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Comanagement of Coal Combustion By-Products and Low-Volume Wastes: A **Southeastern Site**

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Prepared by **Radian Corporation** GeoTrans, Inc. and **Battelle PNL**

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Keywords: Groundwater

Coal ash

Solid wastes Leaching Attenuation

Waste codisposal

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REPORT SUMMARY

Comanagement of Coal Combustion By-Products and Low-Volume Wastes: A Southeastern Site

An insufficient database on the environmental effects of comanagement of power plant wastes could hamper the regulatory approval of the continuation of this practice. This report presents the environmental assessment of comanagement of high-volume coal combustion residues with low-volume wastes at a steam-electric power plant in the southeastern United States.

INTEREST CATEGORIES

Waste disposal and use Waste and water management Land and water quality hydrogeochemical modeling Land and water quality chemistry and physics

KEYWORDS

Groundwater Coal ash Waste codisposal Solid wastes Leaching Attenuation **BACKGROUND** There are several management options available for combustion by-products and other residues generated at steam-electric power plants. Approximately four-fifths of the materials are treated or disposed of on site, typically in ponds or landfills. Many plants comanage high-volume wastes, such as coal ash, with low-volume wastes, such as demineralizer regenerant, boiler-cleaning liquids, and water treatment sludges. EPRI initiated this study in 1988 to provide field data on the environmental performance from the comanagement of these solid and liquid residues.

OBJECTIVES

• To perform an environmental assessment at coal-fired power plant locations that comanage low-volume coal combustion wastes along with the high-volume wastes.

• To determine any benefits resulting from the neutralization of the effects of low-volume waste streams.

APPROACH Three pond sites were selected for an assessment of coal combustion by-product comanagement practices. This report summarizes the results of the study of a site that burns an eastern bituminous coal. In this case, coal ash from the plant is wet-sluiced to a pond situated in a bedrock valley. From late 1988 through 1989, researchers installed numerous groundwater wells and collected core samples and water samples to analyze the composition of the leachate and its migration through and interaction with the subsurface media.

Although hydrogeologic conditions are site-specific, the geology of this site is typical of the piedmont region of the southeastern United States. The management and comanagement practices are representative of typical practices at the steamelectric power plants.

RESULTS Data collected from surface and groundwater monitoring showed no significant increase in ash-derived trace metals in downgradient monitoring wells. Only calcium, magnesium, strontium, and sulfate had higher concentrations in the downgradient wells. Pyrite oxidation is the only low-volume waste by-product having some effects, which were restricted to an area immediately underneath the pond. No other effects of the comanaged low-volume wastes were detected.

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EPRI PERSPECTIVE Comanagement of utility low-volume waste with high-volume residues can be an effective means of treating and disposing of several by-products. In the past, comanagement has traditionally been practiced for convenience, especially when ash is wet-sluiced to ponds. Previous EPRI work has indicated that comanagement does neutralize some low-volume waste streams when handled with high-volume coal ash. Results from the southeastern site study confirm that the comanagement option is a technically viable and environmentally acceptable practice, if appropriately carried out. Results from research at the midwestern and the southwestern sites, which represent different climatic and comanagement conditions, are expected to further substantiate these findings.

PROJECT

RP2485-9

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Comanagement of Coal Combustion By-Products and Low-Volume Wastes: A Southeastern Site

EN-7545 Research Project 2485-9

Final Report, November 1991

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ABSTRACT

The Electric Power Research Institute initiated this study to provide environmental data on the co-management of utility high volume and low volume residues. This report presents results from a field investigation at an ash pond located at a 400 MW, coal-fired power plant in the southeastern U.S. The pond receives wet-sluiced fly ash and bottom ash from the generating station as well as low volume wastes from coal preparation, demineralizer regeneration, and boiler cleaning.

A detailed hydrogeochemical characterization of the primary ash disposal pond and surrounding groundwater system was performed. A total of 25 monitoring wells were installed to characterize groundwater flow directions, rates and chemistry. Ash and soil cores were also collected for hydrogeochemical characterization.

The direction of groundwater flow in the shallow aquifer largely follows the surface topography. Flow velocities varied widely with a mean velocity of 3.6×10^{-2} cm/sec (0.9 ft/day). Groundwater accounts for only a small fraction of the input water to the ash pond; the majority of pond water comes from the steam plant. The bulk of the outflow from the ash pond is through the surface discharge to the river, with a smaller fraction (20 - 35%) estimated to discharge to the groundwater between the pond and the river.

The majority of the constituents analyzed were found in statistically equal concentrations in groundwater upgradient and downgradient of the ash pond, or were not detected in either location. Only calcium, magnesium, strontium, and sulfate were found in wells downgradient of the ash pond in concentrations significantly greater than in upgradient wells. Trace metals from the ash were not detected in downgradient groundwaters.

No impact from the co-management of the low volume wastes was detected outside the ash pond. Increases in acidity and dissolved iron and manganese concentrations detected in groundwater near the terminus of the ash sluice line are related to the oxidation of pyrite rejects co-managed with the ash. However, these effects were not detected outside this localized area.

iii

CONTENTS

Sectio	<u>)n</u>			<u>Page</u>
1	INTRODUCTION			1-1
1	Objectives			1-1
	Background			1-2
	Approach			1-3
•				2-1
2	Sile Description			2-1
	Facility Description			2-4
	Regional Environmental Setting			2-4
	Geology			2-5
	Hydrology Descipitation and Rechard	Program (program) December (program)		2-6
	Coochemistry			2-6
	Geochemischy			3_1
3	CHARACTERIZATION METHODS			3-1
	Hydrogeologic Characterization	ten Mathada		3-1
	Drilling and Core collect	tion methods	and Completion	3-3
	Monitoring Well Design, J	Installation, a	and compretion	3-7
	Pond Water Flux Character	rization		3-10
	Water Levels and Meteoro	logical Measure	ements	3-12
	Laboratory Measurements (of Physical Pro	operties	3-13
	Aquifer Tests			3-15
	Sample Collection and Field Me	asurements		3-15
	Sampling Soil and Ash			3-15
	Sampling Groundwater and	Surface Water		3-17
	Field Measurements		· · · · · · · · · · · · · · · · · · ·	3-17
	Sample Quality Assurance	and Quality L	ONTROI	3-17
	Laboratory Analysis			2 21
	Analysis of Aqueous Samp	les		2 21
	Analysis of Solid Sample	S		3-21
	Laboratory Quality Assur	ance and Quali	ty Control	3-24
4	ASH, WASTE, AND SOIL CHARACTERISTICS	5		4 - 1
	Ash and Soil Physical Properti	ies		4 - 1
	Grain-Size Analyses			4-1

CONTENTS (Continued)

ć

Se	ction	Page
	Hydraulic-Conductivity Measurements	4-3
	Porosity and Volumetric Moisture Content	4-6
	Chemical and Mineralogical Properties	4-6
	Low Volume Waste Characteristics	4-12
	Mineralogical Composition of the Waste and Soils	4-21
	Elemental Trends with Depth	4-25
	Geochemical Properties	4-25
	Pore-Water Analysis	4-28
	Cation Exchange Capacity and Exchangeable Cations	4-31
	pH Manipulation Studies	4-33
	Summary	4-48
	Ash and Soil Characteristics	4-48
	Solubility Controls	4-51
	Impact of Codisposal on Leachable Inventories of Trace Elements	4-51
5	GROUNDWATER ANALYSIS	5_1
	Hydrogeology	5-1
	Geology	5-3
	Hydrology	5-12
	Primary Ash Pond Water Balance	5-20
	Saturated Thickness	5-35
	Water Quality	5-39
	Groundwater Quality	5-38
	Pond and Surface Water Quality	5-50
	Summary of Hydrology and Groundwater Chemistry	5-62
6	SUMMARY AND CONCLUSIONS	6 1
	Site Description	6 1
	Hydrogeology	0-1 6 1
	Ash and Soil Chemistry	6.2
	Groundwater Chemistry	6.4
	Co-Management of Wastes	0-4 6 E
	Conclusions	6-6
7	REFERENCES	7-1

CONTENTS (Continued)

<u>Section</u>			Page
APPENDIX	BOILER CHEMICAL CLEANINGS		A-1
APPENDIX	TRANSDUCER CALIBRATIONS		B-1
APPENDIX	ANALYTICAL DATA FOR GROUNDWATER SAMPLES		C-1
APPENDIX	ANALYTICAL DATA FOR SOIL AND ASH SAMPLES		D-1
APPENDIX	PORE WATER, EXTRACTABLE IRON, AND EXCHANGEABLE	IONS	E-1
APPENDIX	DH MANIPULATION CONCENTRATION DATA		F-1
APPENDIX	MONITOR WELL LOGS		G-1
APPENDIX	WATER LEVEL ELEVATIONS		H-1
APPENDIX	I SLUG-TEST ANALYSES		I - 1
APPENDIX	J SOURCE APPORTIONMENT CALCULATIONS		J-1
APPENDIX	QUALITY CONTROL RESULTS		K-1

, .

ILLUSTRATIONS

Figur	$\underline{\mathbf{e}}$	Page
2-1	L-Site Ash Pond System	2-2
2-2	Ash Pond Inputs Flowsheet for L-Steam Station	2-3
3-1	Schematic of Monitoring Well Design	3-5
3-2	Schematic of Hydraulic Potentiomanometer	3-9
3-3	Equipment for Conducting Field Measurements and Collecting Liquid Samples	3-16
4-1	Lithologic Classification Deposits at L-Site	4-2
4-2	Vertical and Horizontal Log Hydraulic-Conductivity Values	4 - 7
4-3	Distribution of Core Sample Porosity Values	4-10
4-4	Sample of Ash and Geologic Material Collected for Chemical and Geochemical Characterizations	4-11
4-5	Major Elemental Composition of Soil and Ash	4-19
4-6	L-Site Ash Compositions Plotted According to System of Roy and Griffin (1982)	4-22
4 - 7	Morphology of Typical Ash Particles	4-24
4-8	Depth Trend for pH in the 2:1 Water-Soil Extracts	4-26
4-9	Depth Trend for Copper in Ash Delta Area	4-27
4-10	Pyrite Oxidation Cycle	4-30
4-11	Log of Aluminum Activity vs pH for All L-Site Core Samples	4-35
4-12	Log of Calcium Activity vs pH for All L-Site Core Samples	4-36
4-13	Log of Ferric Iron Activity vs pH for All L-Site Core Samples	4-37
4-14	Log of Barium Activity vs pH for All L-Site Core Samples	4-39
4-15	Log of Cadmium Activity vs pH for All L-Site Core Samples	4-41
4-16	Log of Chromium Activity vs pH for All L-Site Core Samples	4-42
4-17	log of Copper Activity vs pH for All L-Site Core Samples	4 - 44

ix

ILLUSTRATIONS (Continued)

Figure		Page
4-18	Log of Manganese Activity vs pH for All L-Site Core Samples	4-45
4-19	Log of Manganese Plus Phosphate Activity vs pH for All L-Site Core Samples	4-46
4-20	Log of Nickel Activity vs pH for All L-Site Core Samples	4-47
4-21	Log of Strontium Activity vs pH for All L-Site Core Samples	4-49
4-22	Log of Zinc Activity vs pH for All L-Site Core Samples	4-50
5-1	Geotechnical Borings and Monitoring Well Locations at L-Site	5-2
5-2	Unweathered Bedrock Topography at L-Site	5-5
5-3	Geologic Section B-B' Parallel to Dam	5-7
5-4	Geologic Section A-A' Perpendicular to Dam	5-8
5-5	Potentiometric-Surface at L-Site	5-14
5-6	Screen Completion Intervals for Monitoring Wells LMW-22, LMW-15, and LMW-14	5-16
5-7	Water-Level Elevations for LMW-22, LMW-21, LMW-14, LMW-15, and the Primary Ash Pond	5-17
5-8	Groundwater Level Fluctuations in L-Site Monitoring Wells	5-19
5-9	Screen Completion Intervals for Monitoring Wells LMW -05, -06, and -07	5-21
5-10	Drawdown Plots and Type-Curve Matches for the Multiple-Well Pumping Test	5-25
5-11	Water Inflow and Outflow Components to Primary Ash Pond	5-31
5-12	Potential Groundwater Flow Paths at the L-Site	5-33
5-13	Estimated Groundwater Velocities at the L-Site	5-36
5-14	Saturated Thickness of Deposits Above the Unweathered Bedrock Surface	5-37
5-15	Site Map Showing Three Categories of Monitoring Well Locations: Background, Ash, and Downgradient	5-43
5-16	Isoconcentration Contours of Calcium in Groundwater Downgradient of Ash Pond	5-51
5-17	Isoconcentration Contours of Sulfate in Groundwater Downgradient of Ash Pond	5-52

.

ILLUSTRATIONS (Continued)

Figur	<u>e</u>	<u>Page</u>
5-18	L-Site Map Showing Well Transect Used in Table 5-8	5-55
5-19	L-Site Event II, Groundwater Concentrations at Depth	5-56
5-20	L-Site Event II, Groundwater pH at Depth	5-56
5-21	Pond Temperature, pH, and Sulfate Concentration at Depth, August	5-59
5-22	L-Site, Pond Water Quality Over Time	5-60

TABLES

<u>Table</u>		Page
3-1	Liquid Sample Collection Specifications	3-18
3-2	Field Analysis of Liquid Samples	3-19
3-3	Test Methods and Method Detection Limits for Aqueous Samples from L-Site	3-22
3-4	Summary of Quality Control Limits for Analysis of Aqueous Samples from L-Site	3-25
4-1	Saturated Vertical Hydraulic-Conductivity Values for Core Samples from the L-Site	4 - 4
4-2	Summary of Initial Moisture Content, Dry Bulk Density, Particle Density and Porosity Values	4-8
4-3	Summary Statistics for Chemical Composition of Soils and Ash from L-Site	4-15
4 - 4	Fraction of Mean Total Elemental Concentrations Extracted into Hydroxylamine Hydrochloride Solution	4-20
4-5	Summary of Mineralogical Analyses for Ash and Soils from the Ash Delta and a Control Location at the L-Site	4-23
4-6	Summary of Pore Water Extracts and Solid Samples	4-29
4-7	Cation Exchange Capacity and Exchangeable Cations of L-Site Soils and Ash	4-32
4-8	Proposed Solubility Controls for L-Site Fly Ashes and Soils	4-52
4-9	Leachable Inventories of Trace Elements in L-Site Samples	4-54
5-1	Horizontal Hydraulic-Conductivity Values Measured from Slug Tests at the L-Site	5-23
5-2	Calculated Groundwater Velocities for the L-Site	5-34
5-3	Summary Statistics for Groundwater Quality Results from Event I Samples	5-39
5-4	Summary Statistics for Groundwater Quality Results from Event II Samples	5-41
5-5	Comparison of Event II Groundwater Results Using a Non-Parametric Duncan's Multiple Range Test	5-45
5-6	Estimated Solids Loadings of Streams Routed to Ash Pond	5-46

xiii

TABLES (Continued)

<u>Table</u>		Page
5-7	Calculated Chemical Composition of Boiler Chemical Cleaning Waste at L-Steam Station	5-49
5-8	Groundwater Concentration Along Upgradient-Downgradient Transect	5-54
5-9	Chemical Characteristics of River and Pond Waters from L-Site, Event II	5-57
5-10	Chemical Characteristics of Sluice Waters from L-Site Event II	5-61
5-11	Chemical Characteristics of Groundwater in the Vicinity of Well LMW-17, Event II	5-63

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SUMMARY

The L-site is located at a 400 MW coal-fired steam station in the southeastern U.S. Fly ash and bottom ash are sluiced to a disposal pond system consisting of two unlined settling basins constructed in 1973. The ponds discharge to an adjacent river. Several low volume wastes are co-managed in the pond system, including pyrite rejects, demineralizer regenerant, and boiler chemical cleaning wastes.

The geology of the site is typical of the piedmont region of the southeastern United States where metamorphic bedrock has undergone extensive chemical weathering. The unweathered bedrock consists of granitic gneisses and mica-rich schists. A partially weathered bedrock deposit lies above the unweathered bedrock, which is overlain by extensively weathered bedrock (saprolite).

The primary ash pond appears to be a source of both recharge and discharge for the shallow groundwater flow system. Shallow groundwater discharges into the pond on the upgradient side of the pond and pond water discharges to the groundwater system on the downgradient end near the dam.

In situ horizontal hydraulic-conductivity values for the aquifer materials, obtained from slug tests and a multiple-well pumping test, ranged over approximately three orders of magnitude from 1.2×10^{-4} to 8.7×10^{-2} cm/sec. The vertical saturated hydraulic conductivities for unconsolidated deposits at the L-site were measured in the laboratory and ranged over approximately four orders of magnitude from 2.26 x 10^{-7} to 1.97×10^{-3} cm/sec. Groundwater velocities were estimated to range from about 4×10^{-3} cm/sec (0.1 ft/day) to greater than 1.2 X 10^{-2} cm/sec (40 ft/day), with a mean velocity of about 0.9 ft/day. These high velocities are due to the large hydraulic gradient between the pond and river, and the high hydraulic-conductivity values of the saprolite.

Concentrations of several constituents in ash leachates, including Al, Ba, Cu, Fe, and Mn, appear to be controlled by solubility relations with the ash. In the underlying soils, similar solubility controls affect concentrations of Al, Ba, Fe, and Mn so that precipitation reactions are not expected to influence mobility of dissolved constituents in leachate moving from the ash into the underlying soils. Major and trace element concentrations in hydroxylamine hydrochloride extracts of ash and soil samples were consistent with this hypothesis, and showed no enrichment in leachable material at the ash/soil interface, where precipitation reactions are most likely.

Other geochemical measurements, including cation exchange capacities and amorphous iron adsorption capacities made on soil samples from the L-site, indicate low attenuative capacity for these soils through adsorption mechanisms. This was consistent with the relatively coarse grain size and high degree of chemical weathering of the saprolite soils.

The ash pond's effects on downgradient groundwater quality are limited to increased concentrations of Ca, Mg, Sr, and SO_4 over background groundwater. Of these constituents, only SO_4 currently has published water quality secondary standards for drinking water. The mean SO_4 concentrations measured downgradient of the ash pond were approximately half the water quality limits.

