
Molybdenum	16	6	25	5	1.4	0.5	mg/L Mo
Potassium	24,000	580	970	490	310	200	mg/L K
Selenium	5	0.4	0.6	0.20	0.10	0.08	mg/L Se
Sodium	8,700	770	2000	740	360	170	mg/L Na
Zinc	1,300	<10	<0.1	<0.1	<0.1	<0.1	mg/L Zn
Boron	430	130	2	3	3	3	mg/L B
Chloride	550	550	1900	420	100	30	mg/L Cl
Cyanide		<10	<0.1	<0.1	<0.1	<0.1	mg/L CN
Fluoride		25	1.3	1.2	0.7	0.5	mg/L F
Nitrate		50	76	40	10	<5	mg/L NO_3
Phosphate	2,800	<100	<1	<1	<1	<1	mg/L PO_4
Sulphate	11,000	5,200	2500	1200	740	430	mg/L SO_4

major cations and anions (sodium, potassium, chloride and sulfate) over the range of 0-2 bed volumes of liquid transport. As and Se were initially released at levels ~½ mg/L.

Putting these results into perspective, Brown et al. (1976) compared the trace element concentrations found in fly ash percolate to the drinking water standards adopted by the World Health Organization (1970) and found several of the percolate trace constituents to exceed the European standards. These standards are shown in Table 2-18.

Table 2-18. European Standards for Drinking Water and Drinking Water Sources. (World Health Organization, 1970)

Standards of Chemical Quality

Toxic Chemical Substances . . . The concentrations given below should not be exceeded in piped water supplies:

		Upper limit of concentration
Arsenic	(as As)	0.05 mg/l.
Cadmium	(as Cd)	0.01 mg/l.
Chromium	(as Cr hexavalent)	0.05 mg/l.
Cyanide	(as CN)	0.05 mg/l.
Lead	(as Pb)	0.1 mg/l.
Selenium	(as Se)	0.01 mg/l.

In addition to the substances listed, there are other substances, such as mercury, tin, vanadium, berryllium, molybdenum, silver, uranium, and thiocyanate, the presence of which in drinking water should be controlled, but insufficient information is at present available to enable levels to be given. It is considered that barium should not be present at concentrations of more than 1.0 mg/l.

Constituents in water which may give rise to trouble in piped supplies of drinking water:

. . .

		Approximate level at which trouble may arise
Chloride	(as Cl)	200 mg/l. Under no circumstances should the level exceed 600 mg/l.
Copper	(as Cu)	0.05 mg/l. at pumping station, 3.0 mg/l. after 16 hr. contact with new pipes.
Fluoride	(as F)	0.8-1.5 mg/l.
Hydrogen sulphide	(as H_2S)	.05 mg/l.
Iron	(total as Fe)	0.1 mg/l. as water enters distribution systems.
Magnesium	(as Mg)	Not more than 30 mg/l. if there are 250 mg/l. of sulphate, if less sulphate, up to 125 mg/l. may be allowed.
Manganese	(as Mn)	0.05 mg/l.
Nitrate	(as NO_3)	Recommended: less than 50 mg/l. Acceptable: 50-100 mg/l. Not recommended: more than 100 mg/l.
Phenolic compounds	(as Phenol)	Less than 0.001 mg/l.
Sulphate	(as SO_4)	250 mg/l.
Zinc	(as Zn)	5 mg/l.

A similar comparison of Table 2-17 with the United States drinking water standards shows excesses of arsenic and selenium. Brown et al. concluded that some care should be exercised when disposing these wastes so that adequate attenuation of hazardous elements would be attained.

In summary, there have been a number of studies on the leaching of solid wastes from coal-fired power plants. The results show that toxic substances are released from the wastes and that the concentration of certain of these can exceed the drinking water standards by factors of 10x or even 100x (e.g., initial Cr release in Brown's study exceeds U.S. drinking water standards by 180x). Also it may be noted that the concentration of some of the toxic materials are highly dependent upon pH. If the soils in the disposal area have the ability to buffer the pH to high values, there is a possibility of reduced transport of many of the potentially hazardous elements.

SECTION 3

THE ATTENUATION OF LEACHATE MATERIALS IN SOILS

As the various trace elements and compounds present in leachates percolate through the soils beneath buried wastes, physical and chemical processes occur which may cause the retention of certain elements while releasing from the soils other naturally present elements. The uptake and attenuation of leaching contaminants is a process complicated by competing uptake mechanisms and evolving leachate chemical properties. Currently the literature looks at many of these things individually, but a comprehensive model is yet in the future.

Many of the previous works addressing the subject of soil uptake of solubilized trace elements specifically deal with nutrient availability to plants. These studies, many of which are reviewed by Jenne (1968) and Lindsay (1972), have provided the groundwork for more general studies concerning the potential hazards of trace elements migrating through the soil. For the most part, the literature dealing with plant nutrients has been fairly specific, focusing on the behavior of particular plant nutrients in the presence of colloidal clay particles or wet soil systems. Highly controlled studies of this type fail to account for many of the competing and complicating mechanisms occuring in actual soil systems. Caution must therefore be exercised in drawing any conclusions about trace element mobility based upon nutrient availability studies.

3.1 MODES OF ATTENUATION

It is probable that all the basic modes of attenuation have been identified. What has not been satisfactorily completed is the determination of the relative importance of each in various aqueous systems. Suggested modes include (Fuller and Korte, 1976; Jenne, 1968; Lindsay, 1972; Griffin and Shimp, 1978):

1) a) electrostatic adhesion of ions within the diffuse double layer near the particle surface,
    b) complexing with organic matter, in which case ions may become an integral part of an organic molecule, or the organic compounds may behave colloidally and possess a certain degree of ion exchange capacity,
    c) adsorption by mineral species (specific adsorption) involving hydrous oxides of iron, aluminum or manganese, and
2) precipitation which is brought on by changes in the solubility balance which occur because of changes in ion activities or the solution pH.

The relative contribution of each of these mechanisms is debatable since it is generally not easy to differentiate which mode is responsible for trace element uptake. Precipitation reactions, however, are sometimes recognizable because of abrupt sorption increases upon altering slightly the system pH, or the ion activities or ionic strength. The pH may also cause abrupt changes in sorption in the range near the point (pH) of zero charge for the clay or hydrous oxide colloid. At this point, further change in the solution pH may alter the polarity of the particle surface charge, thus altering the species being exchanged.

3.1.1 Adsorption Mechanisms (Ellis and Knezek, 1972; Parks, 1967; van Olphen, 1977)

The attachment of charged aqueous species to soil particles is generally referred to as adsorption, although a number of distinct mechanisms may be responsible for the net adsorption phenomenon. A large part of the sorptive capacity of a soil is due to the electrostatic attraction between aqueous ions and a particle surface charge. The ions may be held relatively loosely by simple electrostatic adhesion, being readily displaced by non-specific exchange ions, or more tightly bound by specific bonding mechanisms such as hydrogen or coordinate bonding, exhibiting degrees of non-exchangeability. This latter case is referred to as "specific adsorption" and includes the adsorption of uncharged aqueous species as well as adsorption of charged species on similarly charged surfaces.

The nature of particle surface charge is fundamental to the understanding of the adsorption process. The brief discussion which follows is basically after that of van Olphen (1977).

For clay colloidal systems, the particle charge may be considered to consist of an inherent or permanent negative surface charge and a variable (positive or negative) charge which is dependent upon the hydrogen ion activity (pH) of the sol. The inherent surface charge occurs in clays because of an isomorphic substitution of Al^{3+} for Si^{4+}, or Mg^{2+} for Al^{3+}, or similar substitution within the clay lattice. This results in an imbalance of charge for the particle which is apparently always negative for clays (Mitchell, 1976). The pH dependent portion of the particle charge involves the broken bonds which occur at the particle surface and results from adsorption of peptizing ions at the particle surface.

The sol has no net electric charge, therefore the ions within the solution phase must balance the electric charge on the particles. This balance is satisfied by the electric double layer concept, numerous models of which are given in the literature (e.g. Guoy, Stern-Guoy, Graehme, etc. (van Olphen, 1977)). All models postulate an increase in concentration of charge balancing ions, called counter ions, in the vicinity of the particle surface. Coincident with this there is also a deficit of ions possessing charge of the same sign as the particle. The nature of this charge distribution is addressed in the various models, e.g. a Poisson-Boltzmann distribution is assumed in some models.

An important aspect of this double layer is its influence on the stability of the sol. The double layer repulsion is largely responsible for preventing flocculation of the colloidal particles.

3.1.1.1 Ion Exchange

In a colloidal system or sol, ions may be held near the colloid particles in a diffuse double layer. The type of bonding determines how tenaciously the ions are held. If ions are held by electrostatic attraction, they are easily replaced by others of higher valence or stronger concentration in a process called ion exchange. This action is confined to the counter ion atmosphere surrounding the particle (van Olphen, 1977) and is a relatively rapid process (Jenne, 1968).

Following Helfferich (1962), Gast (1979) suggests that ion exchange is reversible, diffusion controlled, and stoichiometric. In most cases it is also suggested that there is some selectivity with preference for one ion over another. This preference is generally attributed to the difference of crystalline structure and hydration sizes between ions. Ions with smaller hydrated size or larger crystalline size are generally preferred over other ions of the same valence.

If the clay exhibits a negative surface charge, then cations will comprise the counter ion atmosphere. In this region there will be a deficit of anions as compared to the equilibrium solution concentration (deHaan and Bolt, 1963). The double layer anions are considered bound by the stability requirements of the double layer system but, like the cations, are exchangeable. In general, the total anion adsorption (typically expressed as meq/100 gms) is considerable less than the cation adsorption, but is not necessarily negligible. If the clay sheet edges are positively charged due to exposed lattice ions, then an analagous double layer exhibiting a dominating anion exchange capacity may also exist; however, due to the small total surface area of the clay plate edges, this contribution is small.

3.1.1.2 Specific Adsorption

The variable surface charge associated with clay particles is due to the interaction of surface atoms with aqueous ionic species. In the case of chemisorption, the bonds involve sharing of electrons between the charge deficit surface atoms and the solution cations -- this results in very strong bonds. Somewhat weaker bonds occur in physical adsorption when hydrogen bonding or van der Waals attraction forces are involved. Both processes are referred to as specific adsorption.

The particle charge in this case is pH dependent and is established by the preferential adsorption of peptizing ions (so named because of their influence in peptizing or dispersing the sol). These peptizing ions constitute the inner coating of the electric double layer with the counter ions forming the outer coating.

Essential to the understanding of the specific adsorption process and its pH dependence is the knowledge that anions are adsorbed in excess along the clay particle edge. For this to occur, complex anions must be formed which bind to the edges in such a manner that only a portion of the negative charge site of the anion is used, hence the negative charge along the particle edge. Many of the known peptizing anions have a specific reactivity with aluminum and magnesium which results in the formation of complex anions or insoluble salts. Figure 3-1 below demonstrates this phenomena with the polymetaphosphate anion.

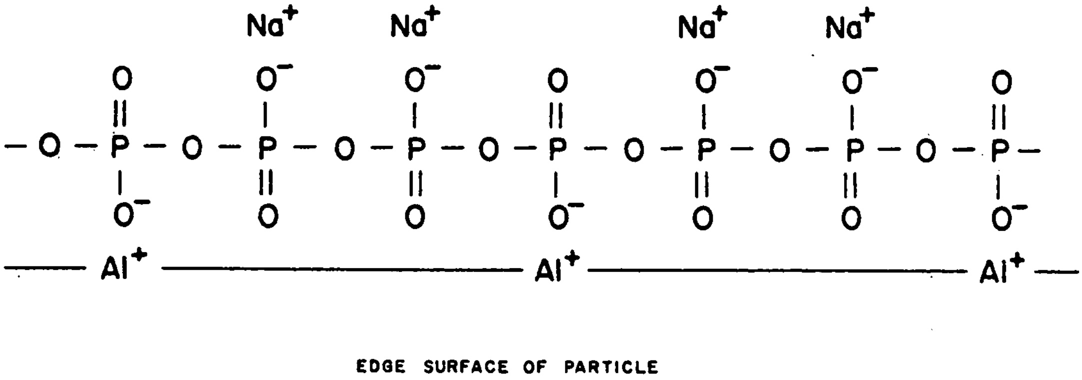


Figure 3-1. Specific Adsorption at the Edge
Surface of the Clay Particle. (van Olphen, 1977)

The excess of negative edge charge now may be satisfied by the electrolyte cations. If they are of the same type as appeared at the broken bond, e.g. aluminum or magnesium, these cations are called potential determining ions (PDI). In general PDI occur whenever the ions in solution are the same as those forming the crystalline structure of the particle and may be cationic or anionic. An example pertinent to soils is petization of aluminum hydroxide sols where the PDI are Al^{3+} or OH^- (or possibly more complex ions).

The oxides and hydrous oxides of aluminum, manganese, and iron are typically involved in specific adsorption characterized by the bonding of disassociated water molecules forming surface hydroxide groups or hydroxo complexes which are negatively charged if the OH^- activity is high (high pH) or positively charged if the H^+ activity is high (low pH). At some intermediate pH, referred to as the zero point of charge, (ZPC), surface charge is zero, being composed of an equal number of positive and negative adsorption sites. (If the ZPC arises from only the interaction of H^+, OH^-, the solid, and water alone, it is referred to as the isoelectric point (IEP).) In this case, the surface potential becomes zero and the electric double layer disintegrates. This need not coincide with neutral pH as Marshall (1975) demonstrated in a table similar to Table 3-1. Although the ion exchange capacity is not necessarily zero

Table 3-1. Isoelectric Points of Oxides and Hydrous Oxides of Iron and Aluminum (after Marshall, 1975)

Precipitate or Mineral	Notes	Isoelectric pH
$Al(OH)_3$ ppt.	From chloride	8.1
$Al(OH)_3$ ppt.	From sulfate	7.1
$Al(OH)_3$ ppt.	Amorphous	8.3
Gibbsite	$Al(OH)_3$	4.8
Bayerite	$Al(OH)_3$	6.2-7.4
Corundum	Al_2O_3	2.2
$Fe(OH)_3$ ppt.	From chloride	7.1
$Fe(OH)_3$ ppt.	From sulfate	7.05
$Fe(OH)_3$ ppt	Amorphous	8.5
Limonite	$FeO \cdot OH$	3.6
Lepidocrocite	$FeO \cdot OH$	5.4
Goethite	$FeO \cdot OH$	3.2
Hematite	Fe_2O_3	2.1

at the ZPC, it is, of course, a minimum with the finite amount of exchange capacity being attributed to ion adsorption and chemisorption. The inherent negative surface charge of the clay particles will cause the oxide coated clay to exhibit its ZPC at a lower pH than a comparable simple oxide having the same degree of chemisorbed surface charge.

In contrast to the electrical double layer ion exchange model, Jenne (1968) presents a good deal of evidence supporting the concept of specific adsorption of trace metals onto the hydrous oxide surface coatings of colloidal particles. It seems reasonable, however, that both the ion exchange mechanisms and the specific adsorption mechanisms should contribute to the observed data pertaining to the exchangeable and non-exchangeable ion sorption capacities, as suggested by the work of Elgabaly and Jenny (1943). Numerous other works suggest the presence of exchangeable and non-exchangeable mechanisms of ionic sorption: Hodgson (1960); Menzel and Jackson (1950); Demumbrum and Jackson (1956a,b); Fieldes and Schofield (1960); Gilbert et al. (1976). On the other hand, evidence given by Kinniburgh et al. (1975) tends to support the hydrous oxide model as overwhelmingly determining the sorption of trace elements. Additionally, solubility studies performed on fly ash (Theis and Wirth, 1977) indicate that the trace metal content of ash particles is concentrated in surface layers of iron and manganese oxides. Because the stability of the hydrous oxide precipitates is dependent upon pH together with reduction-oxidation potential, Eh, the specific sorption onto these oxide coatings may also be affected by the system pH. Outside the stable Eh-pH field for precipitated hydrous metal oxides, trace metal sorption cannot take place. Jenne (1968) presents Eh-pH stability fields for iron and manganese oxides, which are surmised to be the principal adsorbing species in water-soil systems. Lindsay (1972) presents additional solubility data for iron and manganese, as well as several other important trace metals, including Zn, Cu and Mo.

Hingston et al. (1972) report surface anion adsorption at a pH more alkaline than the ZPC. The specific adsorption of anions from incompletely dissociated acids occurs as the acid dissociates at the metal surface and the acid H^+ combines with OH^- in the inner Helmholtz plane (i.H.p.) to form water. The water is easily replaced by the free anion of the dissociated acid. This occurs when the pH is near a pK_a (negative logarithm of the ionization constant for a weak acid) of the acid. They also observed that specific adsorption shifts the ZPC toward more acidic pH's.

The anions of fully dissociated acids are not adsorbed unless the surface charge is positive, a condition which occurs on the acid side of the ZPC. There is no evidence that an anion in the absence of its acid can be adsorbed on a neutral or negative surface (neglecting adsorption on the positively charged edge of clays) (Hingston et al., 1972).

3.1.2 Precipitation

Generally speaking, most trace metal isomers demonstrate decreasing solubility with increasing pH. Notable exceptions are $Fe(OH_3)$, $Cu(OH)_3^-$, several oxides of Mo and hydroxides of Zn (Lindsay, 1972), and anionic forms of Cr, As and Se (Griffin and Shimp, 1978). Trace element solubility in groundwater systems is affected not only by the pH and Eh but also by the partial pressures of oxygen (P_{O_2}) and carbon dioxide

(P_{CO_2}), as well as by the presence of anions such as carbonates and phosphates (Lindsay, 1972). The presence of carbonate ions may encourage the formation of a number of insoluble precipitates (Garrells and Christ, 1965). This precipitation, of course, affects the immobilization of the trace elements in the soil. Ponnamperuma et al. (1966) provide additional Eh-pH-P_{CO_2}-P_{O_2} relationships for iron and manganese in flooded soils. In their 16 week studies they found that the pH equilibrated to a point near 7 for both the soil pH and the soil solution pH. In acid soils this was attributed to either the potential of the $Fe(OH)_3$-Fe^{2+} system or, for reduced acid soils high in iron, to the $Fe(OH)_3$-H_2O-CO_2 system. For alkali soils the system is Na_2CO_3-H_2O-CO_2 and for calcareous soils the system is the $CaCO_3$-H_2O-CO_2. The pH values of the flooded soils were nearer 7 than those of the aerobic counterparts.

3.1.3 Dispersion and Diffusion

Two additional mechanisms merit brief mention: dispersion and diffusion. The diffusion process may have two meanings within the context of this paper. Solid state diffusion, also known as lattice penetration, is indeed a fixation mechanism (Jenne, 1968). Here an ion fills a cavity of suitable size in the clay lattice which results from an unoccupied oxygen and hydroxyl octahedra. In a study of montmorillonite clays, Elgabaly and Jenny (1943) identified this process in the substitution of Zn^{2+} with ionic size 0.78 Å for Mg^{2+} which has the identical size. The other process associated with the term diffusion is actually one of dilution which arises from the random thermal motion of ions and molecules (Nye, 1979). The net movement is from high concentration to low concentration and is described by Fick's first law of diffusion, which in one dimension is:

$$F = -D \frac{dC}{dx}$$

where F is the flux, D is the diffusion coefficient, C is the concentration, and x is the direction of movement.

Dispersion in porous media results from the varied tortuosity of the different fluid paths and the frequent diverging of flow streams near the boundaries of the flow field. Biggar and Nielsen (1963) discuss the influence of dispersion on breakthrough of exchangeable ions. Considering only the longitudinal direction, the differential equation describing the dispersion is:

$$D_L \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

where the longitudinal dispersion coefficient D_L is determined from

$$D_L = 1.8 \, \nu \, N_R^{1.205}$$

where ν is the kinematic viscosity and N_R is the Reynolds number. The other terms in the dispersion equation are the average fluid velocity in the longitudinal direction, V_x, and the time, t (Bouwer, 1978). Dispersion is also a dilution type process.

3.1.4 Summary

A number of attenuation mechanisms have been identified, however it is generally uncertain which mechanisms dominate. Jenne (1968) has reviewed many papers and reinterpreted the results convincingly to support his hydrous oxide model. He suggests that organic matter more often plays an indirect rather than a direct role in fixing heavy metals. The reducing environment created by the presence of organic material is shown to support adsorption of heavy metals by hydrous oxides of iron and manganese. Waterlogging of soils in the absence of organics may have an insignificant influence, but the anaerobic environment created in the presence of organics is interpreted as additional evidence for the support of this model. Jenne further shows that much of the data interpreted as supporting a cation exchange model are based upon good correlations; however, the correlations could just as easily have been with surface area (of which CEC is a function) suggesting that adsorption by hydrous oxides (also a function of surface area) could also account for the adsorption. Furthermore, the rate of ion exchange is relatively rapid compared to the rate of fixation by hydrous oxides, the former being on the order of seconds or minutes (Jenne, 1968). With these points in mind, certainly Jenne's arguments bear consideration.

3.2 FACTORS INFLUENCING ATTENUATION

In addition to the wide variability of soil systems, variability in the leaching materials can significantly affect the uptake and attenuation properties. Leachate from municipal landfills may be somewhat acidic and rich in organic acids (Fuller and Korte, 1976; Fuller 1977, 1978) while leachate from ponded fly ash is usually inorganic and highly alkaline (Theis et al. 1976; Holland et al., 1975) although acidic fly ash leachates have been noted in eastern Tennessee (Milligan and Ruane, 1980). This source of variability further points out the necessity for column or batch studies to determine the gross behavior of leachates in soils.