Groundwater within the disposed ash has statistically elevated concentrations of sulfate; metals including iron, nickel, and zinc; and increased acidity. Oxidation of co-disposed pyrite appears to be the source of these constituents. Slow or stagnant groundwater circulation within this portion of the disposed ash and/or further oxidation and coprecipitation of dissolved iron and other metals prevents the migration of these constituents into downgradient groundwater. Section 1 INTRODUCTION

During the process of combusting fossil fuels to generate electricity, power plants produce several waste or by-product streams. The greatest volumes of by-products result from the control of particulate matter and sulfur dioxide (SO_2) emissions produced by fossil fuel combustion. These streams are often called high volume wastes and include bottom ash, fly ash, and flue gas desulfurization (FGD) wastes. In addition, several low volume waste streams are generated at fossil-fuel-fired power plants. These include pyrites, coal pile runoff, floor and yard drains, demineralizer regenerant, treatment sludges and brines, and equipment cleaning wastes. In many power plants, these low volume wastes are co-managed with the high volume streams in ponds or landfills.

In its report to Congress on coal-fired utility waste, the U.S. Environmental Protection Agency (EPA) concluded that "coal combustion waste streams generally do not exhibit hazardous characteristics under current RCRA regulations" (U.S. EPA, 1988). In some instances, the EPA concluded that wastes produced during equipment maintenance and water purification, such as metal and boiler chemical cleaning wastes, may exhibit RCRA Subtitle C characteristics. Based on this information, the EPA "intends to consider whether these waste streams should be regulated under Subtitle C of RCRA based on further study and information obtained during the public comment period" (U.S. EPA, 1988).

OBJECTIVES

The objective of this research project is to perform an environmental assessment at two coal-fired utilities that co-manage low volume wastes and high volume coal combustion by-products in ash ponds. The data from these characterizations will assist utility managers in selecting the appropriate management practices for these materials and will provide data for their prudent regulation.

This report presents the results from the site assessment at one coal-fired power plant in the southeastern U.S. The focus of the environmental assessment was on the subsurface environment -- namely subsurface soils and groundwaters. Data were

collected over a one-year period on the managed by-products and waste streams, soils beneath these materials, and groundwaters upgradient and downgradient from the management area. The scope of the characterizations was modeled after the recent EPAsponsored study of utility sites (A. D. Little, 1985), with greater emphasis on assessing the impacts from co-management practices.

BACKGROUND

In 1984, U.S. electric utilities generated about 70 million tons of coal ash. For a 1,000 MW power plant, the quantity of ash generated may amount to about 300,000 tons per year of solids (depending on capacity factors, heat rates, ash content of coal and other factors). Sluice water volumes for wet-sluiced ash may be up to 900 million gallons per year for a 1,000 MW power plant. Generation rates for low volume wastes are more difficult to estimate because of their variability. But for the same 1,000 MW power plant, generation rates for a continuous low-volume waste stream such as demineralizer regenerant may be as much as 50 gpm, or over 20 million gallons per year. For an intermittent stream such as boiler chemical cleaning waste, the generation rates may be near 80,000 gallons per year (Holcombe, et al., 1987).

There are several management options available for combustion by-products and wastes generated at steam electric power plants. On a national average, approximately one-fifth of the wastes generated are utilized. The other four-fifths are treated or managed on site, typically in ponds or landfills. Approximately 53 percent of the operating units use landfills for the on-site management of coal combustion by-products (U.S. EPA, 1988). Ponds, or surface impoundments, account for about 44 percent of the management facilities at generating units.

The character and quantity of low volume wastes generated at a power plant depend on factors such as fuel, geographic location, environmental regulations, and other site-specific considerations. Low volume wastes such as demineralizer regenerant, floor and yard drains, water and wastewater treatment sludges, and boiler blowdown are generated continuously or produced in batch volumes during the operation of the power plant (Holcombe, et al., 1987). Other streams, such as fireside cleaning and boiler chemical cleaning wastes, are generated during scheduled outages for equipment maintenance.

APPROACH

Two pond sites were selected for an assessment of coal combustion by-product management and co-management practices. The high volume coal combustion by-products at

both sites consist of coal ash and bottom ash; no flue gas desulfurization system is used at either plant. In selecting the two sites for this assessment, EPRI considered the chemical nature of both the high volume by-products and low volume wastes and the environmental settings. The site reported here (L-site) uses eastern bituminous coal. The ash has a neutral to mildly acidic pH (pH is one of the most important parameters affecting chemical concentrations in ash leachates). In contrast, the second plant (C-station), to be discussed in a companion report, burns a subbituminous coal which produces an ash with an alkaline pH. Additionally, the environments of the ash ponds for the two plants are very different; L-site's ash pond is in a bedrock valley with largely residual soils, and the C-station's pond is constructed in an alluvial valley. The contrasts between the two plants give a broader perspective to the assessment of management and co-management.

The following sections of this report present the results from the environmental assessment at L-site.

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Section 2 SITE DESCRIPTION

This section presents a description of the L-site and the regional environmental setting.

FACILITY DESCRIPTION

The site described in this report is located at a 400 MW, coal-fired steam station in the southeastern U.S. L-site has an ash pond system consisting of two unlined settling basins separated by a dike (Figure 2-1). The ponds were constructed in 1973 and have a total surface area of about 60 acres.

Figure 2-2 presents a flowsheet for high volume and low volume streams routed to the ash pond at the L-steam station. Fly ash and bottom ash are sluiced to the primary ash pond, as are most of the plant's low volume wastes.

Fly ash and bottom ash represent the largest volume of materials going to the pond, with rates of approximately 30,000 cubic yards per year. Over the 16-year operating life of the pond, about 500,000 cubic yards of ash have been routed to the ash ponds.

Blowdown from the boiler cycle water is required to maintain the desired water chemistry. Boiler blowdown is a high purity stream, with typical maximum dissolved solids levels of less than 15 mg/L.

The L-steam station personnel use a two-stage boiler chemical cleaning procedure for their three coal-fired units. Each unit is cleaned approximately every three years using ammonium bromate solution to remove copper and a solution of inhibited hydrochloric acid, ammonium bifluoride and copper complexer to remove iron oxides, silica, and residual copper. Finally, the boiler metal is neutralized and passivated with a solution of soda ash. Appendix A presents a summary of boiler chemical cleanings at the L-steam station.





^aPlant data

^bEstimates for 400 MW power plant from Holcombe et al 1987.

^cTotal flow to ash pond is at least 200 million gallons per year. See Section 6, Primary Ash Pond Water Balance, for further discussion of ash pond water balance.

Figure 2-2. Ash Pond Inputs Flowsheet for L-Steam Station

Runoff from a 7-acre coal pile is also co-managed with the ash. The runoff flow rate shown in Figure 2-2 is based on an average annual rainfall of approximately 40 inches.

Cooling tower basin sludge is generated very infrequently -- estimated at about 20 cubic yards per year (Holcombe, et al., 1987). Demineralizer regenerant is treated in a rapid-mix tank neutralization system and then routed to the ash ponds. This operation involves the mixing of acidic and basic regeneration streams for the demineralizers and generates a waste stream with a flow of approximately 2.5 gpm (approximately 1.3 million gallons per year).

Waste from the water washing of the fireside of the boiler is generated infrequently; although volumes of this waste are unknown, reported generation rates range from 400,000 to 2 million gallons per year for this size plant (Holcombe, et al., 1987). The generation rates for floor and yard drains, which are co-ponded with the fly ash, are unknown, but have been reported at about 8 gpm (Holcombe, et al., 1987).

Sludge resulting from softening of the plant makeup water is also sent to the ash pond (about 1 to 2 cubic yards per year), as are pyrite rejects from the coal pulverizers (about 30 cubic yards per year). Water from a drainage diversion system built to keep surface water away from low lying areas in the plant also is discharged to the ash pond.

The sum of these incremental flows to the ash pond is over 500,000 gallons per day, or about 200 million gallons per year (based on the flows assumed in Figure 2-2, the assumptions listed in the text above, and an ash sluice stream with 3.7% solids). However, other estimates of plant input to the ash pond, based on visual observation of the pipe flow rates and plant reliability factors, approach over 400 million gallons per year (see discussions in Section 5).

REGIONAL ENVIRONMENTAL SETTING

<u>Geology</u>

The L-site is located within the Piedmont Province, which is subdivided into four northeastern trending belts. The distinction between the four Piedmont Belts is based primarily on the degree of metamorphism and to a lesser extent on the mineral-ogy of the parent rocks (Patterson and Padgett, 1984).

The L-site is located in the Inner Piedmont Belt which contains moderate to high grade metamorphic rocks. Structurally, the Inner Piedmont Belt consists of lowangled foliated rocks with some zones of broad folding. Numerous fault zones and lineaments have been identified and mapped throughout this area (Snipes, et al., 1981). The predominant orientation of fault zones and lineaments in the area of the L-site is to the northeast, paralleling the Piedmont Belts; a secondary lineament orientation is also present to the northwest. Major fault zones and lineaments have not been mapped in the immediate vicinity of the L-site.

Rocks in the Piedmont Province were originally deposited during late Precambrian and Paleozoic time (Overstreet and Bell, 1965). The original parent rocks consisted of shale, graywacke, felsic and mafic tuffaceous shale, tuff, and lava flows that contained thin interbedded conglomerate, sandstone, limestone, and manganese-rich shale beds (Overstreet and Bell, 1965). Regional metamorphism and igneous intrusions transformed the original sedimentary rocks in the Inner Piedmont Belt into granite, biotite, and hornblende gneisses, mica schists, and amphibolites (Snipes, 1981).

In general, the stratigraphy for the Inner Piedmont Belt consists of metamorphic bedrock overlain by saprolite, a mantle of weathered bedrock that has developed in place. Alluvial and colluvial deposits are present in ancient and currently active stream channels. Saprolite deposits in the area of the L-site have been reported to range in thickness from less than one foot to greater than 100 feet (Snipes, 1981).

<u>Hydrology</u>

Groundwater flow in the bedrock aquifer of the Inner Piedmont Belt is predominantly controlled by the presence of fractures and weathered veins. The permeability of the unfractured metamorphic rocks is extremely low. Well yields in the bedrock aquifer in the vicinity of the L-site have been reported to range from 0 to 400 gpm, with a median yield of 8 gpm (Snipes, 1981).

Groundwater flow in the saprolite is affected by the structure and texture of the parent rocks. Groundwater tends to accumulate and springs typically emerge at the bedrock/saprolite contact because of the lower permeability of the unfractured bedrock (Snipes, 1981). Previous studies indicate a possible correlation between the thickness of the overlying saprolite and the productivity of bedrock wells. Bloxham and others (1970) hypothesized that the greater the saprolite thickness, the greater the productivity of the bedrock well.

Precipitation and Recharge

Average precipitation at the L-site is about 41 inches per year, based on the average yearly precipitation for the years 1984 through 1989. The months of February, June, July, and November are the wettest (3.6 to 4.6 inches per month), with July averaging the highest precipitation. The months of April, May, and December are the driest (2.5 to 2.8 inches per month), with May averaging the lowest precipitation. Precipitation during the remaining months ranges from about 3.1 to 3.4 inches per month.

There are few estimates of recharge available near the site. Ligon and others (1980) attempted to measure recharge using a mass-balance approach on a test plot about 20 miles west of the L-site. Precipitation, surface-water runoff, and soil-moisture storage were measured at the test plot, and potential evapotranspiration (PET) was estimated. The net difference between precipitation and the sum of surface-water runoff, changes in soil-moisture storage, and PET was assumed to be the net recharge to the groundwater system. Precipitation for the period December 19, 1974 to September 18, 1975 was 55 inches; recharge was estimated to be about 19 inches, or 34% of the precipitation. The largest amount of recharge was reported to occur during the summer from residual soil-moisture storage built up during the winter and late spring.

The recharge rate estimated for the test plot is an abnormally high percentage of the precipitation. Recharge typically averages less than 34% of the precipitation. Two potential reasons for the high recharge rate are: 1) the above average precipitation during the nine-month period, and 2) an underestimation of the PET rate. Recharge at the L-site is anticipated to be less than that calculated for the test plot.

Geochemistry

Most of the soils in the area of the ash ponds can be characterized as residual granite/gneissic bedrock. The soils comprise highly weathered mica, quartz, feld-spars, and some hornblende. Kaolinite is present in both the sand and clay size fractions of the soil, probably occurring as an interstratified mineral in the mica. Small amounts of pyrite are found in the soils, which may influence the pH of soil pore waters. The soils in the region have pHs between 5.5 and 6, with cation exchange capacities averaging 4.5 to 7 meq/100 gram. Background groundwater, from this study, has a pH of about 6. Groundwater compositions reflect the granitic geologic environment, i.e., generally lower pH and lower concentrations of calcium,

magnesium, and carbonate than would be found in sedimentary rock aquifers (Stumm and Morgan, 1970).

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Section 3

CHARACTERIZATION METHODS

The methods used in the site assessment are presented in this section in the following order:

- Hydrogeologic characterizations;
- Sample collection and field measurements; and
 - Laboratory analysis.

HYDROGEOLOGIC CHARACTERIZATION

The hydrogeologic characterization included:

- Reviewing available hydrogeologic data for the site;
 - Collecting geologic cores to define the lithology/stratigraphy of deposits surrounding the pond and to measure physical and geochemical properties of the unconsolidated deposits;
 - Installing monitoring wells and piezometers to define hydraulic gradients, to measure in situ aquifer properties, and to characterize the groundwater chemistry; and
 - Measuring hydraulic gradients in the ash pond to characterize the flux of water into and out of the pond.

The hydrogeologic characterization focused on the primary ash disposal pond, since all high volume coal combustion by-products and low volume wastes are pumped to this pond before being routed to the secondary pond. Any constituents released to the environment as a result of these management practices should be more readily identified in the ash deposits and groundwater beneath the primary pond than beneath the secondary pond.

Drilling and Core-Collection Methods

The drilling and core-collection methods chosen for the monitoring well installation attempted to limit aquifer contamination by minimizing or eliminating the introduction of foreign fluids and substances into the borehole. All drilling and corecollection equipment was decontaminated with a mild detergent and steam cleaned before the drilling of each borehole.

<u>Drilling</u>. Three different methods were required at the L-site for monitoring well installation: 1) hollow-stem auger; 2) air rotary, and 3) air hammer. The majority of the boreholes were drilled with a combination of 3 1/4- and 6 1/4-inch ID hollowstem augers. The 3 1/4-inch ID augers were used primarily for geologic sample collection. Typically, the boreholes caved when the 3 1/4-inch ID augers were removed; 6 1/4-inch ID augers were then used to ream the borehole. The 6 1/4-inch ID augers also served as temporary casing during the construction and installation of monitoring wells.

The air-rotary method was required for drilling through bouldery fill material downgradient of the dam and for drilling through the partially consolidated bedrock beneath the saprolite. Oil-free air was injected down the drill stem to cool the bit and to return rock cuttings to the surface. The air-rotary method was also used to drill through bouldery fill material. After the fill material was penetrated, hollow-stem augers were used to complete the drilling and construct the well.

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Air-hammer drilling was used only when monitoring wells were installed in consolidated bedrock. In this method, the hole is advanced by pneumatically impacting the rock with a carbide bit as the bit is slowly rotated. The rotating action of the bit also helps in the cutting action and maintains a straight borehole. The outside diameter (OD) of the air-hammer bit was nominally 4 inches. Before the air hammer was used, a 4-inch ID surface casing was grouted in a 10 3/4-inch borehole to reduce the size of the hole for a more efficient return of drill cuttings and to eliminate borehole caving problems. The grout was allowed to cure for a minimum of 24 hours before any additional work was performed in the borehole.

Two monitoring wells were drilled on the ash delta of the primary ash pond, with a combination of 3 1/4- and 6 1/4-inch ID hollow-stem augers. Drilling on the ash delta required the construction of a temporary platform to support the 24,000-pound drill rig, its associated equipment and personnel during this phase of monitoring well construction. The platform was constructed of plywood and aircraft landing mats. The weight of the rig was distributed over the surface area of the plywood by interlocking the 4-foot by 8-foot by 3/4-inch plywood sheets. The aircraft landing mats were laid on top of the plywood to distribute the weight laterally across multiple sheets of plywood. The weight of the 24,000-pound drill rig was successfully distributed over a 400-square-foot area, resulting in a net pressure of about

60 pounds per square foot. The ash in the area of drilling was capable of supporting in excess of 200 pounds per square foot.

<u>Core Collection</u>. Geologic core was collected during the drilling of monitoring wells at the L-site by four methods: 1) Moss sampler; 2) split spoon; 3) core barrel; and 4) piston core sampler. The Moss sampler is the preferred method for collecting cores in unconsolidated deposits because compaction and disturbance of the core are kept to a minimum during sampling. The Moss sampler works on a wireline system in conjunction with the hollow-stem auger. The sampler is lowered into the hollow-stem augers and locked into the base of the auger flights. The auger flights are then advanced 2 feet and the Moss sampler is retrieved. Clear plastic liners installed in a split barrel were used with the Moss sampler so that the core could be more easily described, subsampled, and packaged for shipping.

A split-spoon sampler was used to collect core in unconsolidated deposits when there was a problem obtaining core with the Moss sampler. Only 22 of the 70 cores were collected with this method. The split-spoon sampler is also lowered into the inside of the hollow-stem auger via a wire-line system. The sampler is mechanically driven 2 feet with a 140-pound hammer to obtain the core. The sample is then retrieved with the wire line and split open to remove the sample.

The main disadvantage of the split-spoon sampler is that it tends to compact the sample during the sampling process, which directly affects some of the physical property measurements on the sample. Hence, use of split-spoon samples was generally limited to lithologic determinations.

The core barrel was used to collect samples of the consolidated bedrock. Unlike the previous samplers, the drill stem and bit must be removed from the borehole and replaced with the core barrel before a sample can be obtained. The core barrel is diamond-tipped and is cooled by water during core collection. The core moves into the interior of the core barrel as the core barrel is advanced.

Monitoring Well Design, Installation, and Completion

<u>Design</u>. All casing and screen materials used at the L-site were made of poly-vinyl chloride (PVC), which is nonreactive in the geochemical environment present at the L-site. Screens were machine slotted to an opening of 0.010 inches. All threaded casing and screen joints were taped with polytetrafluoroethylene tape prior to assembly. Organic solvents or glues were not used.

Monitoring wells were constructed of 2-inch ID schedule-40 PVC casing and screen. The only exception was a 4-inch ID pumping well installed for use in a multiple-well pumping test. Four different screen lengths were used in the monitoring well construction: 1.1 feet, 2.0 feet, 4.0 feet, and 9.0 feet. A sediment trap, ranging in length from 0.5 to 1.5 feet, was attached to the bottom of the screens.

The length of the slotted portion of the screen interval was determined on the basis of the anticipated permeability of the aquifer material in which it was completed. The majority of the monitoring wells were completed in the unconsolidated saprolite and had a 1.1-foot screen interval. Wells completed in the consolidated bedrock and partially consolidated transition zone above the bedrock had screen intervals of 4.0 and 9.0 feet. The longer screens were used to increase the probability of intersecting permeable fractures and zones. All screens had slot size openings of 0.010 inches.

The annular space of the borehole was backfilled with a uniform-size quartz filter sand from the bottom of the borehole to within about 1 foot above the top of the screen. The filter sand used was that recommended by the manufacturer for a screen slot opening of 0.010 inches. A 2-foot bentonite seal, consisting of 1/4-inch diameter bentonite pellets, was placed above the sand to isolate it from the cement grout above. The remainder of the annular space was backfilled with a cement grout. A small amount of bentonite (about 8 percent) was added to the grout to reduce shrinkage. A lockable protective steel casing was installed on all monitoring wells as a security measure. In addition, a 3-foot diameter cement pad was constructed around each well to direct surface water runoff away from the wells. A schematic of the general well design is shown in Figure 3-1.

Drive-point piezometers also were installed at the L-site by mechanically driving the piezometers. The piezometer screen and casing were constructed of flushthreaded, schedule-80 PVC material for increased durability during installation. All threaded joints were taped with polytetrafluoroethylene tape before installation. Two of the piezometers had 2-inch ID casing and the one piezometer installed in the pond had a 1-inch ID casing. Casing intervals were in 2- and 5foot lengths and screen intervals were 1 foot. The bottom of the screen contained a cone-shaped PVC drive point. A filter pack sand and annular sealant were not installed in the drive-point piezometers.


<u>Installation</u>. Monitoring-well installation was dependent on the type of material in which the well was completed and the stability of the borehole after the 3 1/4-inch ID hollow-stem augers were removed.

The majority of the monitoring wells (12) were completed through the center string of the 6 1/4-inch ID hollow-stem augers due to borehole caving problems. Five of the wells did not have a problem with borehole caving and were completed in the open borehole resulting from the 3 1/2-inch ID augers. Three of the wells were completed in consolidated bedrock in a 4-inch diameter open borehole.

Before the casing and screen were installed, sediments in the borehole or hollowstem augers were removed by bailing to ensure that the filter pack was clean and that the bentonite seal was intact. A 6.5-foot long by 4-inch diameter cable-tool bailer was used to remove the sediments.

The previously decontaminated casing and screen were lowered into the hollow-stem auger or borehole and assembled using polytetrafluoroethylene tape at the joints. After the screen and casing were resting on the bottom of the borehole, a second check was made for the presence of sediment on the bottom of the borehole and the accuracy of the well depth.

When wells were completed inside the hollow-stem augers, sand was slowly poured into the augers until about 2 feet of sand was inside the augers. Each auger was then slowly pulled back until the bottom of the auger coincided with the top of the sand. This process was repeated until the sand pack was about 1 foot above the top of the screen.

When wells were constructed in open boreholes, the filter pack sand was installed through a 2-inch ID tremmie pipe. A small amount of deionized water was added to the sand to help prevent bridging in the tremmie pipe. A tremmie pipe could not be used for wells completed in the bedrock; therefore, sand was poured from land surface. A filter pack was not installed in bedrock well LMW-18 because of caving problems. Saprolite material filled the borehole from the base of the borehole to about 25 feet below land surface. No problems were experienced in sampling these wells.

All bentonite seals were installed by pouring the pellets into the open borehole from land surface. The bentonite seal was allowed to hydrate for a mini-mum period of 15 minutes before the borehole annulus was grouted. In a few cases the bentonite seal was above the saturated zone and deionized water was added to hydrate the bentonite pellets.

The borehole annulus was grouted to land surface by following the American Petroleum Institute's established practices. A 1 1/4-inch ID PVC pipe was installed to within 2 feet of the bentonite seal. A cement/bentonite grout was mixed and pumped down the pipe, until a sustained return of grout was observed at the surface. The grout pipe was then removed from the borehole and the grout was allowed to set for a minimum of 24 hours before any additional work was performed on the well.

The final construction step was to install a lockable protective steel casing over the PVC casing on each well. A 3-foot diameter cement pad was constructed around all wells to promote surface drainage away from the well.

<u>Well Development</u>. Development of the 2-inch diameter monitoring wells was performed with a PVC hand pump. The 80-foot depth-to-water in monitoring well LMW-18 required the use of an air-lift pump for development and the 4-inch ID pumping well (LMW-16) was developed with a submersible pump. The procedure for developing the wells was to pump all of the water out of the well casing and let the well recover. This procedure was continued until the pumped water was visibly free of suspended sediments. Typically, the wells had to be evacuated a minimum of three to four times before the water was visibly free of suspended sediments.

A surging tool, consisting of a 1-inch OD PVC pipe with 2-inch OD rubber washers attached to the outside of the pipe, was used to help develop some of the lower permeability 2-inch ID wells. The surging tool was run up and down the well casing forcing water to move into and out of the well screen and filter pack. The surging action of the water helped to rearrange and to remove fine-grained material from the filter pack and screen.

Pond Water Flux Characterization

The movement of water through the base of the pond has a measurable impact on the groundwater downgradient from the ash pond. The rate of movement is dependent on the hydraulic head in the pond and aquifer and the permeability of sediments in the pond.

<u>Hydraulic Potentiomanometer and Pond Piezometer Measurements</u>. One approach to estimating the flux of the pond water through the base of the pond was to measure the

hydraulic gradient across the pond bottom sediments, measure the vertical permeability of the sediments, and calculate the flux rate using Darcy's equation:

$$q = -K \frac{dh}{dL}$$
(3-1)

where:

q is the flux rate, L/T;

K is the vertical hydraulic conductivity, L/T; and

dh/dL is the hydraulic gradient across the pond bottom sediments, dimensionless.

The main advantage to this approach is that parameters that impact seepage through the base of the pond can be measured directly. The main disadvantage is that a large number of spatially distributed measurements are needed to accurately characterize the total flux of water out of or into the pond.

The hydraulic gradient across the pond bottom sediments was measured with two different devices: 1) hydraulic potentiomanometer, and 2) pond piezometer. The hydraulic potentiomanometer has previously been referenced in the literature as a minipiezometer (Winter et al., 1988). The device consists of a small diameter (0.75 inch OD) dual-walled stainless-steel probe with a 6-inch screen attached to the lower end of the inner tubing string (Step 1) (Figure 3-2). The hydraulic potentiomanometer is manually pushed into the pond bottom sediments (Step 2) about $1 \frac{1}{2}$ to 4 feet and the outer protective casing is pulled back about 6 inches to expose the screen interval (Step 3). The hydraulic gradient is determined from the difference in water levels between the pond and screen interval measured with an inverted U-tube manometer. One end of the U-tube manometer is connected to the pond and the second end is connected to the inner tubing string of the hydraulic potentiomanometer. Water is pumped into the manometer with a vacuum pump. After all air has been removed from the system, the water levels in the manometer are allowed to fall until equilibrium is reached. The time period for equilibrium depends on the permeability of the material opposite the screen interval and can range from as little as 15 minutes up to 8 or more hours. The water levels are assumed to be at equilibrium when three consecutive water-level readings, spaced 5 to 15 minutes apart, are approximately the same. The difference in head between the pond level and the sediments below the pond can then be used to calculate the magnitude and direction of the hydraulic gradient across the bottom sediments. The flux rate is calculated from Darcy's equation, given the vertical permeability of the pond bottom material.



The second method used to obtain the hydraulic gradient was to install a small diameter (1-inch ID) piezometer with a 1-foot screen interval. Hydraulic-head measurements were made by extending the casing above the pond surface and measuring the water level with an electric water-level probe.

A problem that was encountered with many of the hydraulic potentiomanometer measurements at this site was an apparent short-circuiting of pond water between the outer casing and pond sediments. This short-circuiting was reflected in the data by a negligible difference in head between the pond and sediments. The high clay content of the bottom sediments prevented the sediments from collapsing around the probe as it was pushed to the desired depth. The voids that developed outside of the probe provided a pathway for equalizing heads between the pond and sediments. Piezometers placed in coarser texture materials (ash or saprolite) did not exhibit this shortcircuiting.

<u>Pond Sediments Core Collection</u>. Cores of the pond bottom sediments were collected with a piston core system, because of the low cohesiveness and high saturation of the bottom sediments. The piston core system used at this site consists of three components: 1) a tripod, 2) a piston, and 3) a plastic core sleeve. The piston forms an air-tight seal inside of the core sleeve and the tripod is used to hold the piston stationary as the core is obtained.

The piston is inserted into the base of the core sleeve, which is then placed at the top of the sediment/water interface. The piston is attached to the tripod, and the plastic core sleeve is manually pushed 2 to 5 feet into the sediment as the piston remains stationary. The suction created at the upper end of the core retains the core in the sample tube as the core sleeve is removed from the sediments. The use of this piston sampler resulted in 100-percent recovery of the two cores collected in the pond.

Water Levels and Meteorological Measurements

<u>Groundwater Levels</u>. Depths to groundwater were measured by two different methods: 1) an electric water-level probe, and 2) pressure transducers. An electric waterlevel probe was used for routine measurements and as a basis for the measurements made using pressure transducers and a data logger. The water-level probe consists of a sensor mounted on the end of an electric cable with depth markings. When the sensor enters the water inside the monitoring well, a buzzer at the surface sounds, notifying the operator. The depth of the sensor is then recorded from the calibrated cable. This depth represents the depth of the water surface below the

measuring point, generally the top of the monitoring-well casing. The elevation of the water surface is determined by subtracting the depth-to-water measurement from the elevation of the measuring point.

Pressure transducers were installed in several wells on the downstream side of the dam in order to collect data more frequently than is feasible using the electric water-level probe. The transducer was installed a short distance below the water surface in the well. The pressure transducers are mounted at the end of a water-proof cable that contains the needed wires for powering the transducer and returning the pressure information to the data logger. The cable also contains thin-diameter plastic tubing for allowing barometric pressure changes to be transmitted to the inside of the transducer. This type of transducer is called a "vented transducer" and is not sensitive to direct changes in barometric pressure because this pressure change is applied to both sides of the sensing device. A barometric pressure change will, however, change the elevation of the water surface, which will be detected by the pressure transducer.

Transducers were calibrated in the field, using the equipment to be used for powering and measuring the transducers. The transducers were calibrated during their initial installation and at the completion of all water sampling events in the wells. Up to ten calibration points were collected, and a calibration curve calculated using linear regressions. Calibration curves are shown in Appendix B. The transducers exhibited excellent linearity; correlation coefficients (r^2) were 0.999 and higher.

Some of the transducers experienced a shift in the intercept and were replaced. The cause of the shift is not known, but nearby lightning strikes are suspected.

A data logger was used to record the output from the transducers. The data logger records time and pressure information in a solid-state memory module, which contains its own battery to protect against data loss. The data logger is connected to a modem and phone line so that 1) the status of the data logger and transducer can easily be determined, 2) data may periodically be retrieved, and 3) the data logger can be reprogrammed if necessary, all without requiring a trip to the site. The data logger was programmed to record water levels at 30 minute intervals. In addition, if a water level change of greater than 0.1 feet occurred, the data logger recorded the new levels. This feature allowed short-lived events to be recorded.

Water-level measurements were made with an electric water-level probe approximately every 2 weeks for all wells around the ash basin. The electric water-level probe was used to confirm the pressure-transducer data whenever the transducers were removed to allow water sampling. The water-level measurements are presented and discussed in Section 5.

<u>Pond Water Levels</u>. Water levels in the primary and secondary ponds are largely controlled by the elevation of the spillways in the control towers. The water levels in the pond vary because of several factors, with the most important one being the rate at which water enters the ponds. The water needs of the generating station vary depending on the demand for power, and thus the discharge from the station also varies. Water also enters the ponds from surface runoff and from yard drains, so that more water enters the ponds during and following storms.

The water level in the primary pond was measured approximately every 2 weeks by referring the water surface to a staff gage permanently mounted on the discharge tower. The utility routinely determines the discharge from the secondary pond into the river. These data are presented in Section 5.

<u>Meteorological Measurements</u>. Meteorological data are available from several sources. The utility maintains a rain gage at the site. Temperature data are measured using a thermocouple incorporated into the CR-21X data logger. Rainfall and temperature data are also available from a weather station about ten miles from the site. Class A pan evaporation data are collected at a university research station about 20 miles away.

Laboratory Measurements of Physical Properties

The following measurements were performed on selected segments of core:

- Saturated hydraulic conductivity constant-head (ASTM D2434-68) and falling-head (Methods of Soil Analysis, 1982) permeameters;
- Bulk density oven dry mass (ASTM D2216-80 or D4643-87) and volume;
- Particle density water pycnometer (ASTM D854-83);
- Porosity calculated;
- Moisture content change in mass upon oven drying (ASTM D2216-80); and
- Grain-size distribution sieve and hydrometer analyses (ASTM D422-63(72)).

Results are discussed in Section 5.

Samples selected for analysis were primarily restricted to the saturated zone, since characterization of the unsaturated zone was not considered important for two reasons: 1) the by-products and waste are managed in a pond, so an unsaturated zone beneath the management site was not expected (and was not found in our investigation); and 2) the water levels between the pond and the river were expected to vary only slightly because of the influences of the pond and the river on limiting fluctuations of the water table.

Most of the samples for physical property measurements were obtained from cores collected at the same depths where the well screens were installed, so that the screened intervals would be well-characterized. In addition, samples collected higher in the borehole were analyzed to provide information over the range of lithologies encountered. No bedrock cores were analyzed because the hydraulic properties of the bedrock would be primarily determined by the presence and characteristics of fractures. A total of 35 samples were analyzed for physical properties, including the two pond bottom cores.

The cores of unconsolidated material were collected in polycarbonate liners, which were capped and wrapped to preserve their water content. Subsamples of the core for physical property analysis were obtained by sawing the polycarbonate liner perpendicular to its axis and quickly recapping. Because some loss of water occurred during this process, the water contents measured in the lab may be low. Some of the samples required repacking at the laboratory because the soil material separated from the walls of the liner during shipment. Repacking was done by tamping the sample in the polycarbonate liner on a hard flat surface until no further compaction occurred.

Aquifer Tests

<u>Slug Tests</u>. Slug tests were performed in 13 monitoring wells to provide permeability information. The tests were performed using a solid PVC cylinder (the "slugger", diameter 1.5 inches, length 20 feet) to displace water contained in the monitoring well. This approach avoided injecting or removing water from the well. A 5-psi transducer was fitted into a cavity at the bottom of the PVC cylinder and was used to measure the water-level change in the monitoring well in response to the insertion of the slugger. Once inserted, the slugger was secured at a constant level. A data logger was programmed to automatically record the transducer output when the water level changed by 0.1 foot or more. As a result, the recovery curves are very well defined.

Tests were performed in all monitoring wells except the following:

- LMW-13, which was the pumping well in the multiple-well pumping test.
- LMW-14 and LMW-15, which were completed in the ash. The water levels in these wells were too close to the surface to allow the slugger to be used.
- LMW-19, LMW-21, LMW-22, and LMW-23, which were too short for testing.
- LMW-18, where the water was too deep for testing with the available equipment.
- LMW-20, which was a privately owned well and inaccessible because of an existing pump installed in the well.
- LMW-07, which had a very low permeability and therefore responded very slowly. A test was attempted in this well, and the initial indications were that several weeks to months would be required for completion of the test.

The test results were analyzed using the type curves developed by Cooper, Bredehoeft, and Papadopoulos (1967). Results are presented in Section 5. The hydraulic-conductivity values determined from slug tests are generally representative of conductivity in the horizontal plane because of the geometry of the test.

<u>Multiple-Well Pumping Test</u>. A multiple-well pumping test was performed on the downgradient side of the ash-pond dam. Water was pumped from LMW-13 at approximately 2 1/2 gpm for 14 hours. Water levels were monitored in this well and in LMW-03, LMW-05, LMW-06, and LMW-16 using pressure transducers and the data logger. Manual measurements were made in LMW-07 since little response was expected because of its low permeability. Pumping rates were controlled by a flow valve installed on the discharge pipe. The pumping rates were measured using a calibrated five-gallon bucket and a stop watch. Results are presented in Section 5.

The pressure transducers were calibrated before and after the test, except for the transducer installed in LMW-03. No response was observed in this well, so its transducer was not recalibrated after the test. To ensure that it responded to changes in water level, the transducer was checked by pulling it up a short distance and observing its output with the data logger. The calibration data are presented in Appendix B.

SAMPLE COLLECTION AND FIELD MEASUREMENTS

This section describes the procedures and quality assurance/quality control program used for environmental sample collection and field measurements at the L-site.

Sampling Soil and Ash

Samples of soil and ash were collected at L-site using continuous core sampling systems described earlier in this section (see Core Collection, page 3-3). The physical condition and features of all core samples were described in the field before the cores were sealed and transported to the analytical laboratory.

Samples destined for geochemical evaluations of reactive components required special sample preservation. These cores were placed in an argon-filled glove box immediately after they were removed from the coring device. The ends of the core were capped and taped while inside the glove box. The cores were then removed from the glove box and the capped ends dipped in wax for a secondary seal. When the wax hardened, the cores were placed inside plastic bags and transported to the analytical laboratory in an ice cooler at 4° C.

Sampling Groundwater and Surface Water

Groundwater samples from monitoring wells and surface-water samples from the river, the ash pond, outlet drains from the secondary ash pond, and seeps were collected during two sampling events. A peristaltic pump was used to collect surface water; for groundwater, either a stainless steel bladder pump, peristaltic pump, or bailer was used. A flow cell and filtration system (Figure 3-3) facilitated in-line water filtration and measurement of critical properties, including pH, Eh, conductivity, and temperature.

<u>Purging Groundwater Wells</u>. Each groundwater monitoring well was purged immediately before sample collection to remove filter-pack water and standing water in the well. Monitoring wells were purged using either a bladder pump or a peristaltic pump with the inlet placed at the bottom of the well screen. Purging was considered complete when the indicator parameters of pH, temperature, conductivity, and dissolved oxygen stabilized and a minimum of one wetted borehole volume plus one-half the sand-pack volume were removed from the well.

To determine when stabilization had occurred, pH, temperature, and conductivity were monitored continuously until two successive readings of all three parameters did not vary by more than ± 0.5 pH unit, ± 1.0 °C, and $\pm 10 \mu$ mhos, respectively. Monitoring



well LMW-07, LMW-20, and piezometer PIEZ-3 were low yield wells, that is, the wells were purged dry before the wetted casing volume and sand pack volume were removed. For LMW-07, the water level was allowed to recover once before the well was sampled. For wells LMW-20 and PIEZ-3, the water standing in the casing was sampled; therefore, these analyses were not used in our primary database. Piezometer PIEZ-3 was placed by the utility in the ash pond dam.