Fuller and Korte (1976) and Fuller (1977, 1978) summarize a number of general variables known to affect the attenuation characteristics of soils, among which are:

1) soil particle size distribution,
2) soil pore size distribution,
3) calcium content of the soil,
4) solution flux through the soil,
5) the presence of oxides and hydroxides of aluminum, iron and manganese, and
6) soil pH value.

An additional factor, which is not entirely independent, mentioned by Griffin and Shimp (1978) is leachate ionic strength.

3.2.1 Soil Particle Size Distribution

The soil particle size distribution largely determines the surface area available for adsorption. It is partly for this reason that clay minerals exhibit a higher sorptive capacity than larger soil fractions. The particle size also determines the influence of the surface charge distribution. On small clay particles the surface charges are highly localized with positive charges along the edges and negative charges on the surfaces. With this localization the surfaces become cation adsorbers and, to a lesser extent, the edges become anion adsorbers. In larger particles, much of the potential is not available for ion adsorption but rather is required to hold the particle together. Montmorillonite clays exhibit especially suitable properties as a waste pit liner because of the small particle size and consequent large surface area, high swelling capacity, and high cation exchange capacity compared to other clays such as kaolinite and illite. It may be, however, that the chief influence of particle size is on the pore size since Fuller (1978) and Fuller and Korte (1976) found CEC and the kind of clay mineral to be the least important influences on leachate attenuation.

3.2.2 Soil Pore Size Distribution

The soil pore size distribution is related to the soil particle size and the soil composition. Included in this latter property should be the ionic species adsorbed on the surface. Smaller pore sizes restrict the flow of liquid through the soil allowing a longer time for leachate ions to be adsorbed or for chemical reactions to occur.

3.2.3 Calcium Content

Closely related to pore size is the calcium or lime content of the soil. If clay has a high sodium content, it will be dispersed and thus exhibit a low permeability, whereas if calcium is present instead of sodium, the clay will be well-flocculated and will have a higher permeability. The dispersion/flocculation process is discussed in a number of texts (e.g. Mattson, 1929; van Olphen, 1977; Bouwer, 1978); the brief discussion of Bouwer is followed here.

Flocculation of clay particles occurs when sufficient attractive forces exist to bind the clay particles. The forces which may contribute include bonds between organic polymers, polyvalent cation bridges, sesquioxide humus complexes, and van der Waals forces (Mustafa, 1979). For purposes of this paper the van der Waals forces are most important. If the clay particles can be close together, these forces will bind the particles together in floccules. Two influences combine to prevent this flocculation if Na^+ ions occupy the exchange sites:

1) the Na^+ ions are hydrated presenting a thick double layer which prevents the particles from being sufficiently close for the van der Walls forces to bind the particles, and 2) the monovalent Na^+ ions do not effectively mask the negative charges of the clay particles themselves, hence an electrostatic repulsive force opposes the van der Waals forces. Generally the divalent cations Ca^{2+} and Mg^{2+} replace the monovalent cations at exchange sites. These ions are not hydrated, hence the particles may be close enough for the van der Waals forces to bind them and the clay is flocculated. The floccules act as large particles increasing the pore spacing and the soil permeability.

3.2.4 Solution Flux through the Soil

Fuller (1978) noted that sharp decreases in the effluent metal concentrations were often associated with accidental reductions in solution flux. Further experimentation showed a flux effect for Cd, Al, Fe and Zn; however, the magnitude of the effect varied. That the concentration of a metal in the effluent should vary with the solution flow rate is not surprising. What is interesting is the variability of the effluent concentration as a function of element species and soil type. Fuller suggests that additional investigative work is needed on this phenomenon.

3.2.5 Influence of Oxides and Hydroxides

The hydrous oxides of Fe^{2+}, Al^{3+}, and Mn^{2+} may coat the soil particle, and the trace element is then probably first adsorbed on the surface of the hydrous oxide. The scenario continues with another hydrous oxide layer coating the adsorbed metal layer, and the sequence continues. An equation first presented by Leeper (1972) was reported by Fuller (1977) to explain a possible adsorption reaction:

$$2FeO \cdot OH + Zn^{2+} \rightarrow ZnFeO + 2H^{+}$$

Because the soil itself is composed of oxides (e.g. Si, Al, Fe, etc.), the potential for aqueous chemical reactions seems dependent only upon the ability of the soil element to permit lattice substitutions within the element structure. In montmorillonite clay about one sixth of the aluminum ions have been replaced by magnesium (Foth, 1978).

3.2.6 pH Values

The soil and leachate pH values are closely tied to the potential for certain ions to precipitate and hence be attenuated by the soil column. The solution pH may also influence adsorption by altering the polarity of the particle surface charge and thereby influencing which species are exchanged. Another possible influence is the soil's ability to buffer the leachate pH and consequently change the ionic species in solution.

3.2.7 Leachate Ionic Strength

Of all the variables one might choose to control in a soil attenuation experiment, ionic strength might be the most desireable. It is a measure of the average electrostatic interactions among ions in an electrolyte and it is a function of molality (and hence concentration); therefore, the attractiveness of controlling this parameter is that the exact ionic species in the leachate would be known. Unfortunately, as Griffin and Shimp (1978) note, "this is not a variable to be controlled." Although the ionic strength of the solution may be established before initial contact with the soil, once in contact the pH and composition of the soil may alter the ionic strength of the leachate. Griffin and

Shimp (1978) assert that the maximum removal for many elements is a function of the ionic strength of the leachate, CEC of the soil, and pH of the leachate.

3.3 REVIEW OF ADSORPTION EXPERIMENTS

Numerous experimental studies have been documented which address the sorptive ability of a particular soil or clay for specific cations or anions. Most of these experiments have been done by scientists interested in plant nutrition while some have been initiated by those concerned with leachates from municipal waste disposal sites. These latter leachates tend to be acidic. These experiments have often been initiated with the intent of verifying a hypothesized uptake mechanism. This section relates experimental evidence on an element by element basis to the basic leachate-soil interaction phenomena discussed previously. Evidence obtained from broad spectrum-type soil column studies will be cited here, as well as in a later section which addresses column studies specifically.

3.3.1 Adsorption of Specific Elements

3.3.1.1 Elements which Form Important Oxides

Adsorption by mineral species is an important attenuation process involving oxide colloids and oxide and hydrous oxide coatings on silicate clays. Two elements in particular, iron and manganese, have received extensive treatment in the literature.

3.3.1.1.1 Iron

Iron occurs naturally in soils and most often with valences of

+2 or +3 (Theis et al., 1982). Leeper (1970) states that the pH must be below 4 for the ferric concentration to reach even micromolar levels. Because of this he further suggests that the ferrous ion and ferri-organic ions of classical type are unstable in neutral or alkaline media.

According to Griffin and Shimp (1978) Fe may be eluted under anaerobic conditions due to the dissolution of the oxide coatings on the clay surfaces. Korte et al. (1976) suggest that hydrous oxides of iron adsorb trace metals, consequently it is probable that trace metals are reversibly released when iron is eluted. Gadde and Laitinen (1974) reported specific adsorption of Pb^{2+} and Cd^{2+} on hydrous ferric oxide.

Artiola and Fuller (1980) looked at the attenuation of iron in their study of the effectiveness of limestone as a liner for municipal landfills. They found that the limestone liner did enhance Fe attenuation and that this attenuation was most influenced by redox. As would be expected the iron moved more slowly in clay than sandy soils. They observed little or no significant competition between Fe and Be, Cd, Ni, or Zn for exchange sites. The authors interpret these findings and those of Korte et al. (1976) as supporting the hydrous oxide model of Jenne (1968).

In a 1972 study, Norvell and Lindsay found that additions of Fe-DTPA were effective in maintaining Fe solubility in soils in the pH range 5.8 to 7.3. Their calculations indicate that Fe-DTPA should be very stable in acid soils, moderately stable in slightly alkaline soils, and unstable in calcareous soils. The experimental data supported this with stability declining with increasing pH. This decline is partially attributed to decreasing solubility of soil Fe and consequent replacement of Fe by Ca in Fe-DTPA. Adsorption of DTPA by the soil was implicated as a major cause of the loss of Fe-DTPA from soultion. This is supported by the rapid initial losses of C^{14}-labeled DTPA which were accompanied by similar losses of soluble Fe. Dissolution and chelation of Fe by DTPA was much less important in the alkaline soils because of the lower solubility of soil Fe at higher pH.

3.3.1.1.2 Manganese

The chemical behavior and geologic occurence of manganese is similar to iron. It is however more electropositive than iron, most of its compounds exhibit a higher solubility than similar compounds of iron, and the sulfides exhibit less stability. Naturally occuring compounds exhibit three valence states (2+, 3+, 4+). The 3+ valence state is unstable in solution. The stable compounds are those of Mn in reducing environments and MnO_2 in oxidizing environments. The reaction between species suggested by Leeper (1970) is:

Oxidizing:

$$Mn^{2+} + 2\ OH^- + (O) = MnO_2 + H_2O$$

Reducing:

$$MnO_2 + 4\ H^+ + 2\ e^- = Mn^{2+} + 2\ H_2O$$

Hemstock and Low (1953) report formation of MnO_2 from a solution with a pH of 2.7 and Mn concentration of 27 mg/L. The long term equilibrium favors production of MnO_2.

Under reducing conditions, Mn^{2+} is less strongly adsorbed than other heavy metals on particles of soil. The compounds of Mn^{2+} are at least slightly soluble up to a pH of 7 in the presence of the usual anions found in surface waters (Krauskopf, 1972).

If the Mn^{2+} is relatively abundant, at high temperatures with $pH > 8$,

$Mn(OH)_2$ precipitates then dehydrates to form MnO (Krauskopf, 1972). The low temperature oxidation products include psilomelane, $BaMn(II)Mn(IV)_8O_{16}(OH)_4$; braunite, $(Mn,Si)_2O_3$; manganite, MnOOH; pyrolusite, MnO_2; and wad, an impure hydrated oxide. The psilomelane often contains Co, Ni, Cu, Pb, W, Ca, and K.

The details of oxidation are not clear, even in laboratory experiments. Some investigators (Hem, 1963; Collins and Buoll, 1970) report general agreement between theoretical predictions and laboratory observations of the Eh and pH of precipitation of simple oxides by oxidation of Mn^{2+}. Hemstock and Low (1953) found a pH dependence for fixed manganese which they interpreted to suggest an oxidation-precipitation reaction producing MnO_2. More recently their experiment has been considered by Leeper (1970) who suggests that the consumption of hydroxide was misinterpreted and that atmospheric CO_2 rather than Mn^{2+} consumed the OH^-, Manganese is soluble at low pH and Leeper (1970) suggests that the acid extracts not only Mn^{2+} but also MnO_2. Since Mn and Fe frequently occur together, it is important to note an influence which Fe may exert. Fe precipitates at a lower Eh and pH than Mn, consequently Mn may coprecipitate with $Fe(OH)_3$ or be adsorbed on the surface. This results in below normal equilibrium concentrations of Mn^{2+} in solution (Krauskopf, 1972).

According to Krauskopf (1972), little information is available on Mn adsorption in soils. It is known that Mn^{2+} is more strongly adsorbed on feldspathic sand than is Ca^{2+}. Acidifying the soil increases Mn availability (Leeper, 1970) suggesting that the ion becomes less strongly held. Hemstock and Low (1953) eliminated lattice substitution as an explanation of the nonexchangeable manganese in montmorillonite clay because the crystal lattice would be rendered unstable according to the Pauling valence rule. They also ruled out the possibility that the manganese ions might be trapped between the clay plates. Sanchez and Kamprath (1959) found that Mn which was added to a sandy loam was initially readily exchangeable, but that upon incubation in the soil under natural moisture conditions for several weeks it became non-exchangeable. When substantial organic peat was added, the manganese remained readily exchangeable as long as the soil was acidic. The addition of lime further reduced the exchangeable Mn levels in the non-organic soil and negated the solubilizing effect in the organic soils. It should be noted that oxidation as well as complexing was suggested as a factor in the evolution of the insoluble Mn. Reddy and Perkins (1976) noted that reducing conditions favor the formation of soluble Mn. They found that fixed Mn increased with pH, and they assumed it to be a precipitation-solubility effect. Additionally, the fixed Mn was found to vary inversely with cation exchange capacity for illite and bentonite clays. In a contradicting study, Griffin and Shimp (1978) found no correlation between Mn eluted from soil by an organic acidic leachate and the soil cation exchange capacity; however, a significant correlation (r=0.95) was obtained for eluted Mn vs. soil clay percentage. Manganese elution was attributed to reduction of surface coatings of Mn compounds on clays brought about by an anoxic environment. Korte et al. (1975) observed only a moderate correlation of acid-eluted soil Mn with clay percentage, a small negative correlation with cation exchange capacity, but a very significant correlation (r=0.99) with the total iron oxide and manganese content.

3.3.1.2 Major Cations

There are a few ions which, because of their natural occurence, should be considered. Their presence results from either the weathering of mineral matter (Al^{3+}, Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}), or the decaying of organic matter as with NH_4^{+}. In soils which have not been extensively weathered and leached, Ca^{2+} and Mg^{2+} are the most abundant exchangeable cations, while in soils which have experienced these processes, Al^{3+} and H^{+} predominate. Certainly Na^{+} and K^{+} are also usually present, at least in minor concentration (Hausenbuiller, 1978).

As has been noted, (Section 3.1.1) a clay particle derives part of its surface charge by isomorphic lattice substitution during formation. The most common substitutions are Mg^{2+} for Al^{3+} in the octahedral sheet as occurs with montmorillonite, and substitution of Al^{3+} for tetrahedral Si^{4+} as occurs with illite. These lattice substitutions are relatively permanent. The K^{+} ion can also be quite immobile when it occupies hexagonal holes of the planar surfaces of adjacent units in illite clays. A potassium bridge (O-K-O) is formed which binds adjacent layers together and produces a nonexpandable clay lattice. The K^{+} ion can be released during further weathering of the soil, but this is a very slow process. The potassium bridge neutralizes some of the lattice charge which partially accounts for the lower CEC of illite compared to montmorillonite (Foth, 1978).

Two factors primarily influence the concentration and mobility of these cations in the soil environment: 1) the adsorption affinity of the cations and 2) the relative concentration of the cations.

The following adsorption series (Hausenbuiller, 1978) demonstrates the two ionic characteristics which chiefly determine the adsorption affinity. The order of decreasing affinity or replaceability is:

$$Al^{3+} > Ca^{2+} \cong Mg^{2+} > K^{+} \cong NH^{+} > Na^{+}$$

The influence of valence is quite clear as lower valenced ions demonstrate lower adsorption affinity. Calcium and magnesium, both at 2+, are roughly equal although Foth (1978) suggests that Ca^{2+} will replace Mg^{2+}. Potassium and sodium are not equal however, and this demonstrates the second characteristic: degree of hydration. The Na^{+} ion undergoes a much greater degree of hydration than either K^{+} or NH^{+} and is consequently lower in the series. With its greater hydration radium Na^{+} cannot get as close to the adsorption site and consequently its adsorption affinity is less.

The relative concentration of the different ions is important in determining the equilibrium state. In sufficient concentrations weakly held ions can dominate both the exchangeable and soluble phases. The anionic composition of the soil solution is also important in this regard. If the anion forms a weakly ionized acid with the cation, this facilitates replacement; whereas, if a strongly ionized acid results, exchange is not enhanced. Examples of this include Na^{+} replacement of H^{+} which forms weakly ionized water with OH^{-}, and addition of Cl^{-} or $SO_4{}^{2-}$ with the Na^{+} in which case Na^{+} does not replace H^{+}.

Because of their natural occurence, perhaps the most important consideration for these final cations is their tendency to be released from adsorption sites in favor of more detrimental species.

3.3.1.3 Anions

The environment at western ash disposal sites is generally neutral to alkaline, which suggests that the pH dependent particle charges on the soil particles will be negative (the inherent charge is also negative). The only positively charged sites for anion adsorption will therefore be along the clay particle edges. Because of the relatively small area of the edges compared to the surface area, anion repulsion is more apparent than anion adsorption although the latter has been reported (deHaan and Bolt, 1963). This lack of adsorption suggests that anions are likely to be relatively mobile.

3.3.1.3.1 Sulfate

In a study by Babcock and Schultz (1963) two solutions with the same cation concentrations but different anion species gave different values for exchangeable sodium because of different activity coefficients. The exchangeable sodium was higher for the sulfate series than for the chloride series. Brown and Carter (1969) added $BaSeO_4$ and a mixture of $BaSO_4$-$BaSeO_4$ to soil columns. They found much less Se leached with the $BaSeO_4$ treatment and they found more Se leached with gypsum solution than with water alone. In essence, the addition of SO_4^{2-} increased the solubility of $BaSeO_4$.

Hem (1970) has stated that the presence of Ba in solution indicates a low sulfate concentration because $BaSO_4$ is relatively insoluble. In fact this is not the case for most cations as cations taken into solution from rocks do not usually form insoluble complexes with SO_4^{2-}. Generally sulfates are readily leached with both $MgSO_4$ and Na_2SO_4 being very soluble.

Chao et al. (1963) studied four soils in the acid to neutral range and found that sulfate was influenced by cations and pH with the latter dominating. Soils saturated with cations demonstrated an order of preference for adsorption of sulfate with Al^{3+} saturated soils adsorbing the most followed by Ca^{2+} and K^+. The soils which adsorbed large amounts of sulfate were high in hydrous iron and aluminum oxides, exchangeable aluminum, and in some cases amorphous material. The sulfate adsorption was adequately modelled using a Freundlich isotherm. There was no apparent maximum adsorption as sulfate concentration was increased.

3.3.1.3.2 Carbonate

Carbonate minerals are very common (Theis et al., 1982) with $CaCO_3$ having a dominating influence on many soil properties (Lindsay, 1979). The soil is generally an open system with regard to carbonate because of the availability of atmospheric CO_2. Lindsay (1979) discusses the carbonate and bicarbonate systems for Ca^{2+}, Mg^{2+}, Na^+, K^+, Mn^{2+}, and Fe^{3+}.

The solution pH and P_{CO_2} determine the equilibrium of $CO_3{}^{2-}$, $HCO_3{}^-$ and $CO_2{}^\circ$ in the soil system (Theis et al., 1982). Ponnamperuma et al. (1966) found that pH values of flooded soils were sensitive to CO_2 charges. These authors suggested that the pH of the flooded alkali, calcareous soils, and acid soils after reduction could be explained by one or more carbonate systems.

Pohland et al. (1982) suggest that the principal influence of carbonate is the effect on the precipitation of major ion species and the subsequent formation of active adsorption sites. Several metal (e.g. Fe, Ca, Cd, Zn, Mn, Pb, Cu, and Ba) carbonates may control the solubility of metals in the absence of strong precipitation agents such as sulfide.

3.3.1.4 Trace Elements

Many of the following elements (Cr, As, Se, Hg, Pb, Zn, Cu, Cd, Ba, Ag, Ni, V, Be) are necessary for plant or animal life, but all have potentially hazardous impacts at certain concentrations.

3.3.1.4.1 Chromium

The chromium ion may be found in either cationic or anionic form, depending on its oxidation state. Cr(VI) occurs as the anionic forms $HCrO_4^-$ or $Cr_2O_7^{4-}$ for pH less than about 7 and reverts to CrO_7^{2-} for pH greater than 7 (MacNaughton, 1975). Cr(III), on the other hand, occurs only as cationic species, principally as the hydrolized forms (Griffin et al., 1977). Griffin et al. (1977) found Cr(III) to be adsorbed by clays in accordance with the Langmuir isotherm relationship assuming a cation exchange adsorption mechanism. As the pH was increased above the zero point of charge (ZPC) for the clay minerals, the Cr(III) was found to be completely adsorbed. Column adsorption studies performed by Korte et al. (1976) did not, however, indicate a strong correlation with CEC. Instead, the most significant correlation with retained Cr(III) was with the amount of soil iron oxide and manganese. In another study (Artiola and Fuller, 1979) the addition of a limestone layer in the soil column further increased adsorption of Cr(III), presumably by a pH effect upon the negative soil particle charge.

Because of the repulsion between the soil particle negative surface charge and the anionic Cr(VI) forms, adsorption of this species is considerably less than the cationic Cr(III). Griffin and Shimp (1978) note that Cr(VI) adsorption (principally $HCrO_4^-$) is greatest for very acidic conditions where the soil clay particles may actually possess a positive surface charge. As the pH is increased above the ZPC, adsorption of $HCrO_4^-$ rapidly diminished, becoming insignificant above a pH of about 7. This study found that increasing ionic strength enhances slightly the uptake of Cr(VI). Gilbert et al. (1976) and MacNaughten (1975) also noted that adsorption of Cr(VI) onto hydrous manganese and iron oxides was negligible; however, he found adsorption of Cr(VI) to decrease with increasing ionic strength, in contrast to the observations of Griffin and Shimp (1978).