<u>Sample Collection</u>. Samples were collected in a prearranged priority so that all collection and handling took place as efficiently as possible. Table 3-1 lists the analytes, sample containers, filtration and preservation requirements, and holding times for liquid samples. Samples were collected by filling the appropriate bottles from the pump discharge tube after removing the flow cell from the sampling train. Field sampling log forms were used to track sample containers, preservation requirements, aliquot (subsample) ID numbers, and other pertinent information during sampling.

Samples of surface water and wastewater were collected by manually inserting the inlet tube of the peristaltic pump about 6 inches into the water at the desired sampling location. Certain ash pond samples were collected at greater depths. To collect samples from the ash sluice line, the inlet tube was inserted into the flowing water stream at the discharge pipe outfall.

Liquid samples were filtered through either glass fiber or 0.45 μ m membrane filters. For certain samples, ultra-filtration using a 0.1 μ m membrane filter was required. The purpose was to remove colloidal material which could pass through the 0.45 μ m filter and influence analytical values for iron, chromium, arsenic, and selenium. To prevent rapid plugging of the membrane filters when heavily sediment-laden water was being sampled, a glass fiber prefilter was placed above the upper filter support screen in the filter holder. Samples were preserved using the reagents and protocols listed in Table 3-1.

Field Measurements

All liquid samples were characterized in the field for the analytes listed in Table 3-2.

Sample Quality Assurance and Quality Control

The quality assurance objectives for sample collection and field measurements were as follows:

Table 3-1

LIQUID SAMPLE COLLECTION SPECIFICATIONS

Aliquot	Species Sought	Filter Material	Preservation	Container Material ^D	Volume Required (mL)	EPA Holding ^b
A	Total Dissolved Solids (Filterable Residue)	Membrane ^a	None	Plastic	250	,
В	Chloride Fluoride Sulfate	Membrane	4°C 4°C 4°C	Plastic	1000	28 days 28 days 28 days
С	Total Inorganic Carbon	Glass fiber	4°C	Glass (amber)	120	
D	Total Organic Carbon	Glass fiber	4°C, phosphoric acid	Glass (amber)	120	28 days
E	Sulfite Thiosulfate	Membrane Membrane	Formaldehyde, tetraborate buffer	Plastic	125	
F	Sulfide	Membrane	Sodium hydroxide, zinc acetate	Plastic	500	7 days
G	Nitrate and nitrite Total Phosphorus Ammonia	Membrane Membrane	Sulfuric acid, pH <2, 4°C Sulfuric acid, pH <2, 4°C Sulfuric acid, pH <2, 4°C	Plastic	500	28 days
н	Cations & Trace Species	Membrane	Nitric acid, pH <2	Plastic	500	6 months
I	Alkalinity	Membrane	Fill container completely	Plastic	125	Collect 5%
J	Extra Aliquot	Membrane	4°C	Plastic	500	for analyti- cal QC
К	Indicators (cations)	None	Nitric acid, pH <2, 4°C	Plastic	125	6 months
L	Indicators (anions)	None	4°C	Plastic	500	28 days
м	Arsenic III and V	Membrane (0.1 um)	Dry ice	Plastic	60	None estb.
N	Chromium III and VI	Membrane (0.1 um)	Hydrochloric acid, pH 3, 4°C	Plastic	250	None estb.
0	Iron II and III	Membrane (0.1 um)	2 mL Hydrochloric acid, 4°C	Plastic	. 1000	None estb.
Ρ	Selenium IV & VI	Membrane (0.1 um)	Hydrochloric acid, pH 1.5, 4°C	Plastic	60	None estb.

^a0.45 μm filter

^bSource: U.S. EPA, 1983, pp. xvi-xviii.

Table 3-2

FIELD ANALYSIS OF LIQUID SAMPLES^a

Analyte	Method	Reference
Temperature	Thermometer	EPA Method 170.1
рН	pH Electrodes	EPA Method 9040
Eh	Potentiometric	ASTM D 1498
Electrical conductance	Wheatstone bridge conductivity meter	EPA Method 9050
Alkalinity	Potentiometric titration	Skougstad, et al., 1979

^aLiquid samples for field analysis included pond water, river water, groundwater, ash sluice water, and seeps.

- To obtain representative samples of soils, ash, groundwater, pond water, and river water;
- To analyze samples immediately for unstable properties that could change rapidly once samples were collected;
- To preserve sample integrity during transport to the laboratory so that the composition and properties of the materials could be determined as accurately as possible; and
- To provide complete, accurate records to document the number and types of samples collected, field measurements, sample preservation, sample handling, and chain-of-custody procedures.

<u>Sampling Quality Control</u>. Quality control procedures were an integral part of each sampling methodology and included procedures that ensured the collection of representative samples that were free from external contamination. The following quality control procedures were followed:

- 1. Sampling equipment was thoroughly rinsed with deionized water between sampling locations to prevent cross-contamination of the samples.
- 2. Field equipment blanks were collected routinely, at a minimum frequency of one per 20 field samples (5%). These consisted of equipment rinses using reagent-grade deionized water of one piece of each type of sampling equipment (groundwater pump, core barrel sleeve, etc.) before sample collection. These samples were labeled as equipment rinse blanks on the sample documentation records. They served as a check on sampling equipment cross-contamination between sampling locations.
- 3. Split samples for duplicate analyses were collected at a frequency of 5% (1 set per 20 field samples). At least one sample split duplicate was collected for each matrix (e.g., groundwater, pond water) sampled.
- 4. Chain-of-custody forms accompanied all samples.

<u>Storage and Transportation</u>. All liquid and solid samples were kept in coolers containing enough ice to keep the samples between 0° and 4°C from immediately after collection until analysis. Liquid samples were packed in a secure, upright position; protective packing was used to minimize the risk of container breakage during shipping; and absorbent material (vermiculite) was used to ensure against leakage during transport in case of bottle breakage. The coolers containing the samples were sealed using duct tape or a suitable packaging tape. Chain-of-custody forms were affixed to the inside top of the coolers and the samples shipped by overnight delivery to the appropriate laboratory.

LABORATORY ANALYSIS

Analysis of Aqueous Samples

Laboratory tests used to measure concentrations of chemical species present in major, minor, and trace concentrations in aqueous samples are listed in Table 3-3. The table lists analytes, method description and references, and method detection limits. Most of these tests are derived from standard tests used to measure water quality. Standard method references are supplied for most techniques in Table 3-3. Methods for alkalinity, total inorganic carbon, silicon, and thiourea were taken from other literature sources, or developed by Radian Corporation personnel. In some cases minor changes were made to standard techniques to apply them to the samples being measured. Actual detection limits are listed with each measurement in Appendix C. In most cases the actual detection limit and the method detection limit are the same, but in some cases samples had to be diluted for a particular test and the actual detection limit increased.

Analysis of Solid Samples

<u>Chemical Analyses</u>. Tests used to measure concentrations of chemical species in solids were similar to those used to analyze aqueous samples, but the solids had to be dissolved in water before the analyses were performed. Several techniques were used to obtain aqueous solutions of solids, depending on the analyte and the desired information. Elements present in minor and trace concentrations were measured in solutions that had been obtained by digesting the solid in a mixture of nitric acid, hydrochloric acid, and tetrafluoroboric acid in a microwave oven. To obtain the concentrations of major elements, the solids were mixed with lithium metaborate and fused. The cooled melt was dissolved in dilute hydrochloric acid and the solution was analyzed for calcium, iron, magnesium, potassium, and sodium using atomic absorption spectrophotometry and for aluminum and silicon using inductively coupled plasma emission spectrometry.

Boron was measured on four of the solid samples by fusing the sample in sodium carbonate and measuring the boron concentration using inductively coupled plasma emission spectrometry. Water soluble anions were determined by extracting the solid with water, measuring the anionic concentrations in the extract using ion chromatography, and calculating the amount of each anion dissolved in water. The weight of water used was twice the weight of the dry solids. Sulfate was extracted with dilute hydrochloric acid and measured in an analogous way.

Table 3-3

TEST METHODS AND METHOD DETECTION LIMITS FOR AQUEOUS SAMPLES FROM L-SITE

Test	Method	Method Detection _Limits	Units
WATER QUALITY VARIABLES Electric Conductivity Filterable Residue Eh Value Temperature pH Value ANIONS AND AMMONIA Alkalinity Ammonia Bromide	Wheatstone Bridge; APHA 205 Gravimetric Analysis; EPA 160.1 Potentiometry; ASTM D 1498 Thermometry; EPA 170.1 Potentiometry; EPA-9040 Titrimetry ¹ Spectrophotometry; SW846-417C Ion Chromatography; EPA 300.0	10 8 NA NA NA 1 0.01 0.04 6	micromhos/cm mg/L mV Degrees C pH Units mg HCO ₃ /L mg N/L mg/L mg HCO ₂ /L
Total Inorganic Carbon Chloride Fluoride Nitrate/Nitrite Organic Carbon Phosphate, Total Silicon Sulfate Sulfide Sulfite Sulfite Thiosulfate Thiourea	Nondispersive Infrared ² Ion Chromatography; EPA 300.0 Ion Chromatography; EPA 340.2 Spectrophotometry; EPA 353.3 Nondispersive Infrared; EPA 415.1 Spectrophotometry ³ Ion Chromatography; EPA 300.0 Titrimetry, EPA 376.1, 376.2 Adapted from EPA 300.0 Titrimetry; Iodine Oxidation Adapted from EPA 300.0 High Performance Liquid Chromatography ⁴	0.2 0.001 0.05 0.5 0.05 1.0 0.5 0.32 0.08 2 0.3 0.5	mg hco ₃ /c mg/L mg N/L mg C/L mg Si/L mg/L mg/L mg/L mg/L mg/L mg/L
ELEMENTS Arsenic Calcium Chromium Copper Lead Magnesium Potassium Selenium Sodium	Hydride Generation AA; EPA 206.3 Flame AA; EPA 215.1 Graphite Furnace AA; EPA 218.2 Graphite Furnace AA; EPA 220.2 Graphite Furnace AA; EPA 239.2 Flame AA; EPA 243.1 Flame AA; EPA 258.1 Hydride Generation AA; EPA 270.3 Flame AA; EPA 273.1	0.002 0.1 0.001 0.002 0.1 0.1 0.002 0.001	mg/L mg/L mg/L mg/L mg/L mg/L mg/L mg/L

Table 3-3

(Continued)

Test Method Limits Units ELEMENTS Iuminum ICPES; EPA 200.7 0.2 mg/L Antimony ICPES; EPA 200.7 0.3 mg/L Arsenic ICPES; EPA 200.7 0.3 mg/L Barium ICPES; EPA 200.7 0.01 mg/L Beryllium ICPES; EPA 200.7 0.002 mg/L Boron ICPES; EPA 200.7 0.66 mg/L Cadmium ICPES; EPA 200.7 0.005 mg/L Calcium ICPES; EPA 200.7 0.03 mg/L Calcium ICPES; EPA 200.7 0.03 mg/L Cobalt ICPES; EPA 200.7 0.03 mg/L Cobalt ICPES; EPA 200.7 0.02 mg/L Iron ICPES; EPA 200.7 0.02 mg/L Iron ICPES; EPA 200.7 0.04 mg/L Lead ICPES; EPA 200.7 0.05 mg/L Maganeseum ICPES; EPA 200.7 0.01 mg/L Maganeseum ICPES; EPA 200.7 0.01 mg/L Maganeseum ICPES; EPA 200.7 0.02 mg/L Manganeseum ICPES; EPA 200.7 0.02 mg/L			Method	
ELEMENTS ICPES; EPA 200.7 0.2 mg/L Antimony ICPES; EPA 200.7 0.2 mg/L Arsenic ICPES; EPA 200.7 0.3 mg/L Barium ICPES; EPA 200.7 0.3 mg/L Beryllium ICPES; EPA 200.7 0.01 mg/L Boron ICPES; EPA 200.7 0.002 mg/L Cadmium ICPES; EPA 200.7 0.002 mg/L Cadmium ICPES; EPA 200.7 0.005 mg/L Calcium ICPES; EPA 200.7 0.005 mg/L Cobalt ICPES; EPA 200.7 0.03 mg/L Cobalt ICPES; EPA 200.7 0.01 mg/L Copper ICPES; EPA 200.7 0.01 mg/L Iron ICPES; EPA 200.7 0.02 mg/L Magnesium ICPES; EPA 200.7 0.04 mg/L Madgnesium ICPES; EPA 200.7 0	Test	Method	Detection	Units
Aluminum ICPES; EPA 200.7 0.2 mg/L Antimony ICPES; EPA 200.7 0.3 mg/L Arsenic ICPES; EPA 200.7 0.3 mg/L Barium ICPES; EPA 200.7 0.01 mg/L Beryllium ICPES; EPA 200.7 0.002 mg/L Boron ICPES; EPA 200.7 0.002 mg/L Cadmium ICPES; EPA 200.7 0.005 mg/L Calcium ICPES; EPA 200.7 0.005 mg/L Calcium ICPES; EPA 200.7 0.03 mg/L Cabalt ICPES; EPA 200.7 0.03 mg/L Cobalt ICPES; EPA 200.7 0.01 mg/L Copper ICPES; EPA 200.7 0.01 mg/L Iron ICPES; EPA 200.7 0.02 mg/L Iron ICPES; EPA 200.7 0.04 mg/L Lead ICPES; EPA 200.7 0.01 mg/L Magnesium ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.02 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L <td>FI FMENTS</td> <td></td> <td></td> <td></td>	FI FMENTS			
Antimony ICPES; EPA 200.7 0.2 mg/L Arsenic ICPES; EPA 200.7 0.3 mg/L Barium ICPES; EPA 200.7 0.01 mg/L Beryllium ICPES; EPA 200.7 0.002 mg/L Beron ICPES; EPA 200.7 0.002 mg/L Cadmium ICPES; EPA 200.7 0.6 mg/L Cadmium ICPES; EPA 200.7 0.005 mg/L Cadmium ICPES; EPA 200.7 0.005 mg/L Calcium ICPES; EPA 200.7 0.003 mg/L Copper ICPES; EPA 200.7 0.01 mg/L Copper ICPES; EPA 200.7 0.02 mg/L Iron ICPES; EPA 200.7 0.04 mg/L Lead ICPES; EPA 200.7 0.05 mg/L Magnesium ICPES; EPA 200.7 0.05 mg/L Malganese ICPES; EPA 200.7 0.05 mg/L Malganese ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.02 mg/L Nickel ICPES; EPA 200.7 0.3 m	Δluminum	ICPES: EPA 200.7	0.2	ma/L
Arsenic ICPES; EPA 200.7 0.3 mg/L Barium ICPES; EPA 200.7 0.01 mg/L Beryllium ICPES; EPA 200.7 0.002 mg/L Boron ICPES; EPA 200.7 0.66 mg/L Cadmium ICPES; EPA 200.7 0.005 mg/L Cadrium ICPES; EPA 200.7 0.005 mg/L Calcium ICPES; EPA 200.7 0.003 mg/L Chromium ICPES; EPA 200.7 0.01 mg/L Cobalt ICPES; EPA 200.7 0.01 mg/L Cobalt ICPES; EPA 200.7 0.01 mg/L Copper ICPES; EPA 200.7 0.02 mg/L Iron ICPES; EPA 200.7 0.02 mg/L Magnesium ICPES; EPA 200.7 0.04 mg/L Manganese ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.02 mg/L Manganese ICPES; EPA 200.7 0.02 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L Selenium ICPES; EPA 200.7 0.3 <	Antimony	ICPES: FPA 200 7	0.2	ma/L
Barium ICPES; EPA 200.7 0.01 mg/L Beryllium ICPES; EPA 200.7 0.66 mg/L Boron ICPES; EPA 200.7 0.66 mg/L Cadmium ICPES; EPA 200.7 0.005 mg/L Calcium ICPES; EPA 200.7 0.03 mg/L Calcium ICPES; EPA 200.7 0.03 mg/L Cobalt ICPES; EPA 200.7 0.01 mg/L Cobalt ICPES; EPA 200.7 0.01 mg/L Copper ICPES; EPA 200.7 0.02 mg/L Iron ICPES; EPA 200.7 0.04 mg/L Lead ICPES; EPA 200.7 0.05 mg/L Magnesium ICPES; EPA 200.7 0.01 mg/L Magnesium ICPES; EPA 200.7 0.01 mg/L Magnese ICPES; EPA 200.7 0.02 mg/L Molybdenum ICPES; EPA 200.7 0.02 mg/L Nickel ICPES; EPA 200.7 0.3 mg/L Selenium ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 0.3 mg/L <td>Arsenic</td> <td>ICPES: EPA 200.7</td> <td>0.3</td> <td>ma/L</td>	Arsenic	ICPES: EPA 200.7	0.3	ma/L
Beryllium ICPES; EPA 200.7 0.002 mg/L Boron ICPES; EPA 200.7 0.66 mg/L Cadmium ICPES; EPA 200.7 0.005 mg/L Calcium ICPES; EPA 200.7 0.005 mg/L Calcium ICPES; EPA 200.7 0.003 mg/L Cobalt ICPES; EPA 200.7 0.01 mg/L Cobalt ICPES; EPA 200.7 0.01 mg/L Copper ICPES; EPA 200.7 0.02 mg/L Iron ICPES; EPA 200.7 0.04 mg/L Lead ICPES; EPA 200.7 0.05 mg/L Magnesium ICPES; EPA 200.7 0.01 mg/L Magnese ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.02 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L Selenium ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 0.3 mg/L Sodium ICPES; EPA 200.7 0.03	Rarium	ICPES: EPA 200.7	0.01	mg/L
Boron ICPES; EPA 200.7 0.6 mg/L Cadmium ICPES; EPA 200.7 0.005 mg/L Calcium ICPES; EPA 200.7 1 mg/L Chromium ICPES; EPA 200.7 0.03 mg/L Cobalt ICPES; EPA 200.7 0.01 mg/L Copper ICPES; EPA 200.7 0.01 mg/L Iron ICPES; EPA 200.7 0.01 mg/L Lead ICPES; EPA 200.7 0.04 mg/L Lead ICPES; EPA 200.7 0.05 mg/L Magnesium ICPES; EPA 200.7 0.01 mg/L Magnesium ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.01 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L Selenium ICPES; EPA 200.7 0.03 mg/L Silicon ICPES; EPA 200.7 0.3	Bervllium	ICPES: FPA 200.7	0.002	mq/L
Cadmium ICPES; EPA 200.7 0.005 mg/L Calcium ICPES; EPA 200.7 1 mg/L Chromium ICPES; EPA 200.7 0.03 mg/L Cobalt ICPES; EPA 200.7 0.03 mg/L Cobalt ICPES; EPA 200.7 0.01 mg/L Copper ICPES; EPA 200.7 0.02 mg/L Iron ICPES; EPA 200.7 0.04 mg/L Lead ICPES; EPA 200.7 0.04 mg/L Magnesium ICPES; EPA 200.7 0.05 mg/L Manganese ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.02 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L Selenium ICPES; EPA 200.7 0.02 mg/L Silicon ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 0.03<	Boron	ICPES: EPA 200.7	0.6	mg/L
Calcium ICPES; EPA 200.7 1 mg/L Chromium ICPES; EPA 200.7 0.03 mg/L Cobalt ICPES; EPA 200.7 0.01 mg/L Copper ICPES; EPA 200.7 0.02 mg/L Iron ICPES; EPA 200.7 0.04 mg/L Lead ICPES; EPA 200.7 0.05 mg/L Magnesium ICPES; EPA 200.7 0.01 mg/L Magnese ICPES; EPA 200.7 0.01 mg/L Magnese ICPES; EPA 200.7 0.01 mg/L Magnese ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.02 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L Selenium ICPES; EPA 200.7 1 mg/L Silicon ICPES; EPA 200.7 0.03 mg/L Silicon ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 0.003 mg/L <td>Cadmium</td> <td>ICPES: EPA 200.7</td> <td>0.005</td> <td>mg/L</td>	Cadmium	ICPES: EPA 200.7	0.005	mg/L
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Cobalt ICPES; EPA 200.7 0.01 mg/L Copper ICPES; EPA 200.7 0.02 mg/L Iron ICPES; EPA 200.7 0.04 mg/L Lead ICPES; EPA 200.7 0.05 mg/L Magnesium ICPES; EPA 200.7 0.01 mg/L Magnesium ICPES; EPA 200.7 0.01 mg/L Magnese ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.02 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L Potassium ICPES; EPA 200.7 0.02 mg/L Selenium ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 0.03 mg/L Siliver ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 0.03 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Strontium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.02 mg/L Vanadium ICPES; EPA 200.7 0.02 <	Chromium	ICPES; EPA 200.7	0.03	mg/L
Copper ICPES; EPA 200.7 0.02 mg/L Iron ICPES; EPA 200.7 0.04 mg/L Lead ICPES; EPA 200.7 0.05 mg/L Magnesium ICPES; EPA 200.7 1 mg/L Magnesium ICPES; EPA 200.7 0.01 mg/L Manganese ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.05 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L Potassium ICPES; EPA 200.7 0.3 mg/L Selenium ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 0.03 mg/L Siliver ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 0.03 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Strontium ICPES; EPA 200.7 0.1 mg/L Strontium ICPES; EPA 200.7 0.02 mg/L Thallium ICPES; EPA 200.7 0.02 <td>Cobalt</td> <td>ICPES; EPA 200.7</td> <td>0.01</td> <td>mg/L</td>	Cobalt	ICPES; EPA 200.7	0.01	mg/L
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Lead ICPES; EPA 200.7 0.05 mg/L Magnesium ICPES; EPA 200.7 1 mg/L Manganese ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.05 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L Potassium ICPES; EPA 200.7 0.02 mg/L Selenium ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 0.3 mg/L Silver ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 0.03 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Thallium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.1 mg/L Zinc ICPES; EPA 200.7 0.02 mg/L	Iron	ICPES; EPA 200.7	0.04	mg/L
Magnesium ICPES; EPA 200.7 1 mg/L Manganese ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.05 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L Potassium ICPES; EPA 200.7 3 mg/L Selenium ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 1 mg/L Siliver ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 0.03 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Strontium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.02 mg/L	Lead	ICPES; EPA 200.7	0.05	mg/L
Manganese ICPES; EPA 200.7 0.01 mg/L Molybdenum ICPES; EPA 200.7 0.05 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L Potassium ICPES; EPA 200.7 0.3 mg/L Selenium ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 0.03 mg/L Silver ICPES; EPA 200.7 1 mg/L Sodium ICPES; EPA 200.7 0.03 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Manganese ICPES; EPA 200.7 0.003 mg/L Strontium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.02 mg/L	Magnesium	ICPES; EPA 200.7		mg/L
Molýbdenum ICPES; EPA 200.7 0.05 mg/L Nickel ICPES; EPA 200.7 0.02 mg/L Potassium ICPES; EPA 200.7 3 mg/L Selenium ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 1 mg/L Silver ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 0.03 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Thallium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.02 mg/L Zinc ICPES; EPA 200.7 0.02 mg/L	Manganese	ICPES; EPA 200.7	0.01	mg/L
Nickel ICPES; EPA 200.7 0.02 mg/L Potassium ICPES; EPA 200.7 3 mg/L Selenium ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 1 mg/L Silver ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 0.03 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Thallium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.02 mg/L Zinc ICPES; EPA 200.7 0.02 mg/L	Molybdenum	ICPES; EPA 200.7	0.05	mg/L
Potassium ICPES; EPA 200.7 3 mg/L Selenium ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 1 mg/L Silver ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 0.03 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Thallium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.02 mg/L Zinc ICPES; EPA 200.7 0.02 mg/L	Nickel	ICPES; EPA 200.7	0.02	mg/L
Selenium ICPES; EPA 200.7 0.3 mg/L Silicon ICPES; EPA 200.7 1 mg/L Silver ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 0.03 mg/L Strontium ICPES; EPA 200.7 1 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Thallium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.02 mg/L Zinc ICPES; EPA 200.7 0.02 mg/L	Potassium	ICPES; EPA 200.7	3	mg/L
Silicon ICPES; EPA 200.7 1 mg/L Silver ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 1 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Thallium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.02 mg/L Zinc ICPES; EPA 200.7 0.02 mg/L	Selenium	ICPES; EPA 200.7	0.3	mg/L
Silver ICPES; EPA 200.7 0.03 mg/L Sodium ICPES; EPA 200.7 1 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Thallium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.02 mg/L Zinc ICPES; EPA 200.7 0.02 mg/L	Silicon	ICPES; EPA 200.7	1	mg/L
Sodium ICPES; EPA 200.7 1 mg/L Strontium ICPES; EPA 200.7 0.003 mg/L Thallium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.02 mg/L Zinc ICPES; EPA 200.7 0.02 mg/L	Silver	ICPES; EPA 200.7	0.03	mg/L
Strontium ICPES; EPA 200.7 0.003 mg/L Thallium ICPES; EPA 200.7 0.1 mg/L Vanadium ICPES; EPA 200.7 0.02 mg/L Zinc ICPES; EPA 200.7 0.02 mg/L	Sodium	ICPES; EPA 200.7	1	mg/L
ThalliumICPES; EPA 200.70.1mg/LVanadiumICPES; EPA 200.70.02mg/LZincICPES; EPA 200.70.02mg/L	Strontium	ICPES; EPA 200.7	0.003	mg/L
Vanadium ICPES; EPA 200.7 0.02 mg/L Zinc ICPES; EPA 200.7 0.02 mg/L	Thallium	ICPES; EPA 200.7	0.1	mg/L
Zinc ICPES; EPA 200.7 0.02 mg/L	Vanadium	ICPES; EPA 200.7	0.02	mg/L
	Zinc	ICPES; EPA 200.7	0.02	mg/L

AA - Atomic Absorption Spectrophotometry
 ICPES - Inductively Coupled Plasma Emission Spectrometry
 NA - Not Applicable

¹From M.W. Skougstad et al., <u>Techniques of Water Resource Investigations, Book 5</u>, USGS, 1979.

²Adapted from Dohrman DC-80 Instrument Instructions, Xertex Corp., Santa Clara, CA, 1985.

¹From C.T. Hallmart et al., In A.L. Page (ed.) <u>Methods of Soil Analysis, Part 2</u>, Soil Sci. Soc. Am., Agronomy Monograph No. 9, 1982. ⁴Developed by Neal Amick for Radian Corp.

<u>Geochemical Analyses</u>. Geochemical analyses on core samples included extraction and analysis of pore water, determination of cation exchange capacity and exchangeable cations, and extractable iron.

Two extraction techniques were used to analyze pore waters: pressure filtration with nitrogen and immiscible displacement with $Freon^{\oplus 1}$ 113. Both sets of pore waters were analyzed for major and trace constituents using a variety of techniques. Metals and boron were analyzed using inductively coupled argon plasma (ICPES) spectroscopy. Anions, such as sulfate and chloride, were analyzed using ion chromatography. Ammonia and iron species were also analyzed using IC. Fluoride was determined using an ion-selective electrode (ISE). Arsenic species were determined using graphite-furnace atomic absorption (GFAA) spectroscopy. Cation exchange capacities (CECs) were determined on all four cores using the ²²Na isotope method (Babcock and Schulz, 1969). Extractable iron was measured on core samples using the hydroxylamine hydrochloride method (Tessier et al., 1985). This method has been shown to give a good estimate for the amount of amorphous iron in samples. Amorphous iron is one of the major adsorbing oxides that contribute to specific adsorption in many samples.

Laboratory Quality Assurance and Quality Control

A number of quality control, quality assurance, and data evaluation activities were performed to determine and to document the reliability of the data.

Quality control activities conducted within the laboratory included:

- Following prescribed procedures;
- Carefully calibrating instruments; and
- Analyzing quality control check samples (calibration check samples), analytical blanks, analytical duplicates, and spiked samples.

Quality control limits for analyses carried out in the laboratory are listed in Table 3-4. If the measuring system did not produce results within the limits stated, corrective actions were taken to bring the test within control limits and the analysis was repeated. If it was not possible to bring the QC test results within the control limits, the data were flagged in the data base. One example of inability to bring a QC test within control limits occurred for some analytical

¹Freon[®] is a trademark of E. I. du Pont de Nemours & Co., Wilmington, Delaware.

Table 3-4

SUMMARY OF QUALITY CONTROL LIMITS FOR ANALYSIS OF AQUEOUS SAMPLES FROM L-SITE

		Correlation	or				Matrix
		for	Check	Analytical	Analytical	Matrix	Spike
Test	Method	Calibration	Sample	Blanks	Duplicates	Spike	Duplicate
1030	<u> </u>	<u>uut tut uut tut</u>	<u>anne ra</u>				
ANIONS AND AMMONIA							
Alkalinity	Titrimetric	NA	None	None	None	None	None
Ammonia	Spectrophotometric	>0.995	60-140%	NS	None	60-140%	RPD <40%
Bromide	Ion Chromatography	>0.995	95-105%	NS	RPD <10%	85-115%	None
Inorganic Carbon	NDIR	>0.995	90-110%	<2 x MDL	RPD <10%	None	None
Chloride	Ion Chromatography	>0.995	95-105%	NS	RPD <10%	85-115%	None
Fluoride	Ion Selective Elect	>0.995	90-110%	NS	RPD <10%	90-110%	None
Nitrate/Nitrite	Spectrophotometric	>0.995	90-110%	NS	None	85-115%	RPD <20%
Organic Carbon	NDIR	>0.995	90-110%	NS	RPD <20%	None	None
Phosphate, total	Spectrophotometric	>0.995	60-140%	NS	RPD <40%	60-140%	None
Silicon	Spectrophotometric	>0.995	60-140%	NS	RPD <40%	60-140%	None
Sulfate	Ion Chromatography	>0.995	95-105%	NS	RPD <10%	85-115%	None
Sulfide	Titrimetric	NA	None	None	NS	None	None
Sulfite	Ion Chromatography	>0.995	95-105%	NS	RPD <10%	85-115%	None
Sulfite	Titrimetric	None	None	NS	NS	None	None
Thiosulfate	Ion Chromatography	>0.995	95-105%	NS	RPD <10%	85-115%	None
Thiourea	HPLC	NS	50-150%	None	RPD <10%	70-130%	None
Elements (1)	Atomic Absorption	>0.995	85-115%	<5 x MDL	No	75-125%	RPD <20%
Elements (2)	ICPES	Within 10%	90-110%	<5 x MDL	No	75-125%	RPD <20%
		of esti-					

NA = Not Applicable
NS = This quality control test was performed but control limit was not specified.
None = This quality control activity was not scheduled and was not performed.
MDL = Method Detection Limit

duplicates; a low analyte concentration made replicate measurements differ by a relatively high percentage even though the absolute difference was small. Appendix K presents the results of the quality assurance program.

Quality assurance activities included:

- Analyzing audit samples (samples of known composition prepared by the Radian quality control group);
- Analyzing some samples by two analytical techniques; and
- Analyzing some samples in Radian's laboratory and in Battelle's Pacific Northwest laboratory.

Data evaluation techniques for quality control included:

- Preparing plots of calculated vs measured alkalinity;
- Calculating charge balances for aqueous samples; and
- Calculating major components of solids as if they were present as oxides, and comparing the sum of the oxides to 100 percent.

Section 4

ASH, WASTE, AND SOIL CHARACTERISTICS

This section presents the results of characterizations of the ash and geologic materials collected at L-site and data on the composition of co-managed low volume waste streams. Samples for physical-property measurements were obtained from cores collected at the depth at which the well screens were installed. In addition, samples collected higher in the borehole were analyzed to provide information over the range of lithologies encountered. Samples for chemical and geochemical analysis were collected from four boreholes -- two located in the ash delta, one in a background control area, and one in an area downgradient of the ash pond. No analyses of low volume waste streams were made for this project, but results from previous investigations are presented for comparative purposes.

ASH AND SOIL PHYSICAL PROPERTIES

The following paragraphs present results of grain-size, hydraulic conductivity, porosity, and moisture-content measurements on geologic materials.

Grain-Size Analyses

The grain sizes of the lithologic materials at the L-site were measured by two methods: 1) a mechanical sieve for particles larger than 75 μ m in diameter, and 2) a hydrometer for particles with a diameter less than 75 μ m. The 75 μ m size corresponds to the lower grain-size limit of a fine sand.

The grain-size analyses indicate that 14 of the 19 samples analyzed have a lithologic classification of sand and the remaining 5 samples are classified as a silty sand (Figure 4-1). The abundance of sand-sized grains in the samples is due to the high mica content of the saprolite, which typically exceeds 75 percent.

As will be discussed later, the hydrologic properties of the mica sand deposits are highly dependent on the orientation of the mica platelets. Hence, the sand classification for these deposits is misleading in that the nonspherical shape of the grains results in hydrologic properties that are not reflective of a well-sorted sand deposit.



Hydraulic-Conductivity Measurements

Saturated vertical hydraulic conductivities were measured on core samples of saprolite, partially weathered bedrock, alluvium, fill, and pond bottom sediments. No vertical permeability measurements were performed on cores of the unweathered bedrock. To maintain the cores' structural integrity, the cores were not removed from the polycarbonate liners before permeability measurements were made. In a few cases, the core samples were disturbed during shipping and were repacked prior to performing the measurement. The vertical hydraulic-conductivity values range over four orders of magnitude from 2.26 x 10^{-7} to 1.97 x 10^{-3} cm/sec (Table 4-1).

The vertical hydraulic conductivity of the pond bottom sediments was measured in two core samples from the southern and northern areas of the primary ash pond. The permeabilities of these cores (2.26 x 10^{-7} and 9.90 x 10^{-6} cm/sec) were the lowest vertical hydraulic conductivities measured at the site (Table 4-1).

The vertical hydraulic conductivity of the alluvium, as measured in four core samples, ranges over four orders of magnitude $(3.38 \times 10^{-7} \text{ cm/sec} \text{ in LMW-09 to } 1.97 \times 10^{-3} \text{ cm/sec}$ in LMW-01) (Table 4-1). The alluvium's lithology ranges from a silty sand to a sand with the highest permeability measured in a silty sand. The dominant mineral in the sand-sized fraction is mica. This large range of permeabilities for essentially the same lithologic unit demonstrates the significant effect the orientation of the mica platelets has on the permeability of the sample. The lower permeability values for the alluvium probably represent samples where the mica platelets are oriented perpendicular to the vertical direction and the higher permeability samples have mica platelets oriented parallel to the vertical direction.

The vertical hydraulic conductivity of the saprolite was measured in 20 core samples and ranges over three orders of magnitude from 3.31×10^{-6} to 1.29×10^{-3} cm/sec (Table 4-1). The lithology of the saprolite ranges from a silty sand to a sand, with the predominant lithology being that of a sand. The largest and smallest vertical hydraulic-conductivity values measured for the saprolite are both for a sand lithology. As was the case with the alluvial deposits, the large range in vertical hydraulic-conductivity values for the saprolite may be due to the orientation of the mica platelets.

The vertical hydraulic-conductivity of the partially weathered bedrock was measured in five cores from monitoring well LMW-12. The vertical hydraulic conductivity ranges over less than one order of magnitude from 4.87 x 10^{-5} to 2.44 x 10^{-4} cm/sec (Table 4-1) and the lithology ranges from a silty sand to a sand.