3.3.1.4.2 Arsenic

Arsenic appears naturally in two oxidation states, As(III) and As(V), with the latter being more prevalent but the former being much more toxic (Doull, Klaassen and Amdur, 1980). At high pH under oxidizing conditions arsenic exhibits anionic behavior as arsenate, $As(V)O_4^{3-}$ and arsenite, $As(III)O_2^-$ or $As(III)O_3^{3-}$ (Theis et al., 1982). Griffin and Shimp (1978) and Frost and Griffin (1977) report on adsorption studies involving both oxidation states. Their results showed that arsenic adsorption onto kaolinite and montmorillonite clays was dependent upon the concentration of arsenic in solution, the amount of arsenic adsorbed increasing with increasing As(V) or As(III) ionic concentration. The amount of As(V) adsorbed varied with pH, at first increasing with increasing pH and later decreasing. This fluctuation seemed to be governed by the relative abundance of the monovalent $H_2AsO_4^-$ species. Although not noted, it seems possible that the decreasing adsorption for high pH could have been due also to a negative surface charge brought about by pH in excess of the clay ZPC's which correspond approximately to the pH's at the adsorption maximums. As(III) showed a similar pH effect for montmorillonite but varied for kaolinite, with adsorption continually increasing with increasing pH.

In experiments with fly ash leachate from power plants in Tennessee, Turner (1981) found that As(V) concentrations varied systematically as a function of pH but the As(III) concentrations remained nearly constant in the pH range 3 to 12. Turner suggests that as an anionic or neutral species, arsenic should be more mobile than most trace metal cations. Surface active solids which have isoelectric points in the basic pH range, such as amorphous iron hydroxide, are likely to adsorb anionic arsenic species. Pierce and Moore (1980) report that specific adsorption of the neutral arsenious acid molecule on amorphous iron oxyhydroxide is important at environmentally realistic concentrations. In their study, Pierce and Moore found that the adsorption isotherms obeyed Langmuir type equations for ionic strength of the solutions at 0.01, a pH range from 4 to 10, and an arsenite concentration range of 10^{-7} to 10^{-5} M.

Korte et al. (1976) found arsenic adsorption to be predominantly correlated with soil clay content. Huang (1975) found arsenic to adsorb in relatively large amounts onto hydrous aluminum oxide coatings of mineral colloids. Adsorption was found to decrease with an increase in concentration of NaCl in solution. This decrease may be attributed to the flocculation resulting from polyelectrolyte binding of the clay particles and a consequent decrease in adsorption sites.

3.3.1.4.3 Selenium

Perhaps because selenium also behaves anionically, many of the investigations on arsenic also include selenium. In the studies of Griffin and Shimp (1978) and Frost and Griffin (1977), Se(IV) was found to behave much like As(V), attaining a maximum adsorption in the vicinity of the zero point of charge for the clay. This was assumed to be due to the distribution of $HSeO_3^-$ with respect to pH. Korte et al. (1976) also studied selenium and found adsorption to be correlated with soil clay content. Griffin and Shimp (1978) concluded that the principal adsorption mechanism was anion exchange of the monovalent species, $HSeO_3^-$. They also suggest that the relative mobility of this element in alkaline conditions presents a potentially high pollution hazard.

3.3.1.4.4 Mercury

Mercury is found in the environment in three oxidation states, namely Hg°, Hg_2^{2+} and Hg^{2+}. In an investigation into the effects of pH and chloride concentration (pCl) upon soil uptake of mercury, Hahne and Kroontje (1973) observed that mercury takes on a number of hydrolized forms at low pH and soluble chloride complexes at low chloride concentrations. They found the retention of Hg(II) by the three major clay types (montmorillonite, kaolinite and illite) to be negligible, indicating a high mobility of Hg(II) in soil systems. MacNaughton and James (1974) measured adsorption of Hg(II) onto SiO_2 particles, finding a pH dependence. Adsorption was found to increase rapidly with pH above a critical value (although never showing greater than a 60% removal from the solution). This critical pH value further depended upon the chloride concentration becoming greater as the Cl^- concentration increased. Above a second critical value, however, adsorption dropped off again. Since the dominant Hg(II) species were thought to be $Hg(OH)_2^o$ and $HgCl_2^o$, electrostatic phenomena were ruled out as important binding mechanisms; instead, chemical free energy was interpreted as controlling adsorption along the lines of the model of James and Healy (1972). Through a soil column study of attenuation and uptake of municipal waste leachate, Fuller (1978) determined mercury to be moderately to highly mobile in a variety of soil types constituting the most mobile of the many trace elements investigated in that study. In contrast to the preceding investigations which suggest that mercury is not very effectively retained by soils, Griffin and Shimp (1978) report observing significant uptake of mercury by clay particles. This study concluded that cation exchange was the mechanism of adsorption and that roughly two-thirds of the mercury was of organic form. The experiments were flawed, however, due to inadequate control of mercury losses in the apparatus.

3.3.1.4.5 Lead

Gadde and Laitinen (1974) measured the adsorption of Pb(II) onto hydrous oxides of iron, manganese and aluminum. They found lead to be most strongly adsorbed for high values of pH and noted significant lead adsorption for pH's below the hydrous oxide zero points of charge (for hydrous ferric oxide this ZPC is about 8.5). They concluded that since adsorption of lead ions was accompanied by a pH dependent release of hydrogen ions (1.6 hydrogen ions at a pH of 6 and 1.3 hydrogen ions at a pH of 5) the adsorption was a specific replacement of weakly acid protons by aquated Pb^{2+} or $PbOH^+$ rather than a "generalized counter ion process such as could occur on a colloid of opposite sign." Appreciable adsorption of lead in the vicinity of the ZPC was attributed to specific adsorption on hydrous manganese oxide. Griffin and Shimp (1976, 1978) hypothesized that the uptake of lead by clay particles is governed by the cation exchange process but influenced by the formation of PbCO precipitates and pH dependent hydrolized lead species. Lowest lead uptake was associated with adsorption of Pb^{2+} for acidic conditions; highest adsorption of lead was associated with the evolution of several hydrolized lead species at pH above 6. Griffin and Au (1977), noting that experimental results showed calcium ions (from $Ca(ClO_4)_2$) to compete with lead cations for exchange adsorption sites, found a "competitive" Langmuir model to be appropriate for predicting adsorption trends. Fuller (1978) found the uptake of lead by several Western soils to be exceeded only by copper, and elution studies showed that sorbed lead was not easily desorbed by water. Lead uptake was most closely associated with soil texture, with fine-textured soils providing the lowest lead mobilization.

3.3.1.4.6 Zinc

Early studies into the exchangeability of Zn in soils revealed that exchangeable Zn was adsorbed by clay minerals in quantities exceeding the calcium exchange capacity (Elgabaly and Jenny, 1943; DeMumbrum and Jackson, 1956a,b). In particular Elgabaly and Jenny measured uptake of zinc and chloride and release of calcium and sodium and the release of zinc and uptake of calcium, sodium and chloride from various bentonite clays. Two important observations are:
1) the chloride adsorption requires a special explanation which results in a surface mosaic model for the clay surface, and 2) the pH of the solution determines the ionic forms of the constituents and hence

influences the adsorption.

In later work, Griffin and Shimp (1978) viewed the uptake of zinc as being principally controlled by ion exchange and precipitation mechanisms. In their soil column study, zinc was adsorbed from a municipal leachate in quantities proportional to the cation exchange capacity (CEC). As the pH was increased, the zinc was precipitated and adsorbed by the clays. In another column study cation exchange capacity was not well correlated with adsorbed quantities of zinc; instead, clay surface area and free iron oxide content provided the best correlation with adsorption (Korte et al., 1976). This same result was corroborated by Artiola and Fuller (1979) and seems to support the hydrous oxide trace metal control model suggested by Jenne (1968). Gadde and Laitinen (1974) found that zinc adsorption onto hydrous manganese and iron oxides increases with increasing pH but evidently reversibly desorbs as the solution pH is subsequently lowered.

3.3.1.4.7 Copper

Some of the early studies on zinc exchangeability included copper (DeMumbrum and Jackson, 1956a,b) and the results are similar, i.e. copper adsorption appears to exceed the desorption of major cations. Menzel and Jackson (1950) found that roughly fifty percent of the copper adsorbed onto the crystal lattice of clay particles was in the form of $Cu(OH)^+$, even though copper in solution was predominantly Cu^{2+}. This is explained by the hydrolysis of Cu^{2+} after adsorption in the bivalent form. They further suggested that this incorporation into the crystal structure was primarily a mode of irreversible adsorption. Griffen and Shimp (1978) included copper in their soil column study and found that the adsorption by clays increased with pH up to approximately 6.5. At pH's above 7.0 the adsorption decreased apparently due to the dissolution of $Cu(OH)_2$ precipitate. As for zinc, they viewed uptake to be a combination of ion exchange and precipitation. They cited ionic competition as preventing sorption in quantities equal to the CEC. Hemstock and Low (1953) observed that copper salts were efficient in extracting manganese in organic combination by virtue of the fact that the cupric ion replaced the manganese in the organic chelate complexes.

3.3.1.4.8 Cadmium

According to Griffen and Shimp (1978) the mobility of cadmium is dependent upon solution pH, ionic strength, and cation exchange capacity at pH near 6. At higher pH values, precipitation becomes increasingly important. In their study Cd was adsorbed from municipal landfill leachate in quantities proportional to the CEC. Ionic competition prevented the sorption quantity from equalling the CEC. As the pH was increased, Cd was increasingly adsorbed by clays.

Korte et al. (1976) had contradictory results and found that CEC was not well correlated with adsorbed Cd. Clay surface area and free iron oxide content were well correlated ($R^2 = 0.94$) with quantities of Cd adsorbed. In an associated study, Artiola and Fuller (1979) confirm these results and find in them support for the hydrous oxide trace metal control model of Jenne (1968). Gadde and Laitinen (1974) found that cadmium adsorption onto hydrous manganese and iron oxide increases with increasing pH and evidently reversibly desorbs as the solution pH is decreased. Gilbert et al. (1976) contrast these findings by suggesting that there is no significant chemisorption of Cd onto hydrous manganese oxides near the ZPC.

3.3.1.4.9 Barium

Barium is chemically similar to calcium although much less abundant. It has been found to replace potassium (as might be expected on the basis of valence alone) in some igneous rock minerals (Hem, 1970). The $Ba(OH)_2$ form is water soluble, but $BaCO_3$ and $BaSO_4$ are not. Barium has been found to form quite stable complexes with the organic matter in peat (Theis et al., 1982). Hem (1970) maintains that the low occurence of barium in natural waters is due to the low solubility of $BaSO_4$, the most common mineral form. The solubility of barium is increased by the presence of chloride and other anions and cations in dilute solution.

3.3.1.4.10 Silver, Nickel, Vanadium, and Beryllium

The adsorption and co-precipitation of silver onto hydrous ferric oxide was investigated by Dyck (1968), who modeled the uptake in terms of Freundlich adsorption isotherms. The model adequately fits the data, and the study revealed a strong pH dependence with silver uptake increasing with pH. Fuller (1978) determined that retention of cationic nickel by several Western soils was most highly correlated with total surface area and cation exchange capacity. Also, anionic vanadium demonstrated a high correlation with total clay content, and beryllium retention showed an association with the clay content and soil surface area.

3.3.1.5 Organic Materials

It is a documented fact that organic matter plays a role in the movement of metal ions through soils. The addition of organic acids (such as might be associated with municipal landfill operations) to soils can lead to the formation of soluble and insoluble metal chelates (Norvell and Lindsay, 1969; Lindsay and Norvell, 1969; Lahav and Hochberg, 1975). Organic acids and compounds also occur naturally in soils, particularly the podzols (a soil group characterized by mats of organic matter in the surface layer and thin horizons of organic minerals overlying gray, leached horizons and dark-brown illuvial horizons; found in coal forests and in temperate coniferous or mixed forests, as the result of the decay of leaf and forest matter), can contribute to the mobility of metal ions in the soil (Stevenson and Ardakani, 1972). Norvell (1972) presents a summary of chelate stability relations as a function of pH for numerous metal ions, including Mg, Cu, Fe, Al, Mn, Cu, Zn, as well as Ca. Increasing pH can lead to dissolution of iron and aluminum chelates, favoring the formation of magnesium and calcium chelates. Copper and manganese may be strongly chelated in alkaline soils.

3.3.2 Specific Column Studies

The attenuation properties of soils are usually determined by the slow percolation of leachates through soil test columns. Generally the influent and effluent trace element concentrations are measured to determine the amount of attenuation attained for each ion species. These studies may emphasize the elements which are eluted from the soils by the leaching solutions (e.g., Korte et al., 1975) or the trace metals initially present in the leachate which finally penetrate the soil column, as in Korte et al. (1976), Fuller and Korte (1976) and Griffin et al. (1976). Artiola and Fuller (1979, 1980) have investigated the additional attenuation capacity for municipal leachate provided by the use of a limestone liner.

In the experiments of Artiola and Fuller, Fuller et al., and Korte et al. the columns were exposed to the flowing leachate for approximately one month which provided a dose of 15 to 20 pore volumes of leachate through the column. The soil pore volume was determined using a technique developed by Heilman et al. (1965). Essentially, leaching was continued until one of three criteria was attained:

1) effluent concentration = influent concentration (breakthrough)
2) effluent not changing and at a concentration less than that of the influent (steady state), or
3) continued absence of the element after leaching.

Typical curves for C/C_0 are shown in Figure 3-2, where C = effluent trace element concentration, and C_0 = the influent trace element concentration. In this figure nickel portrays the first criteria (breakthrough), beryllium the second (steady state) and selenium the third.

In a similar study, Griffin and Shimp (1978) conducted soil column experiments with particular emphasis on the effects of clay liners on pollutant attenuation. The columns were operated at liquid fluxes which required from 6-10 months to percolate 15 pore volumes.

Griffin and Shimp developed an index of attenuation (ATN) which quantifies the attenuation ability of different soils for trace elements. The attenuation index is a measure of how much of the trace element has been retained in the soil after ten pore volumes have passed through the sample. With reference to Figure 3-3, if one considers the area A under the attenuation curve as a quantity proportional to the amount of trace element not retained, then the amount of material retained is proportional

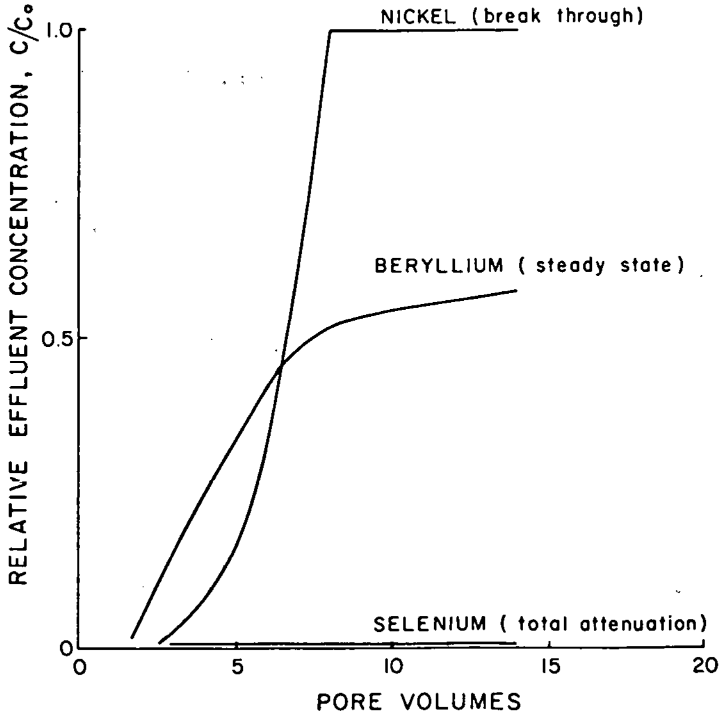


Figure 3-2. Typical Attenuation Curves Obtained from Soil Column Percolation Experiments.

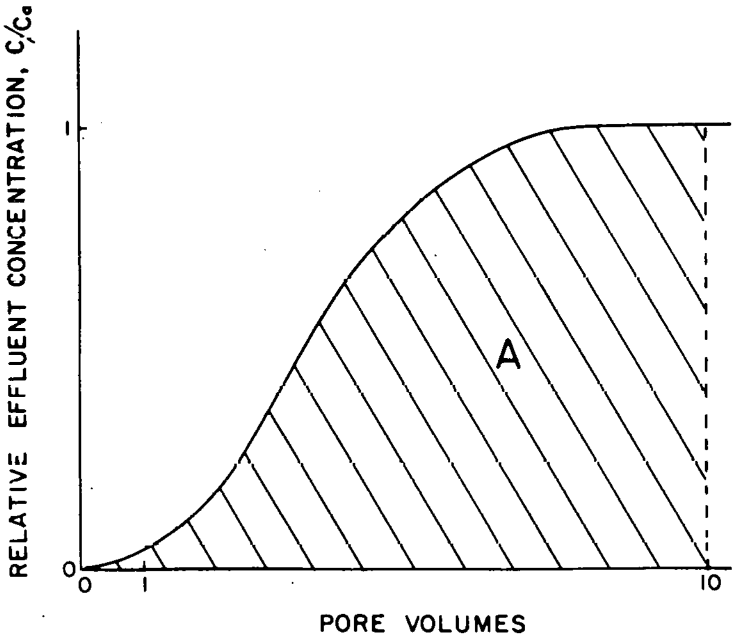


Figure 3-3. Illustration of the Use of an Attenuation Curve for Determination of ATN.

to the quantity 10-A. The relative attenuation then may be expressed by the parameter ATN, viz:

$$ATN = \frac{10 - A}{10} * 100\%$$

The use of this parameter, ATN, allows for the ranking of each trace element with regard to the attenuation of a given soil for that particular element. The results shown in Table 3-2 illustrate an application of ATN in ranking chemical trace elements from municipal leachate flowing through a clay mineral column (Griffin and Shimp, 1978). In this ranking, moderate to highly mobile species were characterized by attenuation numbers less than 50%, and the relative immobile species by attenuation numbers above 95% (e.g. Pb, Zn, Cd, Hg). Those species eluted from the clay with concentrations exceeding the influent are characterized by negative attenuation

Table 3-2. Rank of Chemical Constituents in Municipal Leachate According to Relative Mobility Through Clay Mineral Columns. (Griffin and Shimp, 1978)

Chemical constituent	Mean attenuation number	Principal attenuation mechanism	Relative mobility
Pb	99.8	Precipitation/Exchange	Low
Zn	97.2	Precipitation/Exchange	
Cd	97.0	Precipitation/Exchange	
Hg	96.8	Precipitation/Exchange	
Fe	58.4	Oxidation-Reduction	Moderate
Si	54.7	-----	
K	38.2	Cation Exchange	
NH_4	37.1	Cation Exchange	
Mg	29.3	Cation Exchange	
COD	21.3	Microbial Degradation	High
Na	15.4	Cation Exchange	
Cl	10.7	Dispersion	
B	-11.8	Artifact?	More Eluted Than Applied
Mn	-95.4	Elution from Clay	
Ca	-656.7	Exchanged from Clay	

numbers. Also determined in this study was the dependence of attenuation ability upon the clay type. The performance of the three basic clay types is summarized in Table 3-3. The overall ranking of each clay type from greatest to least attenuation ability was determined to be:

montmorillonite > illite > kaolinite

The soil and leachate pH values were found to affect precipitation mechanisms, with attenuation increasing with pH.

Table 3-3. Mean Attenuation Number (ATN) of Selected Constituents Found in Municipal Leachates for Three Clay Minerals. (Griffin and Shimp, 1978)

Chemical constituent	Mean ATN			
	Montmorillonite	Illite	Kaolinite	All columns
Pb	99.6*	100.0	99.9	99.8
Zn	97.7	98.6	98.1	97.2
Cd	96.7	100.0	97.5	97.0
Hg	98.4	98.1	95.2	96.8
Fe	34.8	82.8	67.6	58.4
Si	39.2	81.6	71.2	54.7
K	50.9	31.0	23.2	38.2
NH_4	54.8	31.0	25.1	37.1
Mg	48.2	19.7	18.1	29.3
COD	24.6	23.2	16.2	21.3
Na	20.6	16.4	9.7	15.4
Cl	9.3	13.5	14.3	10.7
B	-16.1†	-12.8	-11.5	-11.8
Mn	-73.2	-6.4	-266.2	-95.4
Ca	-885.5	-223.3	-190.2	-656.7

*Underlined means are not significantly different (0.05).
†Minus numbers indicate elution.

Griffin and Shimp also proposed the use of a hazard ranking index expressed by:

$$R = Q * HI$$

where: R = hazard ranking factor

HI = hazard index

$$HI = \frac{C}{DWS}(100-ATN)$$

Q = annual production of element

DWS = drinking water standards or other appropriate standard

Table 3-4 lists the relative hazard (based upon the Federal drinking water standards) posed by each of the elements in the municipal leachate investigated by Griffin and Shimp.

TABLE 3-4. Chemical Constituents in Dupage Leachate, Ranked According to Pollution Hazard. (Griffin and Shimp, 1978)

Chemical constituent	Effective concentration / D.W. standard	Hazard index
NH_4	862/0.5	108,440.
B	(29.9 + 3.5)/1.0	3,734.
COD	1340/50	2,109.
Hg	0.87/0.002	1,392.
Cl	3484/250	1,241.
Ca	(46.8 + 307.3)/250*	1,072.
Cd	1.95/0.01	585.
Fe	4.2/0.3	582.
Na	748/270	234.
Mn	(0.02 + 0.02)/0.05	153.
K	501/250*	123.
Mg	233/250*	65.7
Ph	4.46/0.05	17.8
Zn	18.8/5.0	10.5
Si	14.9/250*	2.7

*Actual value not established by EPA; therefore it was assumed to be the same as chloride.