Table 4-1

SATURATED VERTICAL HYDRAULIC-CONDUCTIVITY VALUES FOR CORE SAMPLES FROM THE L-SITE

Stratigraphy	Lithology	Sample <u>Depth (feet)</u>	Well ID	<u>Method of</u> Constant <u>Head</u>	Analysis Falling Head	Vertical Hydraulic Conductivity (cm/sec)
Pond Sediments	Silty Clay	0.4-1.0	Pond-1		Х	2.26x10 ⁻⁷
Fill	Sand*	28.0-28.5	LMW-09		Х	2.96x10 ⁻⁷
Alluvium	Silty Sand	32.6-33.1	LMW-09		Х	3.38x10 ⁻⁷
Fill?	Sand*	30.8-31.5	LMW-09		X	5.05x10 ⁻⁷
Saprolite	Sand*	12.4-12.8	LMW-12		Х	3.31x10 ⁻⁶
Alluvium	Silty Sand	35.1-35.6	LMW-09		Х	3.45x10 ⁻⁶
Pond Sediments	Silty Clay	1.35-1.9	Pond 2		Х	9.90x10 ⁻⁶
Saprolite	Sand*	21.4-21.9	LMW-05		Х	1.62x10 ⁻⁵
Saprolite/Fill?	Sand	31.2-31.6	LMW-02		Х	2.90x10 ⁻⁵
Saprolite	Sand*	17.2-17.7	LMW-13	Х		4.66x10 ⁻⁵
Partially Weathered Bedrock	Sand	36.1-36.6	LMW-12		Х	4.87x10 ⁻⁵
Partially Weathered Bedrock	Sand	25.7-26.1	LMW-12		Х	5.93x10 ⁻⁵
Saprolite	Silty Sand	19.0-19.5	LMW-13	Х		6.01x10 ⁻⁵
Saprolite	Sand	23.5-24.0	LMW-05	Х		7.78x10 ⁻⁵
Saprolite	Sand	30.5-31.0	LMW-08		Х	9.42x10 ⁻⁵
Saprolite/Alluvium	Sand*	30.3-30.8	LMW-10	Х		1.13x10 ⁻⁴
Partially Weathered Bedrock	Silty Sand	34.9-35.4	LMW-12		Х	1.25x10 ⁻⁴
Partially Weathered Bedrock	Sand	37.8-38.2	LMW-12		Х	1.25x10 ⁻⁴
Saprolite	Sand*	21.35-21.85	LMW-13		Х	1.58x10 ⁻⁴
Saprolite	Sand	39.1-39.6	LMW-08	Х		2.00x10 ⁻⁴
Saprolite	Sand*	41.0-41.5	LMW-02		Х	2.01x10 ⁻⁴
Saprolite	Silty Sand*	23.5-24.0	LMW-13		Х	2.12x10 ⁻⁴
Saprolite	Sand	20.3-20.8	LMW-13	Х		2.29x10 ⁻⁴
Partially Weathered Bedrock	Sand*	30.6-31.1	LMW-12	Х		2.44×10^{-4}
Saprolite	Sand	29.6-30.1	LMW-05	Х		2.65x10 ⁻⁴
Saprolite/Fill?	Sand*	30.7-31.0	LMW-17		Х	2.83×10^{-4}
Saprolite	Sand	25.65-26.15	LMW-13		X	3.03x10 ⁻⁴
Saprolite	Silty Sand*	17.55-18.05	LMW-05	Х		3.13×10^{-4}

Table 4-1

(Continued)

				Method of	<u>Analysis</u>	Vertical Hydraulic
Stratigraphy	Lithology	Sample <u>Depth (feet)</u>	Well ID	Constant Head	Falling Head	Conductivity (cm/sec)
Saprolite	Sand	28.0-28.5	LMW-05	X		4.43×10 ⁻⁴
Saprolite	Sand*	20.2-20.7	LMW-05	X		5.70x10 ⁻⁴
Saprolite	Sand*	26.0-26.5	LMW-05	X		5.97x10 ⁻⁴
Saprolite	Sand	18.0-18.5	LMW-13	Х		6.96x10 ⁻⁴
Saprolite	Sand*	15.75-16.25	LMW-05	X		7.70x10 ⁻⁴
Saprolite	Sand*	21.05-21.55	LMW-03	X		1.29x10 ⁻³
Alluvium	Silty Sand*	21.1-21.6	LMW-01	Х		1.97x10 ⁻³

*Based on grain-size analysis

The vertical hydraulic conductivity of the fill material ranges over about three orders of magnitude from 2.96 x 10^{-7} to 2.83 x 10^{-4} cm/sec. In general, the fill material has low vertical hydraulic-conductivity values, because it was compacted during placement.

Frequency plots of the vertical and horizontal log hydraulic-conductivity values indicate distinct differences in conductivity as a function of direction (Figure 4-2). The means of the two sets of measurement differ by more than two orders of magnitude. The differences are probably due to the preferentially horizontal orientation of the mica platelets which reduces the vertical permeability, and to the different measurement methods used in field and laboratory settings.

Porosity and Volumetric Moisture Content

Porosity and moisture-content values were obtained for core samples by measuring the dry bulk density and moisture contents of 35 samples and the particle density of 6 samples. The volumetric moisture content of a sample is equivalent to its porosity if the sample is saturated before the measurement. Porosity values obtained from density measurements on core samples from the L-site are high, ranging from about 29 to 60 percent (Table 4-2). Over 65 percent of the samples have porosity values exceeding 45 percent, with the majority of these samples in the 50- to 55-percent range (Figure 4-3).

The volumetric moisture contents agree with the porosity values calculated from density measurements. Exceptions to this are core samples from LMW-01, LMW-02, and LMW-03, where the moisture contents are significantly lower than the porosity values. These core samples apparently lost water during the approximate five-month storage period prior to their analysis. Hence, the volumetric moisture contents for these cores are not representative of the in situ volumetric moisture contents.

CHEMICAL AND MINERALOGICAL PROPERTIES

Chemical and mineralogical analyses were performed to determine the composition of the coal ash and to obtain evidence of leaching of ash and low-volume waste constituents in soils underlying the ash pond. Analyses were performed on core samples collected at two locations in the ash delta portion of the primary ash pond (LMW-14 and LMW-15) and at a background location (LMW-12). Figure 4-4 is a schematic diagram showing the sampling interval, sample numbers, lithology, and geologic description of the cores.



Table 4-2

SUMMARY OF INITIAL MOISTURE CONTENT, DRY BULK DENSITY, PARTICLE DENSITY AND POROSITY VALUES

			Ir	itial Moi	<u>sture Content</u>	Dry	Particle	
			(iravimetri	c Volumetric	Bulk	Density	
Stratigraphy	<u>Lithology</u>	<u>Well ID</u>	Depth	<u>% q/q</u>	<u>% cm³/cm³</u>	<u>Density</u>	q/cc	<u>Porosity</u>
Saprolite/Alluvium	Sand	LMW-10	30.3-30.8	14.81	28.46	1.92		29.34
Partially Weathered Bedrock	Sand	.LMW-12	25.7-26.1	16.40	30.82	1.88		30.91
Saprolite	Sand	LMW-02	41.0-41.5	4.39	8.09	1.84		32.30
Partially Weathered Bedrock	Sand	LMW-12	36.1-36.6	20.69	37.09	1.79		34.10
Partially Weathered Bedrock	Sand	LMW-12	37.8-38.2	23.60	40.87	1.73	2.78	37.71
Alluvium	SS	LMW-01	21.1-21.6	16.77	27.26	1.63	2.63	38.19
Pond Sediments	SC	Pond-2	1.35-1.9	23.93	39.03	1.63		38.45
Saprolite	Sand	LMW-08	30.5-31.0	19.81	33.75	1.70	2.78	38.71
Saprolite	Sand	LMW-05	29.6-30.1	25.87	40.32	1.56		42.70
Saprolite	Sand	LMW-08	39.1-39.6	27.90	42.45	1.52		44.07
Fill	Sand	LMW-09	28.0-28.5	23.49	35.60	1.52		44.28
Partially Weathered Bedrock	Sand	LMW-12	30.6-31.1	29.99	45.77	1.53	2.78	45.10
Saprolite/Fill?	Sand	LMW-17	30.7-31.0	33.78	50.33	1.49		45.21
Alluvium	SS	LMW-09	32.6-33.1	30.69	44.46	1.45	2.66	45.55
Saprolite	Sand	LMW-13	18.0-18.5	28.78	42.08	1.46		46.25
Saprolite	SS	LMW-13	23.5-24.0	23.34	33.75	1.45		46.83
Saprolite	Sand	LMW-05	20.2-20.7	32.27	45.76	1.42		47.86
Saprolite	Sand	LMW-03	21.05-21.55	19.25	26.31	1.37		49.76
Pond Sediments	SC	Pond-1	0.4-1.0	37.64	49.23	1.31		50.65
Saprolite	Sand	LMW-05	26.0-26.5	35.83	47.18	1.32		51.59
Saprolite/Fill?	Sand	LMW-02	31.2-31.6	22.52	29.59	1.31		51.70
Partially Weathered Bedrock	SS	LMW-12	34.9-35.4	41.45	54.23	1.31		51.90
Saprolite	Sand	LMW-05	28.0-28.5	37.82	49.45	1.31		51.93
Saprolite	Sand	LMW-05	23.5-24.0	40.46	52.75	1.30		52.07
Saprolite	Sand	LMW-13	25.65-26.15	40.67	52.47	1.29		52.57
Saprolite	Sand	LMW-05	21.4-21.9	39.64	50.70	1.28		52.98
Saprolite	SS	LMW-05	17.55-18.05	39.04	49.06	1.26	2.68	53.28
Fill?	Sand	LMW-09	30.8-31.5	39.33	49.81	1.27	2.00	53.44
Saprolite	Sand	LMW-13	17.2-17.7	39.86	49.15	1.23		54.67
Saprolite	Sand	LMW-05	15.75-16.25	44.36	52.84	1.19		56.21

Table 4-2

(Continued)

				<u>Ir</u>	<u>nitial Moi</u> Gravimetri	<u>sture Content</u> c Volumetric	Dry Bulk	Particle Density	
	Stratigraph	y <u>Lithology</u>	<u>Well ID</u>	<u>Depth</u>	<u>% q/q</u>	<u>% cm³/cm³</u>	<u>Density</u>	q/cc	<u>Porosity</u>
4-5	Saprolite	Sand	LMW-12	12.4-12.8	46.10	54.03	1.17		56.92
~	Saprolite	SS	LMW-13	19.0-19.5	50.17	58.33	1.16		57.26
	Alluvium	SS	LMW-09	35.1-35.6	47.67	54.73	1.15		57.79
	Saprolite	Sand	LMW-13	21.35-21.85	50.99	57.14	1.12		58.80
	Saprolite	Sand	LMW-13	20.3-20.8	54.15	58.13	1.07		60.54

SS - Silty Sand SC - Silty Clay





Figure 4-4. Sample of Ash and Geologic Material Collected for Chemical and Geochemical Characterizations

Low Volume Waste Characteristics

The chemical characterization of the low-volume wastes that are co-managed with coal combustion wastes at the L-site was not included in the scope of this project; however, generic data on these waste streams are available from compilations of utility waste management practices. The data summarized below are from the EPRI report <u>Manual for Management of Low-Volume Wastes from Fossil-Fuel-Fired Power Plants</u> (EPRI SC-5281), except as noted.

<u>Boiler Blowdown</u>. Boiler blowdown is required to maintain the high purity standards for water in utility steam boilers. Boiler blowdown contains very low total dissolved solids, generally below the 15 mg/L recommended limit for water quality in high-pressure boilers. Dissolved material typically includes trace quantities of feedwater impurities not removed during treatment such as calcium, sodium, or silicon, trace levels of conditioning chemical such as hydrazine, and dissolved carbonate from air in-leakage. Blowdown is usually generated at the rate of about 150 gpd/MW, although many plants reuse a large portion of the blowdown for other plant operations or recycle blowdown to the boilers after polishing treatment.

<u>Boiler Chemical Cleaning Waste</u>. Boiler cleaning wastes are generated in the process of removing mineral deposits which build up on the internal surfaces of boiler tubes after several years of operation, inhibiting heat transfer to the boiler. The chemical cleaning wastes are somewhat similar to metal finishing industry wastes, containing high concentrations of heavy metals, primarily iron and copper, removed from the boiler and organic or inorganic acids, solvents or complexing agents used in the chemical cleaning solution formulation. Inhibited HCl, citric acid, ammonium bromate, and EDTA are among the commonly used boiler cleaning chemicals. At the Lsite, ammonium bromate is used in conjunction with inhibited HCl in a two-step cleaning process. Additional data on boiler cleanings at the L-site are provided in Appendix A, Tables 1-4.

<u>Coal Pile Runoff</u>. Coal pile runoff volumes are estimated at about 86% of the rainfall incident on the coal storage area. Runoff may contain coal fines and oxidation products of the pyrite present in the coal as an impurity. Pyrite oxidation releases sulfate and iron in the ferrous (+2) oxidation state and increases the acidity of runoff water. Trace metals associated with the pyrite may also be mobilized in acidic runoff.

More alkaline, subituminous coals may contain sufficient buffering capacity to neutralize acidity released by pyrite oxidation. At the L-site, coal pile runoff is estimated at about 70 million gallons per year. The compositions of coal pile runoff samples from several other power plants are listed in Table A-5 in Appendix A.

<u>Cooling Tower Basin Sludge</u>. Cooling tower basin sludge consists of airborne particulates and system debris scrubbed from the air by the cooling water during cooling tower operation and suspended solids settled from the cooling water which collect in the tower basin. Previous analyses of several samples show the material to consist predominantly of clays and iron oxides (EPRI SC-3737, Radian, 1985). Waste volumes are typically a few cubic yards per year. Typical sludge compositions from previous work (Radian 1985) are shown in Table A-6, in Appendix A.

<u>Demineralizer Regenerant</u>. Demineralizer regenerant wastes are produced when the ion exchange beds used to purify boiler make=up water are cleaned of the ions they have removed from the feed water. During regeneration, either acids are used to remove the cations from cation exchange resins, and bases are used to remove anions from anion exchange resins and replace these ions with hydrogen or ions. The waste consists of common salts removed from the feed water in solution with excess acid or base. Average waste flows in coal fired plants are about 100 gpd/MW. Typical compositions found in previous studies (Radian, 1985) are shown in Table A-7 in Appendix A.

<u>Fireside Wash-Water</u>. Fireside wash wastes are generated when particulate materials such as soot or slag are washed off of the boiler tubes, where their accumulation lowers the efficiency of heat transfer to the boiler. Calcium, magnesium, and other elements common to fly ash are the primary dissolved ions in fireside wash waters from coal fired boilers. Chemical additives may be used to enhance the cleaning power of wash solutions, although mechanical washing is generally most effective on the slag deposits typical in coal fired units. Waste generation rates at two plants were 8 and 24 gpd/MW. Typical compositions found in a previous study (Radian, 1987) are shown in Table A-8 in Appendix A.

<u>Floor and Yard Drains</u>. Floor and yard drains collect flows from leaking pump seals, tanks and temporary supply lines together with wash water, continuous flow laboratory sample lines, and other miscellaneous waste streams. Estimated flow rates are 30 to 40 gpd/MW of generating capacity. Oil is generally separated out before disposal. No generalized data on the composition of this waste stream are available. <u>Pyrite Rejects</u>. Several steps are involved in preparing coal for combustion in a utility boiler, including crushing and pulverizing. During preparation, impurities that are harder than the coal may be rejected from the crusher or pulverizer. These rock fragments, typically called coal rejects or pyrites, generally consist of fragments of shale mined from along the edges of coal seams. The waste consists of shale fragments, coal, and a variable amount of pyrite.

Pyrite wastes can generate acidic leachate with high sulfate concentrations as the pyrite (FeS₂) weathers and oxidizes. The volume of pyrite waste generated at a power plant depends on the ash and sulfur content of the coal burned. For several Eastern power plants, volumes ranged between 750 and 1000 tons/year per 100 MW of capacity. The composition of the material also varies considerably depending on the type of coal processed and the impurities it contains. The compositions of samples tested in a previous study (Radian, 1987) are shown in Table A-9 in Appendix A.

<u>Chemical Composition of the Ash and Soils</u>. Soil and ash samples from L-site were analyzed for elements present in major, minor, and trace proportions and for water soluble anions. Three techniques were used to bring the solids or portions of the solids into solution for elemental analysis. A lithium metaborate fusion was used to bring the solids into solution to analyze elements present in major proportions. A mixed acid digestion carried out in a microwave oven was used to dissolve solids for analysis of elements present in minor and trace proportions. Solids were extracted with a hydroxylamine and hydrochloric acid solution to determine the amounts of elements present in water-soluble, dilute acid soluble, manganese-oxiderelated states and amorphous iron. Solids were mixed with twice their weight of water to extract water soluble anions. The moisture present in the samples was taken into account in determining the amount of water to add for the water extraction. Soluble sulfate in dilute hydrochloric acid was measured in four solids.

Table 4-3 presents simple statistics for the chemical composition of soils and disposed ash. The solids are divided into three groups for data analysis: 1) soil samples collected from an area not influenced by ash management, i.e., background soils, 2) ash samples collected from the ash delta in the primary ash pond, and 3) soil samples collected from beneath the ash delta. For each extraction or digestion method, the table lists the number of samples analyzed, the minimum and maximum concentrations of the analytes (elements or anions), and mean and median values for each group of measurements. Complete analytical results for soil and ash samples are given in Appendix D.
SUMMARY STATISTICS FOR CHEMICAL COMPOSITION OF SOILS AND ASH FROM L-SITE Concentrations in mg/L