Milligan and Ruane (1980) conducted a major research effort addressing power plant solid waste disposal which specifically concerns the leaching of scrubber sludge and fly ash buried in northeastern Alabama and eastern Tennessee. In this study, ash leachate samples were obtained from groundwater sampling wells and were found to be mildly acidic and to contain quantities of Al, Be, Cd, Ca, Cr, Cu, Fe, Pb, Hg, Ni, Se and Zn, B, sulfide and sulfate. The leachate was used in columnar studies which involved relatively high liquid flux values -- superficial velocities ~1.3 m/day. Leachate flow was maintained through the soil until the calcium exchange capacity (determined by calculation) of the soil was theoretically exceeded. It was determined that ion exchange could not be a major attenuation mechanism in these experiments; but that the governing phenomena were precipitation and adsorption by hydrous oxides of aluminum, iron and manganese.

Milligan and Ruane (1980) thus emphasized the controversy regarding the dominant attenuation mechanisms. The many conflicting conclusions of other researchers further emphasize the controversy: Griffin et al. (1978) concluded that for Pb, Cd, Hg and Zn, precipitation in the soil column surface layer appeared to be the principal attenuation mode; Fetter (1977) reasoned that heavy metals primarily were attenuated by ion exchange mechanisms; Fuller (1977) specifically noted that ion exchange cannot bind metal ions indefinitely and that eventual migration from the exchange site is inevitable; and Leeper (1972) claimed adsorption reactions with hydrous metal oxides to be major attenuation reactions.

SECTION 4

DISPOSAL SOILS

Although strip mine spoil may be divided into the two categories of topsoil and overburden, this discussion focuses on overburden because it is primarily used in the disposal of power plant solid wastes. A typical disposal scheme involves placing ash in a mined pit with occasional interlayering of the ash with overburden to provide some structural stability. The amount of interlayering is variable and dependent upon current mining operation needs. The pit is closed by placing a final covering of overburden followed by an application of topsoil. The actual chemical nature of the topsoil has little influence on the uptake processes of the soils.

4.1 PROPERTIES OF DISPOSAL SOILS

The particular physical and chemical properties of soils to be used in the disposal of coal ash wastes will be site specific. Certainly, variation is expected between the residual soils of the uplands and the alluvium of the flood plain. Although both may share the same parent material, different processes have influenced the soil development. With respect to the length scales associated with the chemical variability of soils in a given geographical region, Connor, Keith and Anderson (1976) reported that there was no significant variation in trace element concentrations at distances greater than 35 km in the Green River Basin. Most of the variability was noted to be associated with scales of 0.3 to 4.5 km, which suggests that environmental parameters may need to be averaged over the area of a mine.

4.2 WESTERN SOILS

Western soils have the potential for being arid and alkaline (Fuller, 1975) and are generally very different than the soils found in the eastern states. The map in Figure 4-1 outlines the areas where the arid soil classification is appropriate in North America. Essentially the entire western United States - including Wyoming, Colorado,

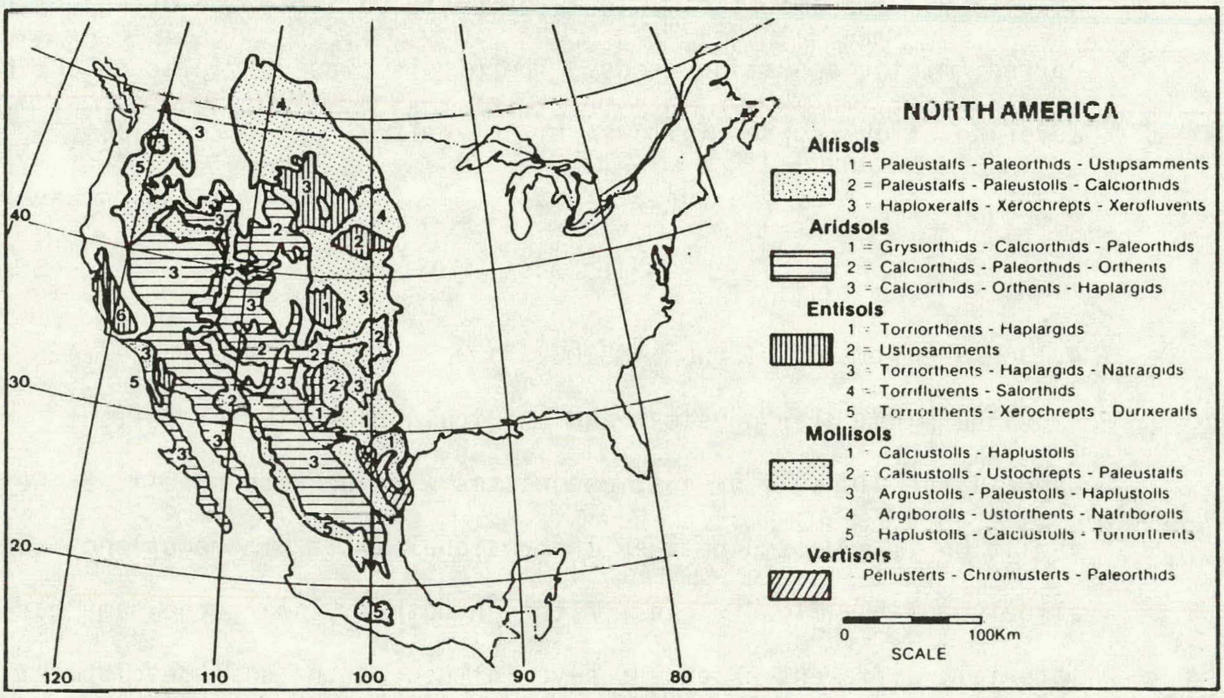


Figure 4-1. Arid-region Soils of North America, Polar Soils Not Shown. (Dregne, 1976)

Utah, Montana and the Dakotas - is characterized by the various types of arid-region soils. The Texas lignite belt does not fall entirely within this arid region and, in some areas, may better be described as possessing subhumid to humid type soils.

4.2.1 Texas Lignite Region

4.2.1.1 Gibbons Creek Mine

The Texas Municipal Power Authority went on-line with a lignite-fired power plant in early 1983. Located near the small community of Carlos in Grimes County, Texas, the plant has a generating capacity of 400 MW and will consume $2.7\text{x}10^6$ tons of lignite per year. The strip mining procedure is the conventional block cut method, and the disposal method for combustion products is an interbedded or layered spoil procedure.

The overburden at all depths has material from the three gradation classes (sand, silt and clay), and the fractions of each vary considerably. A large number of core samples (Texas Railroad Commission, 1981a) have been taken from the overburden in the mine area at depths of 10-200 ft and the results of analysis showed the minimum and maximum values of sand content to be 2.1 and 98.5 percent. The maximum clay content, which is associated with the core with minimum sand content, was 79.7 percent. Clay and silt in the core with 95.8 percent sand were 2.9 and 1.3 percent, respectively. A composite classification of clay or clay loam provides an overall estimate of soil texture.

The range of equilibrium oxidized pH is from 2.7 to 7.93, indicating that the soil is generally acidic, a condition to be expected in a subhumid region such as the East Texas Gulf Coast. The layers which have pH values less than 4.5 generally have concentrations of pyritic sulfur exceeding 0.2 percent. There are, however, other sources of acidity which are indicated by the low sulfur content of some acidic layers. Also, samples from some of the layers with high pyrite concentrations do not oxidize to acid, suggesting the presence of neutralizing material.

Calcium, sodium, potassium, magnesium, chloride, and sulfate appear in the overburden samples. Carbonate and bicarbonate were detected in only two cores, and showed carbonate values of 100-200 mg/kg while bicarbonate values were recorded as less than 100 mg/kg to a high of 800 mg/kg. Calcium and sodium which are the most prevalent exchangeable cations, typically average on the order of 10 and 2 meq/100 g respectively in each core. The base saturation values range from a low of 20 percent to greater than 100 percent (where excess calcium is present), although most values are near 50 percent.

For illustrative purposes, partial data from a sample core (Core Number 3534EE) taken from the Grimes County mine are shown in Table 4-1. This particular core is reasonably representative of the area with one notable exception: at all sampling levels the pH is somewhat more acidic than the average core. The clay fraction varies from 9 to 31 percent, the cation exchange capacity ranges from 6 to 41 meq/100 g, the exchangeable calcium and sodium average 2.7 and 1.9 meq/100 g, respectively, and the percent base saturation varies from 21 to 92 percent. Arsenic levels were noted to be in the mg/kg range and the concentration of selenium was below the minimum detectable level of the analytical apparatus.

Tests were performed on the overburden to determine the concentrations of 14 trace elements. With reference to Table 4-2, the highest, second highest, lowest and second lowest recorded concentration for each element are noted together with the depth at which the event occured. Also given are the weighted averages (weighted

Table 4-1. Overburden Characteristics from a Single Core (Core 3534 EE) at Gibbons Creek Mine. (Texas Railroad Commission, 1981a)

Depth* (ft)	Texture				Equilibrium pH	Acidity		Electrical Conductivity mmhos/cm	Soluble Salts mg/L
	% Sand	% Silt	% Clay	USDA		meq/100g	Equiv. $CaCO^3$ mg/kg		
10.0-31.2	76.0	9.4	14.6	sandy loam	4.2	0.90	450	.5	320
36.4-50.0	81.0	10.0	8.8	loamy sand or sandy loam	4.5	0.89	445	.5	320
50.0-58.6	57.9	19.6	22.5	sandy clay loam	2.8	23.08	11549	-	-
58.9-60.0	69.2	12.4	18.4	sandy loam	4.2	2.18	1091	.5	320
71.1-91	66.8	13.7	19.5	sandy loam or sandy clay loam	2.7	14.15	7081	-	-
91-102	33.0	35.6	31.4	clay loam	2.5	31.65	15838	-	-
108-121.9	79.4	8.4	12.2	sandy loam	2.7	15.36	7686	-	2560
126.4-136.6	38.0	31.1	30.9	clay loam	2.7	29.09	14557	10.0	6400
142.9-145.7	16.6	54.3	29.1	silty clay loam	2.8	8.15	4078	8.0	5120

Depth* (ft)	Cation Exchange Capacity		Exchangeable				Percent Base Saturation	Arsenic mg/kg	Boron mg/kg	Selenium mg/kg	Organic Matter Percentage
			Calcium		Sodium						
	meq/100g	Equiv. Ca^{2+} mg/kg	meq/100g	mg/kg	meq/100g	mg/kg					
10.0-31.2	7.96	1595	0.15	30	2.63	605	47.24	0.8	0.4	<1.5	0.0
36.4-50.0	5.75	1152	0.96	192	1.23	283	51.13	1.5	0.0	<1.5	0.0
50.0-58.9	11.56	2317	0.81	162	0.62	143	21.80	2.3	0.9	<1.5	0.1
58.9-60.0	17.19	3445	1.03	206	1.61	370	20.94	1.6	0.0	<1.5	0.1
71.1-91.0	16.44	3295	2.50	501	0.72	166	30.54	1.7	1.6	<1.5	0.3
91.0-102.	41.01	8218	6.86	1375	1.21	278	31.75	2.4	4.8	<1.5	1.2
108.0-121	10.65	2134	3.41	621	5.31	1221	92.30	1.8	1.7	<1.5	0.4
126.0-136	25.33	5076	6.96	1395	0.64	147	38.25	2.0	3.6	<1.5	0.4
142.0-145	12.12	2429	8.42	1687	1.73	398	>100	0.4	0.3	<1.5	0.2

Table 4-2. Selected Values and Weighted Means of Trace Elements in Soil Samples from Gibbons Creek Mine. (Texas Railroad Commission, 1981a)

	Concentration, mg/kg (Depth, feet)						
	As	B*	Be**	Cd	Cr	Cu	Hg**
High (Depth)	8.9 (10-18)	13.1 (102-108)	3.1 (77.0-80.8)	1.9 (51.0-67.6)	13.4 (58.7-61.6)	19.6 (71-91)	<0.2
Second High (Depth)	5.3 (30.5-31.4)	7.5 (169.0-170.0)	1.5 (29.4-37.4)	1.3 (50-58.6)	8.4 (30.5-31.4)	16.1 (139-141)	<0.2
Second Low (Depth)	0.2 (15.0-19.9)	0.0 (58.9-60.0)	.4 (92-95)	<1.0	1.0 (92-95) (60-64)	2.2 (56-61)	<0.2
Low (Depth)	0.1 (110-115)	0.0 (36.4-50.0)	.4 (53-58)	<1.0 Common	1.0 (110-115)	1.9 (58.9-60)	<0.2
Weighted Mean	2.07	1.01	.96	<0.87[†]	4.95	6.11	<0.2

	Concentration, mg/kg (Depth, feet)						
	Mn*	Mo*	Ni**	Pb	Se	V**	Zn
High (Depth)	367.7 (102-108)	8.3 (10.0-18.0)	5.2 (37.4-54.2)	68.4 (10.0-18.0)	<2.0	25.0 (10.0-18.0)	190.6 (71.1-91.0)
Second High (Depth)	307.9 (10.0-12.9)	5.7 (129.8-132.8)	5.2 (18.0-28.5) (25.4-28.8)	34.7 (102-108)		24.3 (77.0-80.8)	178.0 (30.5-31.4)
Second Low (Depth)	17.2 (36.4-50)	<2.0	2.1 (29.4-37.4)	5.0 (110-115)		4.3 (29.4-37.4)	22.1 (10.0-12.9)
Low (Depth)	14.1 (58.9-60.0)	<2.0 Common	2.0 (92.0-95.0)	4.0 (60.0-64.0)	<1.5	4.1 (92.0-95.0)	20.7 (9-12.5)
Weighted Mean	128	<2.23[x]	3.65	17.6	<2.0[xx]	10.45	49.40

*Sampled in 8 of 9 cores.

**Sampled in 3 of 9 cores only.

[†] Concentrations reported as <1.0 mg/kg were summed as 1.0 mg/kg.

[xx] By weighted thickness, 75 percent of concentrations are recorded as <2.0 mg/kg.

[x] Only values of <1.5 and <2.0 were recorded.

by depth of each tested layer) for each element. Arsenic, for example, was noted to have a weighted mean of 2 mg/kg while selenium was below detectable levels. In general, the mean concentration values of each element are lower than levels which might be considered as toxic to animal or plant life.

4.2.1.2 San Migual (Texas Railroad Commission, 1981b; Brown and Deuel, 1979)

The mine-mouth operation at the San Miguel Power Plant in Atascosa County, Texas, has a generation capacity of 400 MW which is also estimated to require a consumption of 2.7×10^6 short tons of lignite per year.

The topsoil in the mining site is characterized by a texture which includes a silty clay loam, a clay loam and a clay. Depth of the topsoil layers extend from three to six feet. Most is calcareous with pH values greater than 7, and all contain salt and show conductivity values of 1 to 7.4 mmhos/cm.

With respect to the overburden, the results obtained from analysis of three core samples are presented in Table 4-3. The composite texture classification is clay, but it is comprised of approximately 30 percent each for sand and silt and 40 percent clay. Two of the cores showed near neutral pH values with base potentials of 0.23 and 1.04 meq/100 g. One core was distinctly acid, with a composite pH of 3.8 and an acid potential of 5.88 meq/100 g.

Electrical conductivities of the overburden, ~6 mmhos/cm, suggest that the overburden is on the average about as saline as the surface soils. The exchangeable sodium percentage (ESP) varies from 12 to 24 and the sodium adsorption ratio ranges from 10 to 23. The saturation

ration percentages which have an overall value >100 percent, reflect the influence of the excess sodium in the overburden.

TABLE 4-3. Properties of Overburden from San Miguel Mine. (Brown and Deuel, 1979)

Core	Texture				pH		Potential		Salinity		Exchangeable Sodium Percentage (ESP)	Sodium Adsorption Ratio (SAR)
	Sand %	Silt %	Clay %	USDA	paste	1:5	Acid Equiv. mg/Kg	Base $CaCO_3$ mg/Kg	mmhos/cm	mg/Kg		
B296	24.3	31.2	44.5	clay	7.4	7.4		115	7.7	4928	18.9	16.9
MK26	29.2	29.6	41.2	clay	3.8	4.7	2940		5.8	3712	11.8	10.3
MK45	28.9	29.8	41.3	clay	7.3	7.9		520	5.7	3648	24.3	22.7
Overall				clay	near neutral			X	~6	~4000		

Core	Saturation Percentage	Selenium mg/Kg	Boron mg/Kg	Nitrogen mg/Kg	Phosphorus mg/Kg	Potassium mg/Kg	Organic Matter %
B296	131.0	<0.5	2.9	0.03	8.3	2917	0.3
MK26	69.1	<0.5	4.2	0.02	2.8	2083	0.2
MK45	189.8	<0.5	4.5	0.05	9.8	2083	0.5
Overall	>100	<0.5	>3.0	<0.05	<9.8	<2900	<0.5

The nutrient level is low in phosphorous and nitrogen, while potassium is in all cases greater than 2000 mg/kg. The trace metals which were reported, selenium and boron, show overall values of <0.5 and >3.0 mg/kg, respectively. Except for layers near the lignite seams, the amount of organic matter is small, <0.5 percent.

4.2.2 Campbell County, Wyoming

The topsoils in Campbell County are mostly residual, formed from weathered sediments of a parent material which was primarily sandstone and shale (Everett, 1979). The predominant types include sandy loam and loam soils, fine soils from clay shale, coarse soils from sandstone, scoria formed from natural combustion of the thick coal beds, and alluvium (confined to narrow strips along main drainage streams). It should be noted that the scoria, while it appears in the topsoils especially near coal outcrops, also appears in the overburden where it dips to contact the coal seams.

With respect to the overburden, drilling logs of the Shell Oil Buckskin Mine (Scarborough, 1982) indicate a predominance of siltstone and sandstone but with considerable quantities of shale and clay. Much of it is calcareous (usually as calcium carbonate), and pyrite occurs in some strata. Although the texture of the overburden is highly variable, ranging from sand to clay, a composite would be weighted towards the fine-particle end of the scale. In general terms, the overburden is alkaline with a pH range from 6.5 to 8.0 that would be averaged towards the higher end of the range.

Selected test data from analyses performed on one of the cores, Table 4-4, indicate a variability of textures, with the clay fraction ranging from 10-69 percent. The weighted mean pH of these sample intervals is slightly basic, 7.4. Exchangeable sodium percentage values are in the range of 0.44 to 2.34 and the saturation values are on the order of 50 percent. Analyses for selenium generally showed concentrations less than the analytically detectable levels, 0.02 mg/kg, while the average for boron was on the order of 0.2 mg/kg.

Table 4-4. Soil Characteristics of a Sample Core from the Buckskin Mine, Campbell County, Wyoming (Drill Hole Number 28). (Scarborough, 1982)

Sample Interval, feet	Texture % Sand	 % Silt	 % Clay	Class	pH	Conductivity mmhos/cm	Exchangeable Sodium Percentage (ESP)
2-5	71.6	10.9	17.5	sandy-loam	7.0	0.36	0.44
12-14	31.6	49.5	13.9	loam	8.0	1.15	2.34
14-30	19.8	54.7	25.5	silty clay-loam	7.9	0.89	1.28
30-40	24.6	54.7	20.7	silty-loam	7.7	1.41	1.00
40-45	31.8	52.0	16.2	silty-loam	7.7	1.23	1.12
56-60	33.5	44.9	21.6	loam	7.5	1.60	1.17
60-72	71.6	18.6	9.8	sandy-loam	7.7	2.69	1.55
80-101	4.0	26.9	69.1	clay	6.6	3.20	0.74

Sample Interval, Feet	Sodium Adsorption Ratio (SAR)	Saturation Percentage	Selenium mg/kg	Boron mg/kg	Available Phosphorus mg/kg	Available Potassium mg/kg
2-5	0.53	26.4	<0.02	0.17	<0.05	475
12-14	2.44	42.3	<0.02	0.17	<0.05	485
14-30	1.09	50.5	<0.02	0.11	<0.05	555
30-40	1.02	47.7	<0.02	0.20	<0.05	485
40-45	1.03	45.0	<0.02	0.03	<0.05	430
56-60	1.10	49.2	<0.02	0.34	<0.05	475
60-72	1.01	35.1	0.02	0.14	<0.05	475
80-101	0.64	76.8	<0.02	0.28	<0.05	585

Keefer and Hadley (1976) gave a summary of trace elements associated with the near-surface soils, and the overburden rock in the Powder River Basin. An excerpt of their data, Table 4-5, shows information on the eight elemental contaminants for which water quality standards have been set plus uranium. Other than arsenic, the concentrations in the overburden of all indicated elements are within an order of magnitude of the average crustal levels.

TABLE 4-5 Concentrations of Trace Elements in Near-Surface Soils and Rocks, and Overburden Rocks in Powder River Basin. (Keefer and Hadley, 1976)

	Near-surface materials			Overburden Rocks	Average concentration in rocks of the earth's continental crust
	Depth, 6 - 8 inches		Depth, 6.6 ft	Depth, 10-166 ft	
Element	Mean	Range	Range	Range	mg/kg
Arsenic	8.2	-	2.6-8.6	30-70	1.8
Barium	760	300-1,500	700	300-1,000	425
Cadmium	-	-	-	<1-2.5	0.2
Chromium	52	20-100	20-30	30-100	100
Lead	18	10-100	15	<25-30	12.5
Mercury	0.025	0.01-0.04	0.02-0.03	0.02-0.15	0.08
Selenium	0.14	-	<0.1	<0.1-0.4	0.05
Silver	-	-	-	-	0.07
Uranium	3.2	2.2-7	2.0-2.2	2.3-6.9	2.7

4.2.3 Green River Basin

The coal deposits are in the lower part of the Adaville formation (Pittsburg and Midway Coal Mining Company, 1982) and the overburden is dominated by sandstone but also consists of interbedded siltstone, claystone, carbonaceous claystone, and some coal. The formation is approximately 2900 feet thick, with individual coal seams as much as 118 feet thick and with combined coal seam thicknesses in places on the order of 250 feet.

The sandstone is predominantly fine-grained with variations from very fine to medium. Portions exhibit unsuitable acid-base potential characteristics, indeed, of the total overburden which has these characteristics, most is attributable to sandstone. The siltstone, which is the least frequently occurring of the four stratigraphic units, grades from sandy to clay. Claystones are variable in texture and range from well-cemented silty and sandy shale to carbonaceous shales. Near the coal stringers or in carbonaceous claystone, this material may exhibit an undesirable acid-base potential, a high boron level (5 to 7 mg/kg) and a sodium adsorption ratio exceeding ten. However, these layers are relatively thin and, when the overburden is mixed during the mining process, the potential influence of the adverse characteristics will be diluted.

In general, although most properties are variable, the texture of the overburden can be approximated as silty. The pH values are usually in the neutral to slightly alkaline range with low pH's usually associated with the coal stringers, carbonaceous claystones and sandstone. Electrical conductivity, EC, is generally below 8.0 mmhos/cm which may indicate an acceptable concentration of total dissolved solids in overburden groundwater backfill. Although most acid-base potentials are favorable, between 10 and 20 percent of the overburden has values less than or equal to -5.0 tons $CaCO_3$/1000 tons of overburden.

Selected data from one of the 25 test drill holes at the Kemmerer mine (Pittsburg and Midway Coal Mining Company, 1982), are shown in

Table 4-6. The soil texture consists of approximately ½ sand and ¼ of each silt and clay. The pH is near neutral, and the average acid-base potential is on the order of an equivalent of 20 tons $CaCO_3$/1000 tons. Electrical conductivities averaged approximately 3 mmhos/cm and the sodium adsorption ratios ranged from 0.1 to 0.6. The two trace elements which were reported, selenium and boron, exhibited levels of approximately 0.06 and 0.6 mg/kg, respectively.

4.3 SUMMARY OF DISPOSAL MEDIA PROPERTIES

In comparing the overburden characteristics of the four sites, Table 4-7, it may be noted that the textures encompass the categories of clay, clay-loam, and silt. The pH values of samples from the Texas mines are somewhat variable with the Gibbons Creek soils being acidic and those of San Miguel being acidic to slightly basic. On the other hand, the overburdens from the Wyoming mines are, on the average, slightly basic. Electrical conductivities and sodium adsorption ratios for the Texas soils appear to have higher values (although SAR values were not reported for the Gibbons Creek mine). Also, the saturation percentage is higher for the San Miguel mine soils than for the Wyoming overburdens, >100 percent as compared with approximately 50 percent. With respect to trace elements, the San Miguel mine shows concentrations of boron which average >3 mg/kg whereas the western mines have values <1 mg/kg. Average concentrations of selenium at all locations were near or below the analytical detection limits.

Table 4-6. Characteristics of Selected Underburden Depths of Kemmerer Mine. (Pittsburg and Midway Coal Company, 1982)

Sampling Interval, feet	Texture			Class	pH paste	Acid-Base Potential ± tons CaCo₃ equiv/1000 tons	Electrical Conductivity mmhos/cm
	% Sand	% Silt	% Clay				
10-16	38	31	31	clay-loam	4.2	-17.9	1.4
29.9-39.5	70	12	18	sandy loam	4.2	+43.8	3.1
55.5-58.3	16	29	55	clay	7.2	+22.2	1.4
73.8-87.5	67	16	17	sandy loam	6.6	+11.9	2.3
102.6-113.0	41	31	25	loam	7.0	+17.2	4.4
118.4-125.3	14	31	55	clay	7.2	-7.2	3.1
163.4-180.9	66	16	18	sandy loam	7.1	+19.4	3.9
228.9-247.7	14	42	44	silty clay	7.2	+16.9	3.0
371.5-373.3	66	13	21	sandy clay loam	7.4	+164.7	2.0
373.3-379.4	23	33	44	clay	6.7	-3.1	2.0

Sampling Interval, feet	Sodium Adsorption Ratio (SAR)	Saturation Percentage	Selenium mg/kg	Boron mg/kg	Description
10-16	0.6	36.6	0.02	0.80	sandstone
29.9-39.5	0.3	32.2	0.02	0.34	gray sandstone with coal stringers
55.5-58.3	0.3	60.2	0.13	1.33	dark gray soft shale
73.8-87.5	0.2	31.4	0.03	0.77	gray moderately cemented sandstone underlain by dark gray sandstone with coal stringers and pyrite clasts
102.6-113.0	0.1	36.1	0.20	0.90	gray fine-grained sandstone underlain by gray medium-grained sandstone
118.4-125.3	0.2	53.3	0.03	0.93	dark gray hard shale with sand lenses
163.4-180.9	0.2	32.8	0.02	0.57	gray salt and pepper sand with some carbonaceous laminations and pyritic clasts underlain by gray hard silty shale with fossilized shells
228.9-249.7	0.2	40.7	0.07	0.62	very hard sandy fossiliferous shale with coalified plant matter. grades to non-fossiliferous
371.5-373.3	0.2	22.1	0.05	0.29	fine-grained, very well cemented sand stone
373.3-379.4	0.2	44.1	0.14	1.01	gray hard sandy shale

TABLE 4-7 Comparison of Overburden Characteristics for Four Selected Sites

Mine	Texture Classification	pH	Electrical Conductivity	Sodium Adsorption Ratio	Saturation Percentage	Boron mg/kg	Selenium mg/kg
Gibbons Creek	clay to clay loam	acidic	0.5-10.0	-	-	1.0	<2.0
San Miguel	clay	two cores slightly basic and one core strongly acidic -overall is near neutral	~6	16	>100	>3.0	<0.5
Buckskin	clay (near clay loam)	slightly basic	1.0-2.0	1.0	~50	~0.20	<0.20
Kemmerer	silt	slightly basic	1.4-4.4	0.3	~40	<1.0	0.03~0.05

SECTION 5

SUMMARY

Because lignite and subbituminous coal will, in the near future, play a crucial role in meeting the energy demands of industry and the utilities, the hazards of disposing solid wastes from the mines must be recognized and minimized. The principal solid wastes generated by low-rank coal-fired power plants are in the form of fly ash, bottom ash, and sludge materials associated with flue gas desulfurization. As Lacy et al. (1979) point out, a typical 1500 MW plant fired with Texas lignite will likely generate between 300,000 and 500,000 dry tons of FGD sludge per year, and two to three times as much fly ash. At present, these waste materials are disposed of in mining area burial pits.

Understanding the general properties of ash and ash-sludge leachates is essential to pinpointing the potential hazards of the disposal wastes. Coal ash contain a number of oxide elements including those of aluminum, iron, calcium, magnesium, potassium and sulfur, in addition to a variety of trace elements. Sludges arising from the flue gas desulfurization process also contain a large number of trace metals, as well as significant quantities of calcium sulfate and limestone. Lignite and coal ashes show substantial cation and sulfate solubility in water. The leaching of hazardous elements from the ash is generally quite dependent upon pH, typically with significant reductions in elemental concentrations with increasing pH, (although arsenic has been shown to have an anomalous behavior in the range of pH=12). FGD sludge and leachates from the sludge contain concentrations of B, Hg and Se above drinking water standards by a factor of 10x or more (Hart and Delaney, 1978). Brown et al. (1976) found trace element concentrations in fly ash percolate to exceed European drinking water standards.

As these various trace elements and compounds percolate through the soils beneath buried wastes, physical and chemical processes occur which may retain certain elements while perhaps releasing from the soils other naturally present materials. Variability of soil systems and of leaching materials affects uptake and attenuation properties and because of the diverse nature of the soils and leachate there is controversy as to the dominant uptake mechanisms. Fuller and Korte (1976) and Fuller (1977, 1978) note that the several general parameters affect attenuation: soil pore and particle sizes, solution flux through the soil, colloid fraction and type, and the presence of oxides and hydroxides of aluminum, iron and manganese. The mechanisms of attenuation, suggested by Fuller and Korte (1976), Jenne (1968), Lindsay (1972) and Griffin and Shimp (1978) include: ion exchange (specifically those ions held in the counter ion atmosphere of the electric double layer), complexing with organic matter, adsorption by mineral species, and precipitation.

Several column studies have been undertaken to investigate the soils uptake of contaminants in municipal waste leachates. Griffin and Shimp (1978) concluded that precipitation in the column layer was the dominant mechanism for Pb, Cd, Hg and Zn. Fuller (1977) noted ion exchange cannot bind metal ions indefinitely and that some migration from the exchange site will eventually occur. In a column study on the uptake of leachates associated with coal-fired plants in southeastern United States, Milligan and Ruane (1980) noted that ion exchange could not be a major attenuation mechanism because the theoretical ion exchange capacity was greatly exceeded.

With respect to the soils in the primary regions of interest, Texas and Wyoming, data have been summarized for four sites: the Gibbons Creek mine in Grimes County, Texas; the San Miguel mine in Atascosa County, Texas; the Buckskin mine in Campbell County, Wyoming; and the Kemmerer mine in the Green River Basin of Wyoming. The pH ranges from acidic to near-neutral for the Texas mines whereas the values are slightly basic for the two Wyoming areas. Electrical conductivities and sodium adsorption ratios are higher for the Texas overburdens. The levels of boron in the San Miguel soil was >3 ppm whereas the western mines have values <1 ppm. Concentrations of selenium at all sites were near or less than the detection limits of analytical instrumentation.

SECTION 6

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Appendix A

ANNOTATED BIBLIOGRAPHY

This annotated bibliography has been prepared to provide a ready list of references for further study of the information contained in the report. A number of texts are included for their comprehensive treatment of subjects pertinent to the report material. The annotation for these texts necessarily falls short of an abstract of the whole work and further is generally restricted to consideration of those topics germane to the text of the report. Certain older papers have been listed without annotation. The influence of most of these works can be appreciated by noting the frequency with which they are cited in the historic and current literature. They have been included because of their historical importance, however the concepts which they present have so fully become a part of the modern science that the same information may be obtained from the texts cited or from some of the more recent work.

Where appropriate, abstracts of papers have been quoted directly from either the author or journal summaries; however, in some cases these abstracts did not present the content of the papers in a manner which suggested their association to this report. In those cases an abstract has been prepared which closely indicates the value of the paper to readers of this report. With due consideration to the previously mentioned exceptions, articles which are not followed by an abstract are more peripheral in nature with respect to their bearing upon the report material.

Abernathy, R.F. and F.H. Gibson, 1963. "Rare Elements in Coal," U.S. Dept. of Interior, Bureau of Mines, Info. Circ. 8163.

Adams, L.M., J.P. Capp and E. Eisentrout, 1971. "Reclamation of Acidic Coal-Mine Spoil with Fly Ash," U.S. Dept. of Interior, Bureau of Mines, RI 7504.

Addition of fly ash from a bituminous coal to mine spoil improved soil texture, raised the pH, and increased the availability of water. Effect on growth of several grasses and other plants was studied.

Adams, L.M., J.P. Capp and D.W. Gillmore, 1972. "Coal Mine Spoil and Refuse Bank Reclamation with Powerplant Fly Ash," Proceedings of the Third Mineral Waste Utilization Symposium, jointly sponsored by the U.S. Bureau of Mines and IIT Research Institute, March 14-16, Chicago, Illinois.

Fly ash from power plants fired with bituminous coal was used in experimental reclamation of coal mine refuse piles and strip spoil banks. The ash served as a neutralizing agent, diluent, and soil amendment providing some essential plant nutrients as indicated by plant response.

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," J. Envir. Q. 9(3):333-344.

This paper summarized impacts of land-oriented utilization and disposal of various coal combustion residues. Coal residues supplemented soils with Ca, S, B, Mo, and Se but did not provide useful amounts of N, P, and K. Fly ash neutralized acid soil. Many observed chemical and biological effects resulting from fly ash applications to soils resulted from increased activities of Ca^{2+} and OH^- ions.

Allaway, W.H., 1968. "Agronomic Controls Over the Environmental Cycling of Trace Elements," Advances in Agronomy, Vol. 20, pp. 235-274.

This chapter reviews soil selection and management, trace element fertilization, and crop selection and management in relation to plant growth. Current environmental problems involving specific trace elements are reviewed.

Amos, D.R. and J.D. Wright, 1972. "The Effect of Fly Ash on Soil Physical Characteristics," Proceedings of the Third Mineral Waste Utilization Symposium, jointly sponsored by U.S. Bureau of Mines and IIT Research Institute, March 14-16, 1972, Chicago, Illinois.

Mixtures of soil and fly ash showed improved overall engineering properties (i.e. compaction, Atterburg limits) over those shown by each component individually.

Aomine, S., H. Kawasaki and K. Inoue, 1967. "Retention of Mercury by Soils: I. Mercury Residues of Paddy and Orchard Soils," Soil Science and Plant Nutrition 13(6):186-188.

Retention of mercury by soils was investigated in field samples. Among parameters noted were soil gradation and clay mineral type. The mercury source derived from a history of mercurial fungicide use.

Aomine, S. and K. Inoue, 1967. "Retention of Mercury by Soils: II. Adsorption of Phenylmercuric Acetate by Soil Colloids," Soil Science and Plant Nutrition 13(6):195-200.

Mineral colloids were found to be the primary adsorption agent for phenylmercuric acetate although some was also adsorbed by organic colloids. Montmorillonite was more effective at adsorption than kaolinite and this was attributed to particle surface properties.

Appelt, H., K. Holtzclaw, P.F. Pratt, 1975. "Effect of Anion Exclusion on the Movement of Chloride through Soils," Soil Sci. Soc. Amer. Proc. 39(2):264-267.

Studies of the effects of anion exclusion on the movement of chloride (Cl^-) through soils suggest that the nature of the clay mineral, clay content, saturation percentage and iron oxide content together with the cation exchange capacity are important soil characteristics related to the volume of exclusion.

Bailey, E.H., 1945. "Hydrogen-Ion Concentration of the Important Soils of the United States in Relation to Other Profile Characteristics: II. Pedalfers and Soils Transitional Between Pedocals and Pedalfers," Soil Sci. 59(3):239-262.

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A method for obtaining undisturbed soil samples and an installation for performing leachate studies are described.

Barber, R.G. and D.L. Rowell, 1972. "Charge Distribution and the Cation Exchange Capacity of an Iron-Rich Kaolinitic Soil," J. Soil Sci. 23:135-146.

The positive charge on an iron-rich kaolinitic soil was found to increase from 11.1 to 14.2 me per 100 g as a result of lowering the pH from 8.5 to 3.6 in M NH_4Cl solution and the negative charge decreased from 22.2 to 14.4. In 0.002M NH_4Cl the positive charge increased from 0 to 0.3 and the negative charge decreased from 5.6 to 3.2. The variations in charge can be explained by the presence of 3 me per 100 g of permanent negative charge, pH dependent positive and negative charge influenced by the indifferent electrolyte concentration, and the overlap of diffuse layers causing a neutralization of charge.

The ability of this soil to hold cations under field conditions is overestimated by M ammonium acetate at pH 7. Instead, a solution approximating to the pH, composition, and concentration of the soil solution should be used.

Barrows, H.L., M.S. Neff and N. Gammon, Jr., 1960. "Effect of Soil Type on Mobility of Zinc in the Soil and on Its Availability from Zinc Sulfate to Tung." Soil Sci. Soc. Amer. Proc. 24(5):367-372.

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> Studies were conducted on the retention of Cu and Zn by H-Montmorillonite in relation to associated anion, salt concentration reaction time, and pH of the equilibrium solution. Retention was found to be by cation exchange and precipitation. As pH approached ~5, sharp increases in retention were observed. This pH is that associated with formation of precipitates $Zn_2(OH)$ and $Cu(OH)_2$.

Blancher, R.W. and C.E. Marshall, 1981. "Eh and pH Measurement in Menfro and Mexico Soils," In: Chemistry in the Soil Environment, edited by R.H. Dowdy, J.A. Ryan, V.V. Volk and D.E. Baker, Amer. Soc. of Agronomy and Soil Sci. Soc. Amer., ASA Special Publication Number 40, Madison, Wisc., pp. 103-128.

Bloom, P.R., 1981. "Metal-Organic Matter Interations in Soil," In: Chemistry in the Soil Environment, edited by R.H. Dowdy, J.A. Ryan, V.V. Volk and D.E. Baker, Amer. Soc. of Agronomy and Soil Sci. Soc. Amer., ASA Special Publication Number 40, Madison, Wisc., pp. 129-150.

Bohn, H.L., 1976. "Arsenic Eh-pH Diagram and Comparisons to the Soil Chemistry of Phosphorus," Soil Sci. 121(2):125-127.

> Some of the similarities and differences in soil and biological reactions exhibited by phosphorous and arsenic are discussed in terms of redox relations.

Bolt, G.H. and M.J. Frissel, 1960. "The Preparation of Clay Suspensions with Specified Ionic Composition by Means of Exchange Resins," Soil Sci. Soc. Amer. Proc. 24(3):172-177.

> Exchange reactions involving cation-exchange resins and clay suspensions suggest that exchange in one direction is resin dependent while the reverse exchange is strongly dependent upon electrolyte concentration and is insensitive to resin exhaustion.

Boström, K., 1967. "Some pH-Controlling Redox Reactions in Natural Waters," In: Equilibrium Concepts in Natural Water Systems, Advances in Chemistry Series 67, edited by R.F. Gould, Amer. Chem. Soc., Wash., D.C., pp. 286-311.

Bourgeois, W.W. and L.M. Lavkulich, 1972. "A study of Forest Soils and Leachates on Sloping Topography Using a Tension Lysimeter," Can. J. Soil Sci. 52:375-391.

> Leachate was collected using a tension lysimeter and was analyzed for ion content. These values were compared relative to soil properties. For these finest soils the general order of abudance was Na $\geq$ Ca > K > Mg.

Bower, C.A. and E. Truog, 1940. "Base Exchange Capacity Determination as Influenced by Nature of Cation Employed and Formation of Basic Exchange Salts," Soil Sci. Soc. Amer. Proc. 5:86-89.

> Monovalent cations cannot form basic salts, therefore exchange values are true whereas polyvalent cations used in base exchange studies with bentonite clay gave erroneously high base exchange values. Methods of minimizing and correcting these results are discussed.

Boyd, G.E., J. Schubert and A.W. Adamson, 1947. "The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. I. Ion-exchange Equilibria," J. Amer. Chem. Soc. 69(11):2818-2829.

> It is suggested that equations describing base-exchange reactions may be formulated either on the basis of the adsorption mechanism or according to the law of mass action, and these equations are shown to be formally equivalent. Adsorption affinities were shown to be determined chiefly by the magnitude of the charge and the hydrated radius of the ions in solution.

Brown, D.A. and W.A. Albrecht, 1950. "Complementary Ion Effects in Soils as Measured by Cation Exchange between Electrodialyzed Hydrogen Clay and Soils," Soil Sci. Soc. Amer. Proc. 15:133-137.

Brown, J.M. and W.V. Bartholomew, 1963. "Sorption of Gaseous Ammonia by Clay Minerals as Influenced by Sorbed Aqueous Vapor and Exchangeable Cations," Soil Sci. Soc. Amer. Proc. 27(2):160-164.

> Sorption of ammonia by moist and dry clay systems showed that

moisture and ammonia compete for sorption sites on the clay and that the influence of the saturating cations on the clay complex on ammonia sorption may arise in part through differences in the quantity and nature of the sorbed water and in part through other effect(s) of the cations.

Buol, S.W., F.D. Hole and F.J. McCracken, 1980. Soil Genesis and Classification, second edition, Iowa State University Press, Ames, Iowa.

This book is a recent summary of work on pedology including chapters on soil morphology, composition and characterization, soil environment, climatological influences, and detailed discussions of specific soil types.

Busch, R.A., R.R. Backer, L.W. Atkins and C.D. Kealy, 1975. Physical Property Data on Fine Coal Refuse, U.S. Dept. of Interior, Bureau of Mines RI 8062, PB-245 841.

Cameron, K.D. and F.A. Koch, 1980a. "Trace Metals and Anaerobic Digestion of Leachate," J. Water Pollution Control Federation 52(2):282-292.

In this study on anaerobic digestion of municipal landfill leachate, it was found that removal efficiencies were greater than 85% for aluminum, barium, cadmium, mercury, nickel and zinc; 80% for iron; 40 to 70% for chromium, copper, lead, and manganese; 30% for calcium; and less than 10% for magnesium, potassium and sodium. Most of the trace metals were associated with sludge solids.

Cameron, R.D. and F.A. Koch, 1980b. "Toxicity of Landfill Leachates," J. Water Pollution Control Federation 52(4):760-769.