			Sc	oils not Ir	nfluenced b	luenced by Ash		Ash				- 44		<u>sh</u>		
Analyte	DL	n	Minimum	Maximum	Mean	Median	n	Minimum	Maximum	Mean	Median	n	Minimum	Maximum	Mean	Median
<u>Hydroxylam</u>	ine Hydr	och	loride Ex	<u>(tract</u>												
Aluminum	50.0	4	970.0	1300.00	1110.00	1085.00	6	580.0	1100.0	836.67	810.00	5	870.0	1600.0	1148.00	1000.00
Antimony	50.0	4	<50.0	<50.00	<50.00	<50.00	6	<50.0	<50.0	<50.00	<50.00	5	<50.0	<50.0	<50.00	<50.00
Arsenic	75.0	4	<75.0	<75.00	<75.00	<75.00	6	<75.0	150.0	<75.00	<75.00	5	<75.0	<75.0	<75.00	<75.00
Barium	2.5	4	71.0	92.00	85.75	90.00	6	180.0	310.0	232.17	225.00	5	110.0	160.0	128.00	120.00
Beryllium	0.5	4	<0.5	0.75	0.63	0.63	6	<0.5	<0.5	<0.50	<0.50	5	0.7	1.3	0.90	0.82
Boron	150.0	4	<150.0	<150.00	<150.00	<150.00	6	<150.0	<150.0	<150.00	<150.00	5	<150.0	<150.0	<150.00	<150.00
Cadmium	1.2	4	<1.2	<1.20	<1.20	<1.20	6	<1.2	<1.2	<1.20	<1.20	5	<1.2	<1.2	<1.20	<1.20
Calcium	250.0	4	400.0	3500.00	1932.50	1915.00	6	750.0	1800.0	1186.67	1200.00	5	690.0	1400.0	1068.00	1200.00
Chromium	2.5	4	<2.5	<2.50	<2.50	<2.50	6	<2.5	4.3	<2.50	<2.50	5	<2.5	<2.5	<2.50	<2.50
Cobalt	2.5	4	6.5	43.00	22.38	20.00	6	<2.5	3.4	<2.50	<2.50	5	4.0	25.0	13.66	11.00
Copper	5.0	4	<5.0	<5.00	<5.00	<5.00	6	7.0	13.0	9.83	10.40	5	<5.0	<5.0	<5.00	<5.00
Iron	10.0	4	100.0	1250.00	1112.50	1100.00	6	980.0	1300.0	1146.67	1150.00	5	170.0	3600.0	2500.00	2000.00
Lead	12.0	4	<12.0	<12.00	<12.00	<12.00	6	<12.0	<12.0	<12.00	<12.00	5	<12.0	<12.0	<12.00	<12.00
Magnesium	250.0	4	<250.0	560.00	295.00	<250.00	6	<250.0	<250.0	<250.00	<250.00	5	<250.0	510.0	<250.00	<250.00
Manganese	2.5	4	170.0	870.00	477.50	435.00	6	8.5	38.0	24.42	24.00	5	220.0	770.0	454.00	340.00
Molybdenum	12.0	4	<12.0	<12.00	<12.00	<12.00	6	<12.0	<12.0	<12.00	<12.00	5	<12.0	<12.0	<12.00	<12.00
Nickel	5.0	4	<5.0	6.50	< 5.00	<5.00	6	<5.0	<5.0	<5.00	<5.00	5	<5.0	6.6	<5.00	<5.00
Potassium	750.0	4	<750.0	<750.00	<750.00	<750.00	6	<750.0	<750.0	<750.00	<750.00	5	<750.0	<750.0	<750.00	<750.00
Selenium	75.0	4	<75.0	<75.00	<75.00	<75.00	6	<75.0	<75.0	<75.00	<75.00	5	<75.0	<75.0	<75.00	<75.00
Silicon	250.0	4	650.0	1100.00	845.00	815.00	6	120.0	1700.0	1416.67	1400.00	5	560.0	1300.0	868.00	860.00
Silver	2.5	4	<2.5	<2.50	<2.50	<2.50	6	<2.5	<2.5	<2.50	<2.50	5	<2.5	<2.5	<2.50	<2.50
Sodium	250.0	4	530.0	810.00	722.50	775.00	6	550.0	740.0	635.00	640.00	5	590.0	750.0	676.00	660.00
Strontium	0.75	; 4	1.7	8.80	4.75	4.25	6	20.0	38.0	31.33	32.00	5	1.3	4.3	2.68	2.60
Thallium	25.0	4	<25.0	<25.00	<25.00	<25.00	6	<25.0	<25.0	<25.00	<25.00	5	<25.0	<25.0	<25.00	<25.00
Vanadium	5.0	4	<5.0	13.00	7.88	8.00	6	<5.0	17.0	7.65	6.30	5	15.0	34.0	29.00	32.00
Zinc	5.0	4	6.2	9.70	7.65	7.35	6	<5.0	8.9	5.73	5.90	5	<5.0	12.0	5.96	6.40
Anions in A	Aqueous	Ext	racts													
Bromide	1.6	4	<1.60	<1.60	<1.60	<1.60	6	<1.60	<1.6	<1.60	<1.60	5	<1.60	<1.6	<1.60	<1.60
Chloride	1.0	4	1.40	11.70	6.18	5.80	6	<1.00	2.2	1.07	<1.00	5	2.30	3.2	2.78	2.90
Fluoride	0.2	4	<0.20	0.40	<0.20	<0.20	6	<0.20	0.5	0.22	<0.20	5	<0.20	<0.2	<0.20	<0.20
LOI	0.7	4	4.50	10.30	7.03	6.65	6	4.00	24.5	10.35	8.30	5	7.20	12.4	9.56	9.30
Moisture	2.0	4	<2.00	4.65	3.40	3.98	6	<2.00	3.3	<2.00	<2.00	5	2.49	5.2	3.65	3.42
caster the			At 1, April 1	9		1	1.1									

(Continued)

		_	Se	oils not I	nfluenced b	oy Ash	Ash				Soil Beneath the Ash					
Analyte	DL	n	Minimum	Maximum	Mean	Median	n	Minimum	Maximum	Mean	Median	n	Minimum	Maximum	Mean	Median
Anions in A	Anions in Aqueous Extracts (Cont'd.)															
Nitrate Sulfate	3.0 10.0	4 4	<3.00 <5.00	<3.00 <5.00	<3.00 <5.00	<3.00 <5.00	6 6	<3.00 <5.00	<3.0 975.0	<3.00 438.08	<3.00 407.00	5 5	<3.00 174.00	<3.0 520.0	<3.00 386.20	<3.00 501.00
<u>Sulfate in</u>	HCl Ext	rac	ts													
Sulfate	2600	NA	NA	NA	NA	NA	2	2600	4000	2600	<3300	2	3100	3500	3300	3300
Lithium Metaborate Fusion																
Aluminum Calcium Iron Magnesium Potassium Silicon Sodium	a a a a a a	444444	95000 6200 74000 19000 14000 230000 3600	140000.0 46000.0 120000.0 34000.0 16000.0 260000.0 18000.0	116000.00 25275.00 101000.00 25000.00 14500.00 242500.00 9825.00	114500.00 24450.00 105000.00 23500.00 14000.00 240000.00 8850.00	6 6 6 6 6 6	90000 3000 59000 3850 12500 225000 3470	120000.0 7670.0 175000.0 6700.0 28000.0 260000.0 6000.0	109166.67 5861.67 129333.33 5420.00 19816.67 240333.33 4845.00	110000.00 6550.00 136000.00 5385.00 19700.00 240000.00 4800.00	5 5 5 5 5 5 5 5	110000 1300 76000 13000 8700 200000 2300	140000.0 6200.0 115000.0 21000.0 23000.0 280000.0 8000.0	132000.00 2652.00 100200.00 16800.00 13520.00 238000.00 3690.00	140000.00 1600.00 16000.00 16000.00 13000.00 240000.00 2700.00
Microwave [Microwave Digestion															
Aluminum Antimony Arsenic Barium Beryllium	50.0 50.0 75.0 2.5 0.5	4444	10000.0 <30.0 <45.0 220.0 2.0	23000.0 36.0 120.0 370.0 7.3	16500.00 <30.00 69.50 282.50 4.48	16500.00 <30.00 67.75 270.00 4.30	6 6 6 6	16000.0 <50.0 37.5 830.0 5.9	30000.0 <50.0 440.0 1200.0 12.0	22000.00 <50.00 140.00 1036.67 8.13	21500.00 <50.00 37.50 1000.00 7.20	5 5 5 5	20000.0 <50.0 37.5 200.0 2.7	36000.0 <50.0 250.0 280.0 4.8	27600.00 <50.00 102.25 232.00 3.86	27000.00 <50.00 37.50 230.00 3.70
Boron Cadmium Calcium Chromium Cobalt	a 1.3 250.0 2.5 2.5	NA 4 4 4	NA 2.6 5000.0 30.0 17.0	NA 6.4 230000.0 94.0 150.0	NA 4.10 107250.00 59.75 58.25	NA 3.70 97000.00 57.50 33.00	NA 6 6 6	NA <1.2 3500.0 84.0 36.0	NA 7.2 5300.0 140.0 56.0	NA 4.59 4283.33 108.50 44.00	NA 6.00 4200.00 105.00 43.00	NA 5 5 5 5	NA 0.65 1150.0 45.0 47.0	NA 6.7 5000.0 57.5 69.0	NA 3.85 2090.00 49.50 57.70	NA 4.60 1200.00 48.00 59.50
Copper Iron Lead Magnesium Manganese	5.0 10.0 13.0 250.0 2.5	4 4 4 4 4	7.0 57000.0 18.0 4400.0 150.0	39.0 87000.0 61.0 17000.0 2900.0	22.50 69500.00 40.75 8475.00 1037.50	22.00 67000.00 42.00 6250.00 550.00	6 6 6 6	86.0 54000.0 <13.0 1300.0 150.0	120.0 140000.0 62.0 2400.0 500.0	99.50 103666.67 36.50 1833.33 355.00	94.50 110000.00 47.50 1800.00 355.00	5 5 5 5	10.0 62000.0 <13.0 3600.0 640.0	23.0 87500.0 44.0 13000.0 1400.0	16.40 79300.00 25.80 7280.00 956.00	17.00 84000.00 30.00 6600.00 820.00
Molybdenum Nickel Potassium Selenium	12.0 5.0 750.0 75.0	4 4 4 4	<7.6 57.0 5800.0 95.0	20.0 130.0 10000.0 130.0	11.45 82.00 8350.00 113.75	11.00 70.50 8800.00 115.00	6 6 6	6.5 92.0 11000.0 140.0	140.0 130.0 23000.0 1100.0	54.75 107.33 16000.00 453.33	14.50 103.50 16000.00 190.00	5 5 5 5	6.5 38.0 6250.0 150.0	130.0 74.0 16000.0 1000.0	44.85 60.20 10290.00 423.00	13.00 67.00 11000.00 200.00

(Continued)

Soils not Influenced by Ash					Ash				Soil Beneath the Ash								
Ana	alyte	DL	r	n Minimum	Maximum	Mean	Median	n	Minimum	Maximum	Mean	Median	n	Minimum	Maximum	Mean	Median
Micr	rowave	Digesti	on	(Cont'd.)					t. El con								
Sili	icon	250.0	4	11000.0	80000.0	35000.00	24500.00	6	11000.0	21000.0	15166.67	13500.00	5	9700.0	66000.0	43240.00	45000.00
Silv	ver	1.7	- 4	<1.5	7.5	4.88	5.63	6	<1.7	7.5	5.28	7.50	5	<1.7	7.5	4.84	7.50
Sodi	ium	250.0	4	1800.0	14000.0	5250.00	2600.00	6	2100.0	3700.0	2800.00	2650.00	5	700.0	4100.0	1468.00	740.00
Stro	ontium	0.7	5 4	19.0	380.0	229.75	260.00	6	470.0	620.0	536.67	530.00	5	13.0	41.0	21.40	15.00
Thal	llium	25.0	4	30.0	40.0	35.50	36.00	6	40.0	60.0	50.00	50.00	5	<25.0	40.0	32.50	39.00
Vana	adium	5.0	1	48.0	220.0	121.50	109.00	6	120.0	190.0	140.00	135.00	5	160.0	235.0	211.00	220.00
Zind	D	5.0	4	93.0	170.0	124.25	117.00	6	62.0	120.0	83.83	79.50	5	82.0	140.0	109.40	110.00

^a Detection limit not available. DL = Detection Limit n = Number of samples NA Not Analyzed

Figure 4-5 illustrates the major element composition of a background soil, an ash, and a soil under the ash. In this figure the elements are assumed to be present as oxides.

The major elements present in both soil and ash from L-site are silicon, aluminum, and iron. The ranges of aluminum, iron, and silicon concentrations in ash are close to the ranges of the concentrations of these elements in soil. The mean concentrations for these elements are 242,000, 116,000, and 101,000 mg/kg, respectively, for background soil, and 240,000, 109,000, and 129,000 mg/kg for ash. Soil and ash have similar major element concentrations but differ in mineralogy, in physical characteristics such as particle size and shape, and in minor and trace element concentrations. Calcium and sodium concentrations are very low in soil and in ash. Magnesium concentrations are significantly higher in the soils than in the ash. Potassium concentrations are slightly higher in ash than in soil.

Table 4-4 lists the percent of the mean total elemental concentration that was extractable with a hydroxylamine hydrochloride solution, for major elements and for those minor and trace elements with measurable concentrations of hydroxylamine extractables. For the elements not listed in Table 4-4, the concentration in the hydroxylamine hydrochloride extract was less than the analytical detection limit. Chao and Zhou (1983) reported that the extracting medium would extract water-soluble species, species soluble in dilute acid, manganese-oxide-related fractions, and amorphous iron. As expected, the percent of the total element that was extractable. differed for different elements. Less than 3% of total aluminum, iron, and silicon was extracted, and less than 6% of total magnesium and potassium was extracted. Aluminum and silicon were expected to be poorly extracted. The low percent of iron extracted by hydroxylamine hydrochloride indicates that most of the iron is present in forms other than amorphous iron. The low percent of magnesium and potassium indicates that these elements are combined in chemical forms that do not yield to dilute acid extraction. As expected, over 45% of the manganese present was extracted from soils, but only about 7% was extracted from ash. The similar pattern for cobalt extraction suggests that cobalt is associated with manganese. Barium, beryllium, calcium, iron, sodium, strontium, and vanadium were almost extractable from the soil beneath the ash, suggesting that they might be in different forms in the soil beneath the ash than in control soil or the ash. Zinc extractability was very constant for the soil and ash.



Element	Soil Not Influenced by Ash (%)	Ash (%)	Soil Beneath Ash (%)
Aluminum	1.0	0.8	0.9
Barium	30.7	22.3	55.2
Beryllium	14.0	<6.2	23.1
Calcium	7.6	20.3	40.4
Cobalt	37.9	<5.7	23.6
Iron	1.1	0.9	2.5
Magnesium	1.2	<4.6	<1.5
Manganese	46.0	6.8	47.5
Potassium	<5.2	<3.8	<5.6
Silicon	0.3	0.6	0.4
Sodium	7.3	13.1	18.3
Strontium	2.2	5.8	12.9
Vanadium	6.6	5.4	13.7
Zinc	6.1	6.8	5.5

FRACTION OF MEAN TOTAL ELEMENTAL CONCENTRATIONS EXTRACTED INTO HYDROXYLAMINE HYDROCHLORIDE SOLUTION

Figure 4-6 shows L-site ash compositions plotted according to the system proposed by Roy and Griffin (1982). Five of the six ashes fall within the Modic region of the graph and one is in the Fersic region. The ashes differ in iron concentrations and in silica concentrations. The calcic group (CaO + MgO + K_2O + Na₂O) contribution to the overall composition is small and varies little on an absolute basis. The majority of reported compositions for U.S. coal ashes fall in the Modic region (Ainsworth and Rai, 1987). The L-site ashes fall in this same region but have generally lower concentrations of the calcic group and slightly higher ferric group, reflecting the coal mineralogy and the fact that these ashes have been wet-sluiced.

Mineralogical Composition of the Waste and Soils

Mineralogical analyses for ash and soil samples are summarized in Table 4-5. Bulk samples destined for X-ray diffraction (XRD) were ground in a disk mill grinder and formed into a briquette which had a hard, dense surface. The sand fractions were treated in a similar manner. The clay fraction of selected samples was isolated by first dispersing the sample with sodium carbonate and separating the clay by a settling siphon technique. The clays were then Mg-saturated, washed free of excess salts, and analyzed by XRD. The magnetic fraction of ash sample L-16 was separated using a hand magnet prior to analysis. All samples were analyzed from 2° to 42° 2theta using Cu radiation. Specimens destined for scanning electron microscopy energy dispersive x-ray spectroscopy (SEM-EDS) were placed on mounts and coated with gold and carbon.

The results show that the principal components of the ash are quartz, mullite, and glass. Figure 4-7 shows the morphology of typical ash particles. Kaolinite was tentatively identified in one ash clay separated by XRD. A crystalline iron oxide, either magnetite of maghemite, was identified in the magnetic fraction separated by XRD and in the bulk specimen by SEM-EDS. Two other minerals, one high in barium and sulfur (probably barite, BaSO₄) and one high in iron and sulfur (probably pyrite, FeS₂), were also identified by SEM-EDS. In contrast, the soils beneath the ash and in the control location are primarily composed of mica (probably muscovite), kaolinite, quartz, and feldspar. These minerals were found in both the clay and coarser size separates. Other minerals identified included vermiculite, hornblende, and gypsum.



SUMMARY OF MINERALOGICAL ANALYSES FOR ASH AND SOILS FROM THE ASH DELTA AND A CONTROL LOCATION AT THE L-SITE[®]

<u>Material</u>	<u>Sample</u>	Depth <u>(ft)</u>	<u>Fraction</u>	<u>Quartz</u>	<u>Mullite</u>	Vermi- <u>culite</u>	<u>Mica</u>	Feld- <u>spar</u>	Kaoli- <u>nite</u>	Hema- <u>tite</u>	Magne- <u>tite</u>	<u>Othe</u>
					<u>Ash Delta, Bor</u>	ing LC-19						
Ash	L015	4.3	Whole	x	X							
Ash	L016	8-9	Whole Clay Magnetic	X X	X			X		x	x	tr ^b
Soil	L020	13.8	Whole	×			×	tr ^C	x	tr ^C		
Soil	L021	14-14.5	Whole Clay	x			×		x x			
Soil	L024	20-21	Whole Clay	x x		x x	x	X	×			
Soil	L024	21.5	Whole	x			x	x	X			tr ^d
				<u>C</u> t	ontrol Soil, Bo	oring LC-17						
Soil	L010	24	Whole	×			x	x	x			
Soil	L012	27.8-28.8	Whole Clay				x x	x	x x		Χ.	xe

a Identified by XRD unless otherwise indicated
b Barite and pyrite identified by SEM-EDAX
c Identified by SEM-EDAX
d Gypsum identified by SEM-EDAX
e Hornblende



Elemental Trends with Depth

Figure 4-8 shows the depth profile of pH in a water extract (2:1 water-to-soil ratio). The pH values of the ash were near neutrality in the upper 4 feet of ash and around pH 5 in the lower portions. Lower pH values in the ash zone are attributed to oxidation of pyrite rejects disposed in the ash pond (see detailed discussion in GEOCHEMICAL PROPERTIES).

Depth trends of select elemental concentrations (Ba, Ca, Sr, Mn, Cr, Ni, and Zn) are shown in Appendix D. The trend of copper concentrations with depth in the ash and soil in the ash delta is shown in Figure 4-9. Copper is selected as an example because it would be the most readily identified indicator of contamination from boiler chemical cleaning waste. The copper extracted with the reducing agent (hydroxylamine hydrochloride) represents copper that is more easily weathered or leached than copper in a mineral phase. As shown in Figure 4-9, the more easily weathered copper is below analytical detection limits in the soils beneath the ash, indicating no evident migration and subsequent deposition of copper in the soils. The total elemental analysis of the soils also shows copper concentrations to be unaffected by the ash or low volume waste.

GEOCHEMICAL PROPERTIES

Five core samples were taken at the L-Site for use in the geochemical studies. Four of the cores, LC-19, LC-20-2A, LC-20-2B, and LC-20-3, were obtained from the ash delta near the discharge line (see Figure 4-4). The fifth core, LC-12, was taken downgradient from the pond at the site of monitoring well LMW-07. Core LC-19 was taken from the LMW-14 site and the LC-20 cores were taken from the LMW-15 site. The depths, lithology, and stratigraphic locations of the four ash delta cores are shown in Figure 4-4. Cores LC-19 and LC-20-2A were taken in the ash zone; core LC-20-3 was taken from the soil directly beneath the ash zone. Core LC-20-2B was taken at the ash-soil boundary and because it contains a mixture of both types of materials it was not studied further.