Cartwright, K., R.A. Griffin and R.H. Gilkeson, 1977. "Migration of Landfill Leachate Through Glacial Tills," Ground Water 15(4):294-305.

Sanitary landfill leachate collected by anaerobic techniques was used to investigate the effects of clay and biologic activity on leachate attenuation. Ion exchange capacity, hydraulic conductivity, and the buffering capacity of the earth were identified as important potential pollution parameters.

Cavallaro, J.A., G.A. Gibbon and A.W. Deurbrouck, 1978. A Washability and Analytical Evaluation of Potential Pollution from Trace Elements in Coal, Industrial Environmental Research Laboratory, U.S. EPA, Research Triangle Park, North Carolina, EPA-600/7-78-038, PB-280 759.

Results of a washability study showing the trace element contents of various specific gravity fractions for ten coal samples from four coal producing regions of the U.S. are reported. The concentrations of cadmium, chromium, copper, fluorine, mercury, manganese, nickel, and lead were determined using analytical methods developed in the study. It appears that most of the trace elements of interest are concentrated in the heavier specific gravity fractions which suggests that they are associated with the mineral component.

Chang, A.C., L.J. Lund, A.L. Page and J.E. Warneke, 1977. "Physical Properties of Fly Ash-Amended Soils," J. Environ. Qual. 6(3):267-270.

Amendment of five California soils with coal fly ash altered the water-holding capacity, bulk density, hydraulic conductivity, modulus of rupture on laboratory compacted soils.

Chang, C.Y., M.J. Murtha and G. Burnet, 1979. "Environmental Significance of Power Plant Fly Ash," Proc. of 6th Annual UMR DNR Conference on Energy, University of Missouri at Rolla, Oct. 16-18, 1979, sponsored by the Missouri Dept. of Natural Resources, Jefferson City, pp. 490-501.

This paper discusses the potential environmental impacts of fly ash in regard to fly ash leachate and radioactivity. Discussed also are two processes used to extract metals from fly ash. Recoveries are promising suggesting the possibility of converting ash into useful products while minimizing deleterious effects.

Chapelle, F.H., 1980. "A Proposed Model for Predicting Trace-Metal Composition of Fly-Ash Leachates," Environ. Geol. 3(3):117-122.

A mathematical model is proposed that is designed to predict trace metal composition of leachates produced by coal fly ashes. This model is based on the assumption that the mobilization of trace metals from fly ash is primarily a surface desorption phenomena. The validity of this model is tested using data from published sources. Good correlation is found between predicted trace metal concentrations and measured trace metal concentrations in experimentally produced leachates.

Cherry, D.S. and R.K. Guthrie, 1977. "Toxic Metals in Surface Waters from Coal Ash," Water Resources Bulletin (AWRA) 13(6):1227-1236.

Concentrations of Ti, Mn, Cu, Cr, Zn, As, Se, Co, Cd, and Hg were measured in the water, benthic sediment, plants, invertebrates, and vertebrates of a coal ash basin and its drainage system over a period of two years. All elements were more concentrated in the sediment and biota than in water. Plants had high accumulations of Ti, Mn, As, and Hg; invertebrates showed high accumulations of Co, Hg, Cu, Cr, Cd, and As; while vertebrates greatly biomagnified Se and Zn.

Christensen, P.D., S.J. Toth and F.E. Bear, 1950. "The Status of Soil Manganese as Influenced by Moisture, Organic Matter, and pH," Soil Sci. Soc. Amer. Proc. 15:279-282.

Cleary, R.W. and D.D. Adrian, 1973. "Analytical Solution of the Convective-Dispersive Equation for Cation Adsorption in Soils," Soil Sci. Soc. Amer. Proc. 37(2):197-199.

The integral transform method is used to solve analytically the unsteady-state, one-dimensional convective-dispersive equation describing cation adsorption in soils. Adsorption is described by a linear isotherm. The derivation of the mathematical solution is presented in detail to help those unfamiliar with the integral transform method.

Coal Mine Waste: A Bibliography with Abstracts, 1979. NTIS, Springfield, Va., Search Period: 1964-Jan. 1979.

Coleman, N.T., 1952. "A Thermochemical Approach to the Study of Ion Exchange," Soil Sci. 74(2):115-125.

Calorimetrically measured heats of neutralization were used to calculate ΔH's which in turn correspond closely to those measured for the direct exchange of the cations concerned. The data show that calorimetrically measured heats of ion exchange are of similar magnitude to those calculated from equilibrium constants by means of the Van't Hoff equation.

Coleman, N.T., D. Craig and R.J. Lewis, 1963. "Ion-Exchange Reactions of Cesium," Soil Sci. Soc. Amer. Proc. 27(3):287-289.

Exchange-sorption and displacement of Cs were studied in the presence of both Ca and K salts with a number of clays using column leaching procedures. Cesium sorption was found to be much larger from Ca than from K solutions. All except a very small proportion of the sorbed Cs was displaced on leaching with 1N KCl, but many times as much remained after leaching with equal volumes of 1N $CaCl_2$. It appeared that significant amounts of Cs can be "fixed" against displacement with Ca but at the same time remain exchangeable to K.

Coleman, N.T., R.J. Lewis and D. Craig, 1963. "Sorption of Cesium by Soils and Its Displacement by Salt Solutions," Soil Sci. Soc. Amer. Proc. 27(3):290-294.

Cesium was sorbed by montmorillonite, illite, and kaolinite in quantities corresponding to exchange saturation and was displaced readily on leaching with 1N KCl or $CaCl_2$. Vermiculite and heated (600°C, 12 hr.) K-montmorillonite bound Cs tightly against displacement by $CaCl_2$ and $AlCl_3$, but not by KCl or NH_4Cl. Prolonged

leaching with 1N KCl removed 97.5% of the Cs sorbed by heated K-montmorillonite, while 1N $CaCl_2$ eventually displaced 88%. The exchange-displacement behavior of Cs on vermiculite and heated K-montmorillonite suggests that its sorption in interlayer spaces leads to interplanar distances which admit K and NH_4 ions but greatly restrict the entry of Ca.

Cooper, H.B., 1975. "The Ultimate Disposal of Ash and Other Solids from Electric Power Generation," In: Water Management by the Electric Power Industry, edited by E.F. Gloyna, H.H. Woodson and H.R. Drew, Water Resources Symposium Number Eight, Publ. by Center for Research in Water Resources, The University of Texas at Austin, Austin, Tx., pp. 185-195.

This paper reviews and discusses some of the problems associated with disposal of combustion products.

Copenhaver, E.D. and B.K. Wilkinson, 1979. Movement of Hazardous Substances in Soil: A Bibliography, Volume I: Selected Metals, Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio, EPA-600/9-79-024a, PB80-113103.

A bibliography which contains abstracts on articles for 1970 to 1974 covering transport, transformation, and soil retention of arsenic, asbestos, beryllium, cadmium, chromium, copper, cyanide, lead, mercury, selenium, zinc, halogenated hydrocarbons, and other hazardous substances.

Day, A.D., T.C. Tucker and J.L. Thames, 1979. Reclamation and Water Relations of Strip Mine Spoils in Northern Arizona, 1976-1978, Industrial Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio, EPA-600/7-79-258, PB80-152861.

Doran, J.W. and D.C. Martens, 1972. "Molybdenum Availability as Influenced by Application of Fly Ash to Soil," J. Environ. Quality 1(2):186-189.

In a research effort combining laboratory and greenhouse procedures, applications of fly ash to soils increased soil pH and available molybdenum. There is a potential for molybdenum to reach toxic proportions.

Dowdy, R.H. and T.B. Hutcheson, Jr., 1963. "Effect of Exchangeable Potassium Level and Drying on Release and Fixation of Potassium by Soils as Related to Clay Mineralogy," Soil Sci. Soc. Amer. Proc. 27(1):31-34.

Study of six soil series suggests illite as the source of K released by drying; whereas moist fixation was associated with vermiculite, and fixation at moisture levels below 4% was attributed to montmorillonite. The moist K equilibrium value for these soils was 0.45 ± 0.10 me exchangeable K per 100 g of soil.

Elbabaly, M.M., 1950. "Mechanism of Zinc Fixation by Colloidal Clays and Related Minerals," Soil Sci. 69(3):167-173.

Zinc adsorption was studied with respect to mineral crystal structure. In minerals with Al in octohedral arrangement, zinc is thought to be fixed in holes not occupied by Al ions. Some of the zinc adsorbed on the surface (complex monovalent form) may enter the inner layer of the electrical double layer, where it cannot be exchanged with neutral organic salts.

Ellis, J., 1980. "A Convenient Parameter for Tracing Leachate from Sanitary Landfill," Water Res. 14(89):1283-1287.

El-Nahal, A.M. and L.D. Whittig, 1973. "Cation Exchange Behavior of a Zeolitic Sodic Soil," Soil Sci. Soc. Amer. Proc. 37(6):956-958.

The abnormal cation exchange behavior of a strongly saline-sodic soil was attributed to the presence of the zeolite analcime. The use of Li, Mg, or Ba for the displacement of Na gave a fair measure for the exchange properties of the nonzeolitic portion of the soil. Extraction with NH_4 or K gave abnormally high exchange capacity due to the release of Na from the analcime.

Elseewi, A.A., A.L. Page and S.R. Grimm, 1980. "Chemical Characterization of Fly Ash Aqueous Systems," J. Environ. Quality 9(3):424-428.

Measurements of the solubility of Ca, Mg, Na, K, OH, CO_3, HCO_3, Cl, SO_4, and B were made on fly ash from a western coal fired power plant. The high pH and salinity were attributed to dissolution of Ca^{2+} and OH^- ions. It was concluded that the aqueous fly ash system does not represent a true equilibrium state.

Emerson, W.W. and M.G. Dettmann, 1960. "The Effect of pH on the Wet Strength of Soil Crumbs," J. Soil Sci. 11(1):149-158.

The clay-clay attractive forces were greater in crumbs from acid soils than crumbs from soils which are similar but contain free $CaCO_3$. Two causes suggested for this are: (a) positive charges on the edge faces of the clay crystals; (b) exchangeable trivalent cations on the clay. Liming an acid soil decreases the attractive forces between clay particles within soil crumbs, however any free $CaCO_3$ in the soil may result in a sufficiently high concentration of electrolyte in the soil solution to reflocculate dispersed clay.

Engineering-Science, 1980. Analysis of Selected Trace Metals in Leachate from Selected Fossil Energy Materials, Final Report, prepared for Dept. of Energy and ASTM, Engineering-Science, McLean, Va.

The results of leachate testing revealed extreme variability in results for the EPA extraction procedure and ASTM's Methods A and B. The results of the three extraction procedures were, in general, not statistically different.

Epler, J.L., F.W. Larimer, T.K. Rao, E.M. Burnett, W.H. Griest, M.R. Guerin, M.P. Maskarinec, D.A. Brown, N.T. Edwards, C.W. Gehrs, R.E. Milleman, B.R. Parkhurst, B.M. Ross-Todd, D.S. Shriner and H.W. Wilson, Jr., 1980. Toxicity of Leachates, Municipal Environment Research Laboratory, U.S. EPA, Cincinnati, Ohio, EPA-600/2-80-157.

The toxicities of several solid waste extracts (including power plant fly ash, bottom ash, and scrubber sludge) were evaluated. The leachates were notably tested in the absence of soil. The power plant waste extracts varied from low to moderate in toxicity rating.

Farquhar, G.J. and F.A. Rovers, 1976. "Leachate Attenuation in Undisturbed and Remoulded Soils," In: Gas and Leachate from Landfills: Formation, Collection, and Treatment, Proceedings of a Research Symposium held at Rutgers University, New Brunswick, New Jersey, March 25-26, 1975, Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio, EPA-600/9-76-004.

This paper discusses the attenuation and dilution of leachate from municipal landfills. Some of the limitations of column studies are mentioned.

Fisher, G.L. and D.F.S. Natusch, 1979. "Size Dependence of the Physical and Chemical Properties of Coal Fly Ash," Chapter 54 in: Analytical Methods for Coal and Coal Products, Volume III, edited by C. Karr, Jr., Academic Press, New York, pp. 489-541.

Most of the soluble fraction of fly ash is derived from the particle surface layer which is rich in trace elements. A discussion is presented on the reasons and supporting data for the suggested particle size dependence of physical and chemical properties of fly ash.

Follett, E.A.C., 1965. "The Retention of Amorphous, Colloidal 'Ferric Hydroxide' by Kaolinites," Soil Sci. 16(2):334-341.

The sorption and distribution of amorphous colloidal 'ferric hydroxide' particles on the surfaces of kaolinite flakes were

studied by electron microscopy. The sorption reaction was crystallographically specific with particles observed only on basal plant surfaces and was unaffected by the presence of excess NH_4^+, Ca^{2+}, or Al^{3+} ions. Cationic surface-active agents prevented the reaction. Differences observed in colloid distribution and density on the introduction of a competing surface indicated that only one surface of a flake was attracting colloid particles and similar experiments with quartz and gibbsite suggested the silica-tetrahedra surface of kaolinites as the probable site of colloid fixation. The distribution of colloid was unaffected by pH variation, saturation with ammonium acetate, prolonged washing, or ultrasonic vibrations. The colloid was removed only by extraction with sodium dithionite.

Freeze, R.A. and J.A. Cherry, 1979. Groundwater. Prentice-Hall Inc., Englewood Cliffs, New Jersey.

This is a groundwater text for engineers with a substantial chapter on chemical properties and principles. Included are discussions of water and electrolytes, organic constituents, and dissolved gases. The law of mass action is covered under the area of chemical equilibrium which also includes discussions on activity coefficients and free energy. The common-ion effect, oxidation-reduction processes and ion exchange and adsorption are considered.

Frink, C.R. and M. Peech, 1963. "Hydrolysis and Exchange Reactions of the Aluminum Ion in Hectorite and Montmorillonite Suspensions," Soil Sci. Soc. Amer. Proc. 27(5):527-530.

The exchangeable aluminum in hectorite and montmorillonite suspensions was found to remain in trivalent form even upon moderate additions of a base, owing to suppression of hydrolysis on the clay surface as compared to the degree of hydrolysis in the equilibrium dialyzate. The formation of nonexchangeable aluminum was not found to be accompanied by any substantial reduction in exchange capacity, and was, therefore, attributed to precipitation of aluminum hydroxide.

Frost, R.R. and R.A. Griffin, 1977. "Effect of pH on Adsorption of Copper, Zinc, and Cadmium from Landfill Leachate by Clay Minerals," J. Environ. Sci. Health A12 (4 and 5), 139-156.

The removal of Cu, Zn, and Cd from a municipal landfill leachate was attributed to an exchange-adsorption reaction which was affected by pH and ionic competition. At pH's above 6, precipitation contributed significantly to removal of Cu, Zn, and Cd.

Fuller, W.H., 1976. "Residual Management by Land Disposal, Proceedings of the Hazardous Waste Research Symposium," Univ. of Arizona, Tuscon, Ariz. EPA-600/9-76-015.

Fuller, W.H. and J.E. Hardcastle, 1967. "Relative Absorption of Strontium and Calcium by Certain Algae," Soil Sci. Soc. Amer. Proc. 31(6):772-774.

The relative uptake of strontium and calcium was compared using seven different species of algae isolated from fresh water and arid land. Uptake always favored calcium over strontium when the two elements were present in nutrient media together. Strontium was absorbed in addition to the calcium requirement. With Scenedesmus sp., however, strontium actually appeared to compete with calcium.

Fuller, W.H., N.E. Korte, E.E. Niebla and B.A. Alesii, 1976. "Contribution of the Soil to the Migration of Certain Common and Trace Elements," Soil Sci. 122(4):223-235.

Fuller, W.H. and W.T. McGeorge, 1950. "Phosphates and Fixation of Added Phosphates," Soil Sci. 70(6):441-460.

Garland, G.A. and D.C. Mosher, 1975. "Leachate Effects of Improper Land Disposal," Waste Age 6(3):42-48.

Gasser, J.K.R. and C. Bloomfield, 1955. "The Mobilization of Phosphate in Waterlogged Soils," J. Soil Sci. 6(2):219-232.

Geering, H.R., E.E. Cary, L.H.P. Jones and W.H. Allaway, 1968. "Solubility and Redox Criteria for the Possible Forms of Selenium in Soils," Soil Sci. Soc. Amer. Proc. 32(1):35-40.

Based upon solubility measurements made in seven soils, it appears that the Se concentration in solution is dominated by a ferric oxide-selenite adsorption complex. The paper considers theoretically the physical-chemical factors (including redox potential, soil pH, and ions with which Se combines) which are involved in establishing the solubility and oxidation state of Se in soils.

Gonzalez, R.B., H. Appelt, E.B. Schalscha and F.T. Bingham, 1974. "Molybdate Adsorption Characteristics of Volcanic-Ash-Derived Soils in Chile," Soil Sci. Soc. Amer. Proc. 38(6):903-906.

The high adsorption of molybdate by volcanic-ash-derived soils in Chile is thought to be due to the presence of allophane and amorphous aluminum, silica and iron compounds. Competitive studies with chloride, sulfate and phosphate suggest a high affinity of molybdate for the adsorption sites.

Griffin, R.A. and R.G. Burau, 1974. "Kinetic and Equilibrium Studies of Boron Desorption from Soil," Soil Sci. Soc. Amer. Proc. 38(6):892-897.

Kinetics of boron desorption showed two separate pseudo first-order plots which were interpreted as desorption from two separate sites. Equilibrium studies, using a two-site analog of the one-site Langmuir equation solved by multiple regression analysis, corroborated the results obtained in the kinetic studies. A third site was also observed and possible mechanisms for all three sites are discussed.

Griffin, R.A., R.M. Schuller, J.J. Suloway, S.A. Russell, W.F. Childers and N.F. Shimp, 1977. "Solubility and Toxicity of Potential Pollutants in Solid Coal Wastes," Symposium on Environmental Aspects of Fuel Conversion Technology, III, Hollywood, Florida, September 1977.

Griffin, R.A. and N.F. Shimp, 1976. "Leachate Migration through Selected Clays," In: Gas and Leachate from Landfills: Formation, Collection, and Treatment, edited by E.J. Genetelli and J. Cirello, Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio, EPA-600/9-76-004.

The results of a column study on landfill leachates are reported indicating that the most important factors affecting trace element migration through the soil are pH of the solution, cation exchange capacity of the soil, and the ionic composition of the solution matrix.

Grim, E.C. and R.D. Hill, 1974. Environmental Protection in the Surface Mining of Coal, National Environmental Research Center Office of Research and Development, U.S. EPA, Cincinnati, Ohio, EPA-670/2-74-093, PB-238 538/AS.

This report provides extensive and detailed descriptions of current strip mining and reclamation techniques.

Grim, R.E., 1968. Clay Mineralogy, second edition, McGraw-Hill, New York.

Gureghian, A.B., D.S. Ward and R.W. Cleary, 1980. "A Finite-Element Model for the Migration of Leachate from a Sanitary Landfill in Long Island, New York. I. Theory," Water Res. B. 16(5):900-906.

Gutenmann, W.H., C.A. Bache, W.D. Youngs and D.J. Lisk, 1976. "Selenium in Fly Ash," Science 19 (March 15):966-967.

Biological accumulation of selenium from fly ash is documented.

Halligan, A.S. and G.K. Pagenkopf, 1980. "Factors Influencing the Release of Boron from Coal Ash Materials," Environ. Sci. Technol. 14(8):995-998.

The release of boron from fly ash is investigated from the aspect of ratio of amount of ash to leachate water. An acid wash was performed to determine the maximum amount of material available for leaching. Other parameters discussed include release of boron with time and pH variation with time.

Harner, D., K. Holland, S. James, J. Lacy and J. Norton, 1978. Environmental Overview of Texas Lignite Development, Industrial Environmental Research Laboratory, U.S. EPA, Research Triangle Park, N.C., EPA-600/7-78-003.

Hart (Fred C.) Associates, Inc., 1979. Impact of RCRA on Coal Gasification Wastes, New York, NY, U.S. DOE Report DOE/EV/10286-1*.

Harter, R.D. and G. Smith, 1981. "Langmuir Equation and Alternate Methods of Studying 'Adsorption' Reactions in Soils," In: Chemistry in the Soil Environment, edited by R.H. Dowdy, J.A. Ryan, V.V. Volk, and D.E. Baker, Amer. Soc. Agronomy and Soil Sci. Soc. Amer., ASA Special Publication Number 40, Madison, Wisc., pp. 167-182.

The application and limitations of the Langmuir adsorption isotherm are discussed. The theory for application to soil systems is presented. The authors assert that the model has been used inappropriately and they present some alternative models.

Hassett, J.J., 1976. "Determination of Lead Sorptive Capacities of Selected Illinois Soils Using Titration Curves," Commun. Soil Sci. and Plant Anal. 7(2):189-195.

The capacity of a soil to sorb or bind Pb^{2+} may be determined by titrating the soil with a $PbCl_2$ solution. The addition of Pb to the soil results in a shift in pH. The sorption capacity corresponds to the point of maximum curvature in the titration curve. Sorption capacities obtained in this manner are highly correlated with plant uptake.

Heald, W.R., M.H. Frere and C.T. deWit, 1964. "Ion Adsorption on Charged Surface," Soil Sci. Soc. Amer. Proc. 28(5):622-627.

Equations describing ion adsorption on a charged surface are based on a model of equilibrium between ion pairs at the surface and a diffuse Gouy layer. Selectivity for adsorbed ions is related to the charge density, the constants for ion-pair formation, and the total concentration of ions in the bulk solution. High charge

density material is a special case which results in simplified equations. These simplified equations were confirmed with Dowex-50 resin.