The LC-12 core was taken at the 14- to 16-foot level below ground surface, directly below the water table. The material consisted of brownish-red saprolite with abundant mica. Particle sizes ranged from clay- to silt-size. Core LC-19 was recovered from the 5.6- to 7.3-foot level below the surface of the ash delta. The material consisted of clay- to silt-size gray ash. Core LC-20-2A was recovered from 14.5 to 16.2 feet below the surface of the ash delta. The material consisted of silt- to sand-size gray ash. Core LC-20-3 was recovered from 16.5 to 18.5 feet below the





surface and consisted of reddish brown clay- to silt-size saprolite with abundant mica.

Pore-Water Analysis

Two extraction techniques were evaluated for analysis of pore waters: pressure filtration with nitrogen and immiscible displacement with $Freon^{\otimes 1}$ 113. Appendix E presents the results of analysis of pore waters obtained from the four cores using both extraction techniques. Elemental concentrations in extracts obtained by either method appear to be essentially equivalent. The pH and Eh measurements taken from these extracts were considerably more erratic. The values shown in Appendix E are those taken in situ in the cores before they were unsealed.

<u>Ash Samples</u>. Ash cores LC-19 and LC-20-2A had similar chemistry, with the major characteristics summarized in Table 4-6. The pH of the LC-19 samples was 7.2, whereas LC-20-2A had a lower pH, 6.1. Core LC-19 had a somewhat more reducing Eh. Both samples were quite high in ferrous iron (Fe(II)) and sulfate, which are characteristic oxidation products of the mineral pyrite. Pyrite sulfur was detected in both samples using the Cr^{2+} method of Cutter and Oatts (1987). No aqueous sulfide was detected, a pattern that is consistent with the measured Eh and also typical of pyrite oxidation. Although pyrite would not be associated with the ash stream, it is commonly associated with the reject stream from the coal pulverizers (pyrite rejects). This stream is co-managed in the ash pond.

The oxidation of pyrite is illustrated in Figure 4-10. Reaction (c) is of particular interest in this system because it proceeds in the absence of molecular oxygen (O_2) . The oxidation of pyrite produces acidity (H⁺ and Fe²⁺); therefore, a low pH (<4) is also typical of pyrite oxidation. In this case, however, the pH of the ash was nearly neutral, 6.1 to 7.2. A likely explanation lies in the neutralization of the H⁺ by the alkaline glass fraction of the ash.

None of the constituents normally associated with boiler chemical cleaning waste from this plant (copper, iron, organic complexing reagents, bromide, etc.), except for iron, are present in the pore waters in any significant concentrations. The likely source of the iron in the pore water is the oxidation of pyrite rejects disposed of in the pond, rather than boiler cleaning wastes. Geochemical calculations indicate that the Fe^{2+} concentration is controlled by redox equilibrium between Fe^{2+}

¹Freon[®] is a trademark of E. I. du Pont de Nemours & Co., Wilmington, Delaware.

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SUMMARY OF PORE WATER EXTRACTS AND SOLID SAMPLES

Ash Samples									
		LC-19	<u>LC-20-2A</u>						
рН		7.23	6.13						
Eh (volts)		-0.173	+0.115						
$Fe^{2+}(mg/L)$		70	180						
$SO_4^{2-}(mg/L)$		1150	1280						
Pyrite Sulfur (mg/kg))	250	460						

	11 A.	Soil Samples	NE CONTRACTOR
		LC-20-3 <u>(Below Ash Pond)</u>	LC-14 <u>(Downgradient)</u>
pH south		3.92	4.58
Eh (volts)		+0.438	+0.420
$Fe^{2+}(mg/L)$		318	<0.02
Sulfate (mg/L)		1190	25
Pyrite Sulfur (r	ng/kg)	110	70

 $\begin{array}{rcl} H_{2}0 + FeS_{2} (s) + 7/2 \ 0_{2}^{(a)} & H + SO_{4}^{2-} + & Fe(II) \\ & & & & & \\ & & + \ 0_{2} & & \\ & & Slow & Fe(III) \end{array}$ Fast $& + \ FeS_{2} (s) \\ & & Fe(III) \end{array}$ Fection (b) $Fe^{2+} + H^{+} + 1/4 \ 0_{2} = Fe^{3+} + 1/2 \ H_{2}0 \\ & Feaction (c) \ FeS_{2} (s) + 14Fe^{3+} + 8H_{2}0 = 15Fe^{2+} + 2SO_{4}^{2-} + 16H^{+} \\ & Figure \ 4-10. \ Pyrite \ Oxidation \ Cycle \end{array}$

and Fe^{3+} . The solubility of Fe^{3+} is controlled by amorphous ferric hydroxide [Fe(OH)₃(A)].

<u>Soil Beneath the Ash Pond</u>. The soil sampled directly beneath the ash pond (Core LC-20-3) is also high in ferrous iron and sulfate (Table 4-6). The pH of this soil is also quite low, 3.9, and small amounts of pyrite sulfur are present. These chemical properties are indicative of pyrite oxidation. There are two possible reasons for the lower pH. One is that acidity created by the pyrite oxidation may originate so near the boundary between the ash and the soil that it has not been neutralized by the ash. The saprolitic soil is highly weathered and unlikely to have a significant neutralizing capability. Another possibility is that the large flux of Fe^{2+} from pyrite oxidation in the coal ash above may be displacing acidic ions (H⁺ and Al³⁺) adsorbed in the soil.

As in the ash, no constituents expected from boiler chemical cleaning waste other than iron are present in the pore water below the ash pond. Once again, the source of the iron is most likely pyrite oxidation. Geochemical calculations indicate again that iron concentrations are controlled by a combination of redox equilibria and amorphous ferric hydroxide. Equilibrium with aluminum hydroxide sulfate $[A1(OH)SO_4]$ or jurbanite $[A1(OH)SO_4 \cdot 5H_2O]$ is indicated. Both of these aluminumbearing phases are typical of acidic soils.

<u>Downgradient Soil</u>. The chemical parameters for the downgradient soil sampled by core LC-14 are summarized in Table 4-6. The pH was 4.58, with an oxidizing Eh. The

pore water from this sample contained relatively low concentrations of all dissolved constituents including dissolved iron (<0.02 mg/L) and sulfate (25 mg/L). A small amount of pyritic sulfur was detected, but no effects from its oxidation were observed. The pyrite that does exist in this highly weathered soil may be coated with some other phase that makes it less accessible to oxygen or of a crystal size and morphology that inhibits its reactivity. No constituents attributable to boiler chemical cleaning waste are present. Geochemical calculations indicate equilibrium with an amorphous silica phase (SiO₂) and barite (BaSO₄).

Cation Exchange Capacity and Exchangeable Cations

Table 4-7 presents results of cation exchange capacity (CEC) and exchangeable cation measurements. The individual sample results are shown in Appendix E. The two soil samples, cores LC-12 and LC-20-3, had CECs in the range from 4.5 to 7 milliequivalents per 100 grams. The two ash samples had somewhat lower CECs in the 1 to 2 meq/100 gram range. Both of these ranges are toward the low end for soils, reflecting a relatively low clay mineral content.

The major exchangeable cation in both of the ash samples (cores LC-19 and LC-20-2A) was calcium. The method used to determine exchangeable cations (Reeve and Sumner, 1971) appeared to yield exchangeable Ca far in excess of the measured CEC. This excess may be attributable to the presence of some Ca-containing phase in the ash that is partially dissolved by the reagents used. The nature of this Ca-containing phase is not clear at this time, since no solubility control for Ca has been identified for these samples. Very little exchangeable acidity in the form of aluminum or iron was present in the two ash samples (cores LC-19 and LC-20-A), which is consistent with the near neutral pH.

The major exchangeable cations on the downgradient soil, core LC-12, were aluminum and magnesium. Aluminum is a source of exchangeable acidity whereas Mg is an exchangeable base. The soil under the ash delta (core LC-20-3) had even more exchangeable aluminum, which is consistent with the soil's lower pH. Considerable exchangeable iron, which is also a form of exchangeable acidity, was present as well. The magnesium in core LC-20-3 had been largely replaced by calcium. The source of the exchangeable iron and calcium in core LC-20-3 is presumably the fly ash leachate infiltrating from above.

<u>Extractable Iron</u>. Extractable iron was measured on all four core samples using the acid hydroxylamine hydrochloride method (Chao and Zhou, 1983). This method has been shown to give a good estimate for the amount of amorphous iron in samples.

CATION EXCHANGE CAPACITY AND EXCHANGEABLE CATIONS OF L-SITE SOILS AND ASH (Meq/100g)

<u>Parameter</u>	Downgradient Soil LC12ª	<u>Ash</u> LC20-2Aª	LC19 ^a	Soil Beneath Ash LC20-3ª
CEC	4.68	1.34	1.72	6.37
Exchangeable Cations				
A1	1.19	0.025		4.72
Ba	0.24	0.074	0.024 ^b	0.031
Ca	0.12	1.31	8.78 ^b	2.14
Fe		0.069 ^b	0.0006 ^b	1.75
К	0.46	0.12	0.14 ^b	0.88
Mg	2.26	0.12	0.11 ^b	0.32
Mn	0.12	0.022	0.032 ^b	0.060
Na	0.073	0.012	0.0047 ^b	0.052
Sr	0.0012	0.015	0.054 ^b	0.016
Total	4.46	1.75	9.14 ^b	9.98

^aAverage of duplicate analyses, unless otherwise noted

^bSingle measurement

Amorphous iron is one of the major adsorbing oxides that contribute to specific adsorption in many samples. The results are given in Appendix E. Both soil samples, cores LC-12 and LC-20-3, showed a relatively low extractable iron content of around 100 mg/kg. The ash from core LC-20-2A also showed a fairly low extractable iron content. The ash from core LC-19 had a somewhat higher extractable iron content, possibly reflecting precipitated iron derived from the oxidation of pyrite.

<u>Retardation Capacity of the Soils</u>. Both the CEC and the extractable iron were relatively low in the two soil samples (cores LC-12 and LC-20-3). These low values coupled with the relatively low pH and alkalinity of the soil samples indicate that the soils have little capacity to retard solutes migrating from the ash pond.

pH Manipulation Studies

To learn more about possible solubility controls for various elements in both the ash and soil samples, all four cores were studied using pH manipulation. For this technique, small (3 g) aliquots of the sample were placed in test tubes in a suspension with 30 mL of water and the pH was adjusted using hydrochloric acid or potassium hydroxide. Twenty-four aliquots were adjusted at 0.5 pH increments from pH 2 to pH 12. The samples were equilibrated while being shaken for seven days. Both the pH adjustment and equilibration were carried out in a controlled-atmosphere chamber under N_2 gas. After seven days, the solutions were filtered and analyzed for trace and major elements and species. The analytical results are tabulated in Appendix F. The results were analyzed using a geochemical model (MINTEQ) to determine the single ion activities. The activity is a thermodynamic quantity expressed as the product of the concentration and an activity coefficient. The activity can be looked upon as the "effective concentration," and may be orders of magnitude different from the analytical concentration of an element. The single ion activities were plotted versus pH and compared to activities expected from various possible solubility controls. This technique is useful for identifying reactive solid phases which are present in too low a concentration to be detected by direct methods such as x-ray diffraction.

<u>Major Elements</u>. Major elements are those present in quantities greater than 1 percent by weight in the ash or soil matrix.

<u>Aluminum</u>. In Figure 4-11, the logarithm of the aluminum activity for all four samples is plotted against pH because the behavior of Al in all four samples is fairly similar. Also plotted are the expected profiles for gibbsite $[Al(OH)_3 (Cryst)]$ and amorphous aluminum hydroxide $[Al(OH)_3 (A)]$. The calcu-

lated activities follow the expected pH trend for an aluminum hydroxide phase but lie between the two lines in the pH from 4 to 9, possibly representing a form of gibbsite that is not fully crystalline. Above pH 9, the Al activity more closely follows the gibbsite line. This behavior has been documented by Ainsworth and Rai (1987). The natural pH of the four core samples varied from 3.9 to 7.3. At these pH levels, a mixture of gibbsite and amorphous aluminum hydroxide appears to control Al solubility.

<u>Calcium</u>. The logarithm of Ca^{2+} activity is plotted against pH for all four core samples in Figure 4-12. The most common controls on Ca in soils and fly ashes are gypsum (CaSO₄ 2H₂O) and calcite (CaCO₃), so the expected activities for these two minerals are also plotted. Neither of these two minerals is controlling the calcium activities in the samples. The gypsum line is plotted for a pSO₄ (negative log of sulfate activity) of 2.7, which is an average of the two ash samples (cores LC-19 and LC-2O-2A) and the soil below the ash pond (core LC-2O-3). All three samples appear to be undersaturated with respect to gypsum. The average pSO₄ for the downgradient soil (core LC-12) is 3.7; therefore, the LC-12 samples are in fact an order of magnitude less saturated than they appear in the figure. The calcite is plotted for a pCO₂ of 3.5, which is the atmospheric value.

In the case of gypsum, all samples are undersaturated. Thus it seems likely that gypsum would be a solubility control in the sense that if sufficient calcium and/or sulfate were added to the samples, gypsum would precipitate and limit the concentrations of both constituents. However, many samples would be clearly oversaturated with respect to calcite if the samples were in equilibrium with atmospheric CO_2 . Therefore calcite is not a solubility control in these samples, apparently because of a lack of equilibrium with atmospheric CO_2 . It is likely that, if carbon dioxide diffuses into the ash pond or is produced through biological activity, calcite will eventually become a calcium control. Because of the low pH and small amount of leachable Ca of the soil samples (cores LC-12 and LC-20-2A), calcite is not expected to be an important component of these samples. This hypothesis was confirmed by X-ray diffraction studies, which failed to detect calcite in any of the ash or soil samples.

<u>Iron</u>. The logarithm of the ferric iron activity is plotted versus pH for all four samples in Figure 4-13. The ferric iron concentration in soils phase rather than by one of the crystalline iron oxides, such as hematite (Lindsay,







1979). Because these iron hydroxides are amorphous and have no definite structure, thermodynamic properties have been identified for a variety of iron hydroxides of uncertain compositions. Lindsay (1979) discussed two, amorphous iron hydroxide $[Fe(OH)_3(A)]$, which is freshly precipitated, and what he calls "soil" iron hydroxide [Fe(OH $_3$)(soil)], which is presumably somewhat more crystalline. The $Fe(OH)_3(A)$ is the most soluble iron hydroxide for which constants are available. The $Fe(OH)_3(soil)$ is considerably less soluble. An iron hydroxide of intermediate solubility has also been reported. This intermediate iron hydroxide is an aged precipitate referred to as $Fe(OH)_3(PPT)$. The two most soluble ferric hydroxides, $Fe(OH)_3(PPT)$ and $Fe(OH)_3(A)$, have been plotted in Figure 4-13. The values from the downgradient soil (core LC-12) follow the $Fe(OH)_{3}(PPT)$ line fairly closely. The soil from under the ash pond (core LC-20-3) and the ash samples (cores LC-19 and LC-20-2A) follow the same line at pH greater than 7, but become even more soluble than $Fe(OH)_3(A)$ at pH less than 7. The high solubility of iron may be the result of the rapid dissolution and precipitation of iron resulting from pyrite oxidation in these samples, as discussed in the section on porewater chemistry.

<u>Trace Elements</u>. Trace elements are those present in trace quantities (less than 0.2%) in the ash or soil matrix.

Barium. The logarithm of the Ba^{2+} activities for all four core samples is plotted versus pH in Figure 4-14. Also plotted are expected profiles for barite (BaSO₄) at two sulfate concentrations. The first is for $pSO_4 = 2.7$, which is the average for the three high sulfate samples (the two ash samples, cores LC-19 and LC-20-2A, and the soil from below the ash pond, core LC-20-3). The second is $pSO_4 = 3.7$, which is the average and coal ashes is typically controlled by an amorphous iron hydroxide concentration for the downgradient soil core LC-12. The LC-12 samples fit the barite profile well for $pSO_4 = 3.7$ at pH levels above 5, indicating that crystalline barite is a solubility control for Ba in this soil. The Ba^{2+} activity rises at lower pH because the SO_4^{2-} activity falls well below $pSO_4 = 3.7$, apparently reflecting the increasing solubility of other forms of barium in the samples at the lower pH levels. The SO_4^{2-} activity is suppressed in the samples at lower pH, so that the barium is still in equilibrium with barite. The ash samples (cores LC-19 and LC-20-2A) and the soil below the ash pond (core LC-20-3) appear to be somewhat supersaturated with respect to barite. Barite was identified by SEM-EDX in these samples. Previous work at Battelle has shown barite supersaturation to be relatively common in fly ash systems as a result of the presence of other



ions, particularly strontium (Sr^{2+}) , which coprecipitates with the barite, creating a more soluble phase. This more soluble phase is metastable and can be expected eventually to revert to crystalline barite.

<u>Cadmium</u>. The logarithm of Cd^{2+} activity is plotted versus pH in Figure 4-15 for all four samples. Also plotted are two potential solubility controls, otavite (CdCO₃) and cadmium silicate (CdSiO₃). Neither phase appears to be a solubility control for any of the samples.

The cadmium concentration in solutions equilibrated with the ash at the lowest measured pH level is approximately 0.1 μ g/g. This amount of soluble cadmium compares to 0.3 to 2.6 μ g/g measured for other ashes (Rai et al., unpublished data) and does not appear to reflect any effects from codisposal of boiler chemical cleaning waste (BCCW) in the ash pond.

<u>Chromium</u>. No direct determination of chromium redox status was performed on these samples. Therefore, for this analysis, all chromium is assumed to be present in the Cr(III) state. This is a reasonable assumption because Fe(II), which is present in the two ash samples (cores LC-19 and LC-20-2A) and the soil from below the ash (LC-20-3), rapidly reduces Cr(VI). It may not be a reasonable assumption for the downgradient soil (core LC-12) because of the presence of extractable manganese in the soil (Rai et al., 1988).

The logarithm of the $CrOH^{2+}$ activity [the most common form of Cr(III) in aqueous solution at near neutral pH] is plotted versus pH for all four samples in Figure 4-16. Also plotted are the expected profiles for amorphous chromium hydroxide [$Cr(OH)_3(A)$]. Rai et al. (1988) found that in many soil and fly ash systems, chromium concentrations are controlled by a solid solution of ferric hydroxide and chromium hydroxide. Therefore, a line representing the expected profile for such a solid solution, in which chromium hydroxide is present at the 1% level, is also plotted. In