Hem, J.D., 1967. "Aluminum Species in Water," In: Trace Organics in Water, Advances in Chemistry Series 73, edited by R.F. Gould, Amer. Chem. Soc., Wash., D.C., pp. 98-114.

Experimental work on solubility of aluminum species in water is reported. Considered here are the processes by which aluminum combines with hydroxide ions to form complexes and polymers.

Hingston, F.J., A.M. Posner, R.J. Atkinson and J.P. Quirk, 1968. "Specific Adsorption of Anions on Goethite," Int. Congr. Soil Sci., Trans. 9th (Adelaide, Australia) I:669-678.

Hodgson, D.R. and W.N. Townsend, 1973. "The Amelioration and Revegetation of Pulverized Fuel Ash," In: Ecology and Reclamation of Devastated Land, edited by R.J. Hutnik and G. Davis, Gordon and Breach, London, pp. 247-271.

Properly treated pulverized fuel ash can be effectively used in conjunction with vegetation reclamation. The pH tends to be fairly high and must be corrected, but often it is not reasonable to reduce the pH to an ideal level. Mixture with lime causes cementation, mixture with clays is not effective and may reduce permeability if too little clay is added, and mixture with organics prevents cementation.

Hunsaker, V.E. and P.F. Pratt, 1970. "The Formation of Mixed Magnesium-Aluminum Hydroxides in Soil Materials," Soil Sci. Soc. Amer. Proc. 34(5):813-816.

By the use of potentiometric titration curves and X-ray diffraction analysis, the formation of mixed Mg-Al hydroxide in soil materials is detected. The precipitate forms when the suspension, which contains Mg^{2+}, is raised from a pH of 8.2 to 8.5. The materials which support this precipitation by supplying reactive Al are gibbsite, Al sesquioxide, allophane, and exchangeable Al.

Hunsaker, V.E. and P.F. Pratt, 1970. "The Solubility of Mixed Magnesium-Aluminum Hydroxide in Various Aqueous Solutions," Soil Sci. Soc. Amer. Proc. 34(5):823-825.

The solubility of mixed Mg-Al hydroxide is influenced by the pH as well as the composition of the solvent. Neutral and slightly acid NH_4OAc released much more Mg-Al hydroxide than did neutral

NaCl solutions. The effectiveness of the NH_4 salts is primarily a result of their buffer capacity, which tends to maintain the suspension at a slightly acid pH.

Hunt, L.B., 1932. "A Study of the Structure of Electrodeposited Metals," J. Phys. Chem., XXXVI, Part 2, Jul-Dec, pp. 2259-2271.

Iskander, I.K. and J.K. Syers, 1972. "Metal-Complex Formation by Lichen Compounds," J. Soil Sci. 23(3):255-265.

Lichen compounds caused chemical weathering of water suspensions of biotite, granite, and basalt. Cations were released from silicate materials as a result of metal-complex formation rather than from reactions directly involving hydrogen ions. Citric, salicylic, and p-hydroxy-benzoic acids and EDTA usually released considerably greater amounts of cations than did the lichen compounds.

Jackson, M.L., 1963. "Aluminum Bonding in Soils: A Unifying Principle in Soil Science," Soil Sci. Soc. Amer. Proc. 27(1):1-10.

The aluminum ion bonds through oxygen to form a variety of functional groups underlying diverse properties of soils, including cation-exchange capacity, several functional groups of soil acidity, polymeric interlayer precipitates of hydroxy alumina formed by chemical weathering during soil genesis, aluminum-affected root functions, anion retention sites, and bands involved in soil aggregation and disaggregation. Aluminum bonding supplies a unifying principle for the soil system much as hydrogen bonding has served to unify many properties of water and aqueous organic systems including living water.

Jacobs, H.S. and M.M. Mortland, 1959. "Ion Movement in Wyoming Bentonite During Electro-osmosis," Soil Sci. Soc. Amer. Proc. 23(4): 273-276.

Rates of cation removal from Wyoming Bentonite during electro-osmosis were $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$. Rates of K^+ and Na^+ removal were proportional to the amount of these ions remaining in the system. Transference numbers of Na^+ and K^+ were near unity during the early stage of electro-osmosis. The water flowrate per milliequivalent of cation removed was greatest for Ca^{2+}, intermediate for K^+, and least for Na^+.

James, R.O. and T.W. Healy, 1972. "Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface. I. Co(II) Adsorption on SiO_2 and TiO_2 as Model Systems," J. Coll. and Interface Sci. 40(1):42-52.

Isotherms of adsorption density versus pH and concentration for Co(II), Fe(III), Cr(III), and Ca(II) adsorption on SiO_2 and for Co(II) adsorption on TiO_2 have been determined. For Co(II) adsorption on SiO_2 the zero point of charge pH is 2.0, while on TiO_2 it is 5.6. The primary hydration sphere of free metal ions is apparently not altered in the adsorption process. The qualitative correlation between adsorption and hydrolysis is shown to break down when examined in detail.

James, W.D., C.C. Graham, M.D. Glascock and A.G. Hanna, 1982. "Water Leachable Boron From Coal Ashes," Environ. Sci. and Technol. 16(4): 195-197.

Water leachable boron for a number of fly ashes is determined. There is agreement with proposed thermal fixation models.

Jeffrey, J.W.O., 1960. "Iron and the Eh of Waterlogged Soils with Particular Reference to Paddy," J. Soil Sci. 11(1):140-148.

Jenny, H., 1932. "Studies on the Mechanism of Ionic Exchange in Colloidal Aluminum Silicates," J. Phys. Chem., Vol. XXXVI, Part 2, pp. 2217-2258.

This is an early classical work on ion exchange which presents the current thought on retention mechanisms. Also presented are the two isotherm models (Freundlich and Langmuir) and a mass action model.

John, M.K., 1974. "Waste Water Renovation through Soil Percolation," Water, Air, and Soil Pollution 3:3-10.

Laboratory experiments using soil columns of one acid and two alkaline soils demonstrated the potential for the acid soil to reduce cation concentrations in the effluent while cation concentrations in the alkaline soils were enriched. Cations analyzed included Ca, Mg, K and Na.

John, M.K., 1972. "Lead Availability Related to Soil Properties and Extractable Lead," J. Environ. Quality 1(3):295-298.

In a study which correlated the amount of lead in plants to extractable lead, it was found that lead availability was related to soil pH, extractable aluminum, and total nickel. Organic matter seemed to have no influence on lead availability.

Jones, J.H. and A.V. Lewis, 1960. "Weathering of Fly Ash," Nature 185:404-405.

Available Ca, B, K, Al, Fe, and P declines with the age of the ash with the decline being particularly rapid for Al, Ca, and B. This phenomenon was observed in a well drained soil.

Kanehiro, Y. and G.D. Sherman, 1956. "Effect of Dehydration-Rehydration on Cation Exchange Capacity of Hawaiian Soils," Soil Sci. Soc. Amer. Proc. 20(3):341-344.

In at least some instances, dehydration provides an irreversible reduction in cation exchange capacity. In general the exchange capacity for a soil varies with moisture content.

Kay, R.L., 1967. "The Effect of Water Structure on the Transport Properties of Electrolytes," In: Trace Inorganics in Water, Advances in Chemistry Series 73, edited by R.F. Gould, American Chemical Society, Wash., D.C., pp. 1-17.

Kohls, D.W., 1962. Reconnaissance of Trace Elements in Texas Coal and Lignite, Mineral Resource Circular No. 43, Bureau of Economic Geology, University of Texas, Austin, Tx.

Kubota, J. and W.H. Allaway, 1972. "Geographic Distribution of Trace Elements Problems," In: Micronutrients in Agriculture, edited by J.J. Mortvedt, P.M. Giordano and W.L. Lindsay, Soil Sci. Soc. Amer., Madison, Wisc., pp. 525-554.

Kun-Huang, H. and C. Tsen-tuo, 1959. "Certain Physico-Chemical Properties of the Pinchen Clay and the Function of Its Free Iron Oxide and Organic Matter," Soil Sci. Soc. Amer. Proc. 23(4):270-273.

The specific surface and standard free energy of adsorption of water vapor were both decreased by removal of organic matter. Deferration decreased the "available" water and specific surface. but increased the free energy of adsorption. Binding forces of cations at exchange sites were little affected by presence of organic matter or iron oxide.

Lai, T.M. and M.M. Mortland, 1968. "Cationic Diffusion in Clay Minerals: I. Homogeneous and Heterogeneous Systems," Soil Sci. Amer. Proc. 32(1):56-61.

Diffusion of Na or Cs ion in vermiculite saturated with Na, K, or protonated p-phenylenediamine, and in kaolinite and bentonite saturated with Na or K ion, was measured at various times. Heterogeneous and homogeneous diffusion systems were suggested on the basis of change or lack of change of apparent diffusion coefficients with diffusion time. This was in accord with the structure of clay minerals used and conformed with a mathematical model derived originally for solving the grain boundary problem. The diffusion coefficients of external surface and of interlayer surface of Na ion in Na-vermiculite were evaluated.

Leggett, G.E. and C.D. Moodie, 1963. "The Release of Fixed Ammonium from Soils by Sodium as Affected by Small Amounts of Potassium or Ammonium," Soil Sci. Soc. Amer. Proc. 27(6):645-648.

Data are presented to indicate that small quantities of NH_4 or K, even when present with large amounts of Na, are extremely effective in preventing release of fixed NH_4 from soils. Rate studies conducted under alkaline conditions at room temperature indicate that fixed NH_4 is released slowly by Na. The logarithm of rate of release decreased linearly with time in a similar manner to the release of fixed K as noted by others.

le Roux, F.H., J.G. Cady and N.T. Coleman, 1963. "Mineralogy of Soil Separates and Alkali-Ion Exchange-Sorption," Soil Sci. Soc. Amer. Proc. 27(5):534-538.

Vermiculite and a regularly interstratified biotite-vermiculite (hydrobiotite) were separated from a soil derived from granite-diorite alluvium. Measurement of cation-exchange capacities and amounts of Rb sorbed irreversibly led to the conclusion that such minerals, concentrated in silt and coarse clay, contributed some 40% of the CEC and nearly all of the K or Rb fixing capacity of the soil.

le Roux, F.H. and N.T. Coleman, 1963. "Ion Sorption by Soil Separates and Exchange Equilibria Involving Sodium, Potassium, and Rubidium," Soil Sci. Soc. Amer. Proc. 27(6):619-623.

Alkali ion sorption and exchange studies with soils and size separates containing biotite-hydrobiotite-vermiculite showed specific adsorption of K, Rb, and Cs on part of the exchange capacity, with reversible ion-exchange on the remainder, Na-K exchange constants for nonfixing sites varied with ion saturation and for different soils.

Levy, R. and E. Mor (Muravsky), 1965. "Soluble and Exchangeable Cation Ratios in Some Soils of Israel," J. Soil Sci, 16(2):290-295.

Two approaches were used to test the relationship between the sodium-absorption ratio and the exchangeable sodium ratio. The first approach was to survey the existing relationship for about 250 soil samples, and the second was to compare exchange isotherms obtained by a batch equilibrium procedure. Some insight into the soils exchange behavior was gained by determination of the exchange isotherms.

Libicki, J., 1978. Effects of the Disposal of Coal Waste and Ashes in Open Pits, Industrial Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio, EPA-600/7-78-067, PB-284 013.

The extent of groundwater deterioration due to fly ash leachate is examined through groundwater monitoring at two experimental disposal sites. In addition laboratory tests were conducted to determine the physical-chemical properties of the ash and its leachate. Particular pollutants investigated included TDS, Cl, SO_4, Na, K, Ca, Mg, NH_4, PO_4, CN, phenols, Cd, Sr, Cu, Mo, and B.

Lindsay, W.L., 1979. Chemical Equilibria in Soils, John Wiley and Sons, New York.

A basic test which includes a comprehensive discussion on twenty different element species. The discussion includes redox reactions and standard free energies as they affect solubility relationships.

Lindsay, W.L., 1972. "Zinc in Soils and Plant Nutrition," Advances in Agronomy, Volume 24, edited by N.C. Brady, Academic Press, New York, pp. 147-186.

This chapter is basically a review of the current knowledge concerning zinc as it is found in soils and its availability to plants. The discussion includes the use of zinc in fertilizers to control zinc deficiency in plants. The content of zinc in soils is considered especially in regard to its concentrations and distribution in the soil profile, its mineral occurences and valence states, adsorption phenomena, interactions with organic matter, ion activity - pH relationships, and metal chelation. Availability of zinc to plants is discussed in the light of factors considered to affect availability and the influence of chelation on adsorption by plants. Methods of testing for zinc availability and procedures for correcting zinc deficiency are reviewed.

Lindsay, W.L., M. Peech and J.S. Clark, 1959. "Determination of Aluminum Ion Activity in Soil Extracts," Soil Sci. Soc. Amer. Proc. 23(4):266-269.

A method is presented for calculating the Al^{3+} activity from measurements of the concentration of Al, pH, and the ionic strength of the soil extract. The validity of the method was established by verifying the existence of a theoretical equilibrium relationship between the Al^{3+} and H^+ activities in soil extracts.

Lisk, D.J., 1972. "Trace Metals in Soils, Plants, and Animals," In: Advances in Agronomy, Volume 24, edited by N.C. Brady, Academic Press, New York, pp. 267-325.

A review of the occurences, toxicities and chemistry (physical, inorganic, and organic) of some of the trace elements.

Low, P.F., 1981. "Principles of Ion Diffusion in Clays," In: Chemistry in the Soil Environment, edited by R.H. Dowdy, J.A. Ryan, V.V. Volk, and D.E. Baker, Amer. Soc. of Agronomy and Soil Sci. Soc. Amer., ASA Special Publication Number 40, Madison, Wisc., pp. 31-46.

Mahalingam, P.K., 1973. "Ameliorative Properties of Lignite Fly Ash in Reclaiming Saline and Alkali Soils," Madras Agric. J. 60:1055-1057.

Manz, O.E., 1970. "Ash from Lignite," U.S. Dept. of Interior, Bureau of Mines, Info. Circ. 8488.

This paper provides information on alternative uses of fly ash and contains data on properties for ashes from a number of countries.

Marion, G.M., D.M. Hendricks, G.R. Dutt and W.H. Fuller, 1976. "Aluminum and Silica Solubility in Soils," Soil Sci. 121(2):76-85.

The applicability of equilibrium relationships to the mobility of Al and Si in open systems (soil columns) was examined in nine soils representing six soil orders. Gibbsite, halloysite, kaolinite, and montmorillonite appeared to control the solubility of Al and Si. X-ray diffraction measurements confirmed their presence in the soils. A model for describing soluble Al as a series of $Al(OH)_z^{3-z}$ ($z=0-5$) monomers was evaluated. The monomer model was in agreement with the electrophorectic properties of aqueous Al and the solubility of solid phase Al.

Marshall, C.E., 1977. The Physical Chemistry and Mineralogy of Soils; Volume II: Soils in Place, John Wiley and Sons, New York.

The discussion ranges through pedology, weathering, hydrothermal synthesis of minerals, and influence of climate. Field studies have included lysimeter and index mineral studies. Consideration is given to characterization of the pedological environment and its products and mineralogical analysis. Of most relevance to this report are the chapters dealing with chemical analysis of soils and ionic properties of the exchange complex and the soil solution. The thrust of the book is on soil development and all topics are considered in that light.

Martin, J.P. and S.J. Richards, 1959. "Influence of Exchangeable H and Ca, and of Na, K, and NH_4 at Different H Levels on Certain Physical Properties of Soils," Soil Sci. Soc. Amer. Proc. 23(5):335-338.

Increasing exchangeable K or NH_4 only slightly reduced aggregation of the <50 μm particles of three soils but greatly reduced

water conductivity as determined on laboratory-compacted samples. Increasing exchangeable H increased the dispersing action of Na, K, and NH_4.

Martin, J.P., S.J. Richards and P.F. Pratt, 1964. "Relationship of Exchangeable Na Percentage at Different Soil pH Levels to Hydraulic Conductivity," Soil Sci. Soc. Amer. Proc. 28(5):620-622.

The same quantities of exchangeable Na reduced hydraulic conductivity more in acid than in neutral soil. Hydraulic conductivity was highly correlated (negatively) with Na calculated as a percentage of the ammonium acetate extractable Ca, Mg, K, and Na.

Mattigod, S.V., G. Sposito and A.L. Page, 1981. "Factors Affecting the Solubilities of Trace Metals in Soils," In: Chemistry in the Soil Environment, edited by R.H. Dowdy, J.A. Ryan, V.V. Volk and D.E. Baker, Amer. Soc. Agronomy and Soil Sci. Soc. Amer., ASA Special Publication Number 40, Madison, Wisc., pp. 209-222.

Mattson, S., 1932. "The Laws of Soil Colloidal Behavior: VIII. Forms and Functions of Water," Soil Sci. 33:301-323.

Mattson, S., 1930. "The Laws of Soil Colloidal Behavior: II. Cataphoresis, Flocculation, and Dispersion," Soil Sci. 28(5):373-409.

Mattson, S., 1929. "The Laws of Soil Colloidal Behavior: I.," Soil Sci. 28(3):179-220.

Mattson, S. and L. Wiklander, 1940. "The Laws of Soil Colloidal Behavior: XXI A. The Amphoteric Points, the pH, and the Donnan Equilibrium. Part A. Theoretical," Soil Sci. 49:109-134.

Mattson, S. and L. Wiklander, 1940. "The Laws of Soil Colloidal Behavior: XXI B. The Amphoteric Points, the pH, and the Donnan Equilibrium. Part B. Experimental," Soil Sci. 49:135-153.

McGeorge, W.T., 1945. "The pH of Soil Separates," Soil Sci. 59(5):375-378.

McGeorge, W.T., 1945. "Base Exchange - pH Relationships in Semiarid Soils," Soil Sci. 59(4):271-275.

The interrelationships between base-exchange capacity, adsorbed

sodium, and soil pH are investigated. Sodium saturated soils all exhibited the same pH at 1:10 soil to water ratio regardless of pH used to achieve saturation.

McGeorge, W.T., 1945. "Isohydric pH, pH of Soil Paste, and pH of Exchange Neutrality," Soil Sci. 59(3):231-237.

With proper methodology consistency in soil pH can be achieved. In comparative experiments essential agreement was found between pH on a soil paste with a moisture content near the moisture equivalent, the pH of exchange neutrality of Mattson, and the isohydric pH of Puri and Sarup.

Mehlich, A., 1981. "Charge Properties in Relation to Sorption and Desorption of Selected Cations and Anions," In: Chemistry in the Soil Environment, edited by R.H. Dowdy, J.A. Ryan, V.V. Volk and D.E. Baker, Amer. Soc. Agronomy and Soil Sci. Soc. Amer., ASA Special Publication Number 40, Madison, Wisc., pp. 47-76.

This paper considers different components of the ion exchange capacity (constant negative, variable charge, and total negative cation exchange capacity, and anion exchange capacity and anion adsorption capacity) in relation to different ions and soil minerals. The nature of the charges and properties of the ligands are discussed.

Merwin, H.D. and M. Peech, 1950. "Exchangeability of Soil Potassium in the Sand, Silt, and Clay Fractions as Influenced by the Nature of the Complementary Exchangeable Cation," Soil Sci. Soc. Amer. Proc. 15:125-128.

An attempt to develop a rapid laboratory method for determining the amount of potassium a soil can supply to crops from exchangeable and nonexchangeable potassium is reported. The contribution of supplied potassium from the sand, silt, and clay fractions was also determined.

Metry, A.A. and A.J. Fazzini, 1980. "Microencapsulation Process for Stabilizing Hazardous Industrial Wastes," Plant Engineering, Sept. 4, 1980.

Microencapsulation using coal fly ash as the pozzolan is proposed for the stabilization of other hazardous wastes.

Miller, J.R. and R.F. Reitemeier, 1963. "The Leaching of Radiostrontium and Radiocesium through Soils," Soil Sci. Soc. Amer. Proc. 27(1):141-144.

Experiments were conducted in the greenhouse to determine the downward movement of Cs^{134} and Sr^{89} in five soils under intensive leaching with deionized water, 0.005N NaCl, and 0.005N $CaCl_2$. After leaching with 300 inches of the above liquids, 96.6 to 100% of the Cs^{134} was found in the zone of application. In the leaching experiment with Sr, the $CaCl_2$ produced the greatest movement of Sr^{89} and the deionized water the least. The maximum distance Sr^{89} penetrated into the soils when leached with 30 inches of water was 1.3 inches, and with 300 inches of water the distance was 4.3 inches.

Miller, R.J., J. Schepers, J. Hassett and D.S. Brown, 1973. "The Partial Molal Volumes of Several Ionic Forms of Montmorillonite in Dilute Suspensions," Soil Sci. Soc. Amer. Proc. 37(6):844-846.

A high precision magnetic float densitometer was used to determine the density of dilute suspensions of Na^+, Li^+, K^+, and Al^{3+}-montmorillonite. The method of intercepts was then used to calculate the partial molal volume of the clay. After correction for the cations, the apparent densities of the clays were determined and found to be less than expected; suggesting that the clay-ion associated water is different than normal.

Minnick, L.J., 1967. "Reactions of Hydrated Lime with Pulverized Coal Fly Ash," U.S. Dept. of Interior, Bureau of Mines Information Circular 8348.

Minnick, L.J., 1968. "Reactions of Calcium and Magnesium Compounds with Pulverized Coal Fly Ash," Presented at Annual Meeting of AIME, New York, Feb. 25-28, 1968, American Institute of Mining, Metallurgical, and Petroleum Engineers, NY, 50 pp.

Misra, U.K., R.W. Blanchar and W.J. Upchurch, 1974. "Aluminum Content of Soil Extracts as a Function of pH and Ionic Strength," Soil Sci. Soc. Amer. Proc. 38(6):897-902.

The concentration of aluminum in the soil extract cannot presently be predicted from ion activity product considerations alone. Empirical equations were developed which predict aluminum concentration from estimates of pH and ionic strength of the soil extract. The calculated and determined aluminum values for several soils were compared.

Moran, S.R., G.H. Groenewold, J.A. Cherry, 1978. Geologic, Hydrologic, and Geochemical Concepts and Techniques in Over Burden Characterization for Mined-Land Reclamation, Report of Investigation, ND Geol. Survey no. 63.

Morgan, J.J., 1967. "Applications and Limitations of Chemical Thermodynamics in Natural Water Systems," In: Equilibrium Concepts in Natural Water Systems, Advances in Chemistry Series 67, edited by R.F. Gould, Amer. Chem. Soc., Wash., D.C., pp. 1-29.

Morgan, M.E., R.G. Jenkins and P.L. Walker, Jr., 1981. "Inorganic constituents in American Lignites," Fuel 60(3):189-193.

Both the discrete mineral phases and the ion-exchangeable inorganic constituents of lignites from Texas, Montana, and North Dakota have been studied. The ion-exchangeable cations and the carboxyl groups with which they are associated were characterized by ion exchange methods utilizing ammonium acetate and barium acetate respectively.

Muljadi, D., A.M. Posner and J.P. Quirk, 1966. "The Mechanism of Phosphorous Adsorption by Kaolinite, Gibbsite and Pseudeboehmite. Part I. The Isotherms and the Effect of pH on Adsorption," Soil Sci. 17:212-229.

O'Connor, J.T., M.H. Virshbo, C.J. Cain and C.J. O'Brien, 1973. "The Composition of Leachates from Combustion By-Products," Paper presented at the ASCE National Environmental Engineering Division Conference Symposium on Wastewater Effluent Limits, Univ. of Michigan, Ann Arbor, Mich., July 18-20, 1973.

Olomu, M.O., G.J. Racz and C.M. Cho, 1973. "Effect of Flooding on the Eh, pH, and Concentrations of Fe and Mn in Several Manitoba Soils," Soil Sci. Soc. Amer. Proc. 37(2):220-224.

Measurements of Eh, pH, and concentrations of Fe and Mn in the soil solutions of flooded soils indicated that the concentrations of Fe and Mn increased with reduction. pH changes were found to be relatively small. The experimentally measured concentrations of Fe in the soil solution were much greater than predicted by the observed Eh and pH values. Iron was found to be complexed with organic matter; these complexes were negatively charged and relatively stable. Manganese in soil solution was partly complexed with organic matter in relatively unstable complexes.

Oster, J.D. and P.F. Low, 1963. "Activation Energy for Ion Movement in Thin Water Films on Montmorillonite," Soil Sci. Soc. Amer. Proc. 27(4): 369-373.

Activation energies for the movement of Li^+, Na^+, and K^+ along montmorillonite surfaces were determined by a conductometric method at water contents corresponding to one and two molecular layers. The order of activation energies at each water content depended on the organization of the adsorbed water and on

ion-surface interaction. Relative organization of water on the different clays was obtained by using adsorption isotherm data to calculate relative partial molar entropies. The relative ion-surface interaction on the different clays was estimated from the locations of the ions with respect to the surfaces as determined by X-ray analysis. Activation energy of each ion was greater at the higher water content, indicating that adsorbed water markedly influences ion movement.

Patel, N.C., 1974. "The Release of Metal Ions to Ground Water by Soils," Office of Water Research and Technology, Wash., D.C., PB-269 759.

Using soils with different pH, cation exchange status, and genesis the adsorption of Ca, Ba, and Cr was investigated. Metal equilibrium treatments isolated fractions of exchangeable, chelated and nondisplaceable complexed metals. The resulting soil-metal complexes demonstrated a stability increase with increase in soil organic matter. It is suggested that for soils high in organic content, highly acidic, and with high CEC which are equilibriated with cations of high electronegativity and high valences, the stability constant will be high.

Persse, F.H., 1975. Strip-mining Techniques to Minimize Environmental Damage in the Upper Missouri River Basin States, U.S. Dept. of Interior, Bureau of Mines Information Circular 8685.

Plass, W.T. and J.P. Capp, 1974. "Physical and Chemical Characteristics of Surface Mine Spoil Treated with Fly Ash," J. Soil and Water Conservation 29(3):119-121.

Fly ash amendments to surface mine spoil neutralized acidity, added plant-available phosphorous, lowered spoil density, and increased the subsurface moisture content.

Pollard, B.C., J.B. Smith and C.C. Knox, 1972. Strippable Lignite Reserves of North Dakota: Location, Tonnage, and Characteristics of Lignite and Overburden, U.S. Dept. of Interior, Bureau of Mines Information Circular 8537.

Ponnamperuma, F.N., E.M. Tianco, and T. Loy, 1967. "Redox Equilibria in Flooded Soils: I. The Iron Hydroxide Systems," Soil Sci. 103(6): 374-382.

Ponnamperuma, F.N., 1972. "The Chemistry of Submerged Soils," Advances in Agronomy, Volume 24, edited by N.C. Brady, Academic Press, New York, pp. 29-96.

This is a major review of the chemistry of submerged soils with discussion of such topics as electrochemical changes, chemical transformations, and equilibrium thermodynamics. The major soil characteristics of concern include absence of oxygen, the oxidized mud-water interface, and mass exchanges between mud and soil. Discussions of electrochemical phenomena center around redox potential, pH, and specific conductance. The chemical transformations of a number of elements in soil systems are considered; among those are iron, manganese, carbon, silicon, and some trace elements. The section on mineral equilibria considers redox and carbonate systems.

Reed, G.D., D.T. Mitchell and D.G. Parker, 1976. "Water Quality Effects of Aqueous Fly Ash Disposal," Paper presented at the 31st Annual Purdue Ind. Waste Conf., Purdue Univ., West LaFayette, Ind., May 4-6, 1976, pp. 337-343.

The results of a batch leachate test are reported. Mass transfer coefficients were determined based upon the data for calcium. Initially magnesium went into solution and then transferred back out. An inverse proportionality existed between fly ash concentration and equilibrium concentrations of magnesium, sulfate, and silica. The rate of chemical transfer for the batch tests was rapid.

Reitemeier, R.F., 1946. "Effect of Moisture Content on the Dissolved and Exchangeable Ions of Soils of Arid Regions," Soil Sci. 61:195-214.

For a number of arid region soils, an increase in moisture content of the soil led to an increase in pH and soluble ions. Various clay-loams and sandy-loams from four western states were tested.

Richburg, J.S. and F. Adams, 1970. "Solubility and Hydrolysis of Aluminum in Soil Solutions and Saturated-paste Extracts," Soil Sci. Soc. Amer. Proc. 34(5):728-733.

Three soils that had exhibited different "critical" pH values in field experiments were analyzed for Al solubility. Soil-solution Al at several soil pH levels for each soil was evaluated *in situ* by room growth of cotton seedlings; Al was also determined analytically after displacement from soil columns as 1/3-bar moisture. Other soil samples were equilibrated with KCl and $CaCl_2$ solutions and soil solutions were analyzed for H, Ca, Mg, Mn, K, NH_4, SO_4, and Al. Thermodynamic equations and constants were used to distribute solution Al among the ionic species of Al^{3+}, $AlSO_4^+$, and $AlOH^{2+}$ or $Al_6(OH)_{15}{}^{3+}$. The ion-product of $(Al^{3+})(OH^-)_3$ was much larger and considerably more pH-dependent with $AlOH^{2+}$ as the assumed hydrolytic product of Al^{3+} and H_2O than with $Al_6(OH)_{15}{}^{3+}$ as the product.

Ritter, W.F. and R.P. Eastburn, 1978. "Leaching of Heavy Metals from Sewage Sludge through Coastal Plain Soils," Commun. in Soil Sci. and Plant Analysis 9(9):785-798.

Industrial sludge, anaerobically digested municipal sludge, and anaerobically digested municipal-industrial sludge were applied to soil columns and leached with distilled water. The leachate was analyzed for As, B, Cd, Cl, Cr^{6+}, Cr^{3+}, Cu, Fe, Hg, Ni, Pb, Se and Zn. Under the test conditions it was determined that hazardous amounts of Cd, Cr, Cu and Zn would not be leached to groundwater.

Roethel, F.J., I.W. Duedall, H.B. O'Connors, J.H. Parker and P.M.J. Woodhead, 1980. "Interactions of Stabilized Scrubber Sludge and Fly Ash with the Marine Environment," J. Test Eval. 8(5):250-254.

Roffman, H., 1976. "Disposal of Coal-fired Utility Wastes," Industrial Wastes 22(5):36-39.

An overview of some of the hazards involved in the disposal of utility wastes and suggestions of items for consideration in the selection of a disposal site.

Rogers, R.B. and W.F. Kean, 1980. "Monitoring Ground-Water Contamination at a Fly Ash Disposal Site Using Surface Electrical Resistivity Methods," Ground-Water 18(5):472-478.

Rohrman, F.A., 1971. "Analyzing the Effect of Fly Ash on Water Pollution," Power 115(8):76-77.

Romney, E.M. and J.D. Childress, 1965. "Effects of Beryllium in Plants and Soil," Soil Sci. 100(3):210-217.

The soil effects of beryllium were studied using batch equilibrium tests on clay systems. In kaolinite clays the divalent cations, Ba, Ca, and Mg, competed with ^{7}Be for sorption sites and also replaced adsorbed ^{7}Be. These cations did not compete effectively in bentonite systems. Since Be shows a strong chemical resemblance to Al, it is able to undergo isomorphic substitution in secondary clay minerals along with the cation-exchange reactions.

Ruggiano, L.M. and E.S. Poulson, 1980. "Geotechnical Evaluation of Stabilized FGD Sludge Disposal," paper presented at second conference on Air Quality Management in the Electric Power Industry, Austin, TX, Jan. 24, 1980.

Results of laboratory and field studies suggest that a commercially available process for stabilization of FDG sludges

provides for an environmentally sound program for the disposal of these wastes. The ASTM shake extraction procedure was used to obtain leachate data. The structural characteristics of the disposal product are the focal point of the report.

Shuman, L.M., 1974. "The Effect of Soil Properties on Zinc Adsorption by Soils," Soil Sci. Soc. Amer. Proc. 39(3):454-458.

The Langmuir isotherm was found descriptive of zinc adsorption in testing which involved eight different zinc concentrations equilibriated with four different soils. The isotherm exhibited two linear regions; one associated with low zinc concentrations corresponding to very high bonding coefficients and low adsorptive capacities, and the second which was associated with high zinc concentrations in the equilibriating solution. Cation exchange capacity was related to adsorptive capacity. Colloid content and organic matter both influenced adsorptive capacities and bonding energies.

Sidle, R.C. and L.T. Kardos, 1977. "Adsorption of Copper, Zinc, and Cadmium by a Forest Soil," J. Environ. Qual. 6(3):313-317.

Batch equilibrium studies were performed using spiked solutions. Time dependence was investigated and adsorption data for all three metals was better fit by the Freundlich isotherm than the Langmuir isotherm.

Sidle, R.C., L.T. Kardos and M. Th. van Genuchten, 1977. "Heavy Metals Transport Model in a Sludge-treated Soil," J. Environ. Qual. 6(4):438-443.

A transport model which described cation adsorption in terms of the Freundlich adsorption isotherms severely underpredicted movement of Cu, Zn, and Cd in a forest soil. Inclusion of assumed levels of chelated components enhanced the predictions of the model somewhat suggesting other processes are also involved.

Sieling, D.H., 1946. "Role of Kaolin in Anion Sorption and Exchange," Soil Sci. Soc. Amer. Proc. 11:161-170.

Sillén, L.G., 1967. "Master Variables and Activity Scales," In: Equilibrium Concepts in Natural Water Systems, Advances in Chemistry Series 67, edited by R.F. Gould, Amer. Chem. Soc., Wash., D.C., pp. 45-56.

Sillén, L.G., 1967. "Gibbs Phase Rule and Marine Sediments," In: Equilibrium Concepts in Natural Water Systems, Advances in Chemistry Series 67, edited by R.F. Gould, Amer. Chem. Soc., Wash., D.C., pp. 57-69.

Simonson, C.H. and J.H. Axley, 1963. "High Frequency Titrimetry of Soils and Clays: Methodology, Theory, and Nature of the Ba-Mg Exchange Reaction," Soil Sci. Soc. Amer. Proc. 27(1):26-31.

Apparent dissociation of Ba from exchange sites was determined by comparing titration curves for strongly and weakly dissociated salts. For many soils and clays the curves may be divided into four regions representing loose, moderate, moderately strong, and strong bonding.

Smith, R.L., 1981. The Impact of RCRA (PL 94-580) on the Use or Disposal of Solid Wastes from Texas Lignite-fired Utility Boilers: A Literature Survey, Final Report prepared by Raba-Kistner Consultants, Inc., San Antonio, Texas, for Texas Energy and Natural Resources Advisory Council, Energy Development Act Project #80-L-10-2.

Background information on Texas lignites and their ashes is provided in this survey.

Sommerfeldt, T.G. and H.B. Peterson, 1963. "Effect of Anions on Amount of Sodium Adsorbed by Sodium-Saturated Utah Bentonite," Soil Sci. Soc. Amer. Proc. 27(6):641-644.

The amount of Na adsorbed by Na-saturated bentonite, following equilibration with various Na salt solutions, was affected by the anions and the ionic strength of the equilibrating solution. Different possibilities for these results are discussed. It was concluded that the adsorption capacity of the bentonite varied with the anion environment as well as pH.

Sondreal, E.A., W.R. Kube and V.L. Elder, 1968. Analysis of the Northern Great Plains Province Lignites and Their Ash: A Study of Variability, U.S. Dept. of Interior, Bureau of Mines Report of Investigation (RI) 7158, Wash., D.C., PB-180 073.

Sposito, G., 1981. "Cation Exchange in Soils: An Historical and Theoretical Perspective," In: Chemistry in the Soil Environment, edited by R.H. Dowdy, J.A. Ryan, V.V. Volk and D.E. Baker, Amer. Soc. Agronomy and Soil Sci. Soc. Amer., ASA Special Publication Number 40, Madison, Wisc., pp. 13-30.

Stöber, W., 1967. "Formation of Silicic Acid in Aqueous Suspensions of Different Silica Modification," In: Equilibrium Concepts in Natural Water Systems, Advances in Chemistry Series 67, edited by R.F. Gould, Amer. Chem. Soc., Wash., D.C., pp. 161-182.

Styron, C.R. III and Z.B. Fry, Jr., 1979. Flue Gas Cleaning Sludge Leachate/Liner Compatibility Investigation: Interim Report, Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio, EPA-600/2-79-136.

The ability of various liners to serve as barriers to percolation of leachates from FGD sludges was investigated in laboratory tests.

Swaine, D.J. and R.L. Mitchell, 1960. "Trace-Element Distribution in Soil Profiles," J. Soil Sci. 11(2):347-368.

Some trace elements (Co, Ni, Cu, Mn, Zn and Pb) demonstrated increased mobilization in conditions of restricted drainage.

Theis, T.L., 1975. "The Potential Trace Metal Contamination of Water Resources through the Disposal of Fly Ash," Paper presented at the 2nd National Conference on Complete Water Reuse, Chicago, Illinois, May 4-8.

Tiller, K.G., J.F. Hodgson and M. Peech, 1963. "Specific Sorption of Cobalt by Soil Clays," Soil Sci. 95(6):392-399.

Comparison of the specific sorption of Co^{2+} by soil clays with sorption by pure minerals suggests that care must be exercised when applying data obtained on pure minerals to soil systems. The minerals showed a wide variation in the amounts of Co^{2+} adsorbed whereas the soils did not. Tests to determine the influences of organic matter, the influence of previous saturation of the specific sorption sites by transition metal ions, and the influence of amorphous material on reactions of soil clays with Co^{2+} suggest these influences are not significant.

Tyler, G., 1978. "Leaching Rates of Heavy Metal Ions in Forest Soil," Water, Air, and Soil Pollution 9:137-148.

The leachability of Mn, Zn, Cd, Ni, V, Cu, Cr, and Pb was studied in two purely organic spruce forest soils: one control soil and one similar soil heavily polluted by Cu and Zn from a brass foundry in southern Sweden. Artificial rainwater, acidified to pH 4.2, 3.2, and 2.8 was used in the experiment. The 10% residence times, estimated from the experimental data, varied from 3 yr (Mn) to 70 to 90 yr (Pb) in the control soil and from 2 yr (V) to >200 yr (Pb) in the polluted soil with a precipitation water of pH 4.2. Residence times for most elements studied (except V and Cr) decreased with pH of precipitation water.

Tyree, S.Y. Jr., 1967. "The Nature of Inorganic Solute Species in Water," In: Equilibrium Concepts in Natural Water Systems, Advances in Chemistry Series 67, edited by R.F. Gould, Amer. Chem. Soc., Wash., D.C., pp. 183-195.

In the range of pH exhibited by most natural water and in the concentration range greater than millimolar, few metal ions exist as simple hydrated cations, and relatively few oxyanions exist as simple monomeric species. The hydrated cations are good buffers toward bases, the metallate ions toward acids. As pH is raised in solutions of many hydrated cations, isopolycations are produced, and ultimately, hydrous metal oxides precipitate. As pH is lowered in solutions of many metallate ions, isopolyanions are produced, and ultimately, hydrous oxides precipitate. Salts of the intermediate isopolyions precipitate in some cases. Where the results are unambiguous, the nature of the intermediate species can be described. Kinetics are thought to have been neglected in studies of such solutions up to the present time.

Walton, H.F., 1943. "Equilibria in a Carbonaceous Cation Exchanger," J. Phys. Chem. 47(5):371-382.

In an investigation of exchange reactions with a carbonaceous cation exchanger, the law of mass action was obeyed for sodium-potassium, sodium-calcium, and calcium-barium, but was not a good model for sodium-hydrogen and calcium-hydrogen exchange. Most exchanges were reversible. As the pH was increased, the uptake of calcium increased.

Wiklander, L. and L. Fredrickson, 1946. "Studies on the Sorption of Sodium Arsenate and Sodium Arsenite by Soil and Synthetic Iron and Aluminum Oxide," Aeta Agr. Suecana 1:345-376.

Williams, C.R., R.L. Smith and C.F. Raba, Jr., 1981. "Environmental Engineering Aspects of Fly Ash Disposal," Paper presented at 1981 Fall meeting of the Texas Section ASCE, Houston, Texas, Sept. 25, 1981.

This work reviews briefly some of the findings of some of the major investigators in the field and discusses the application of these findings by an engineering consulting firm.

Wilson, B.D., 1929. "Extraction of Adsorbed Cations from Soil by Electrodialysis," Soil Sci. 28(6):411-421.

The recovery by electrodialysis of potassium, calcium, magnesium, and aluminum from clay soils to which the acetates had been added was investigated. Both adsorption and release were studied for conditions where each acetate was added individually to an electrodialyzed soil, and to an electrodialyzed soil made alkaline. Potassium and calcium exhibited the highest recovery rates and magnesium followed. Aluminum was adsorbed when the soil was saturated with hydrogen or calcium, but was not appreciably extracted by electrodialysis.

Woolson, E.A., 1977. "Fate of Arsenicals in Different Environmental Substrates," Environmental Health Perspectives 19:73-81.

The current knowledge of arsenic (As) transformations in the environment, as well as some gaps in this knowledge, are reviewed. These transformations involve As chemical and biochemical transformations in air, waters, sediments, and soils. Arsenic moves in a dispersive manner through air and water and is in physical and chemical equilibrium in many substrates. It is oxidized, reduced, methylated, volatilized, incorporated into biotic tissues, excreted, adsorbed, and desorbed. Oceanic sediments become the eventual sink for As.

The rates of As movement and transformation vary with environmental conditions. Besides inorganic As, various methylated arsenicals are found naturally at environmentally sensitive equilibrium concentrations, which are probably maintained biotically.

An As-transformation model has been constructed from rate constants derived from field observations. The environmental factors affecting these rate constants are discussed.

Woolson, E.A., 1969. The Chemistry and Toxicity of Arsenic in Soil, Ph.D. Thesis, Univ. Maryland, Univ. Microfilms, Ann Arbor, Mich. (Diss. Abstr. 31, B, p. 20).

Yee, M.S., H.L. Bohn and S. Miyamoto, 1975. "Sorption of Sulfur Dioxide by Calcareous Soils," Soil Sci. Soc. Amer. Proc. 39(2):268-270.

At room temperature, air-dry calcareous soils sorbed 0.4 to 1.6 g of SO_2/100 g of soil within 10 to 15 min from a dry air stream. The SO_2 sorption capacity increased with increasing SO_2 concentration in the air stream. Moisture in the air and soils greatly increased the sorption capacities and the initial sorption rates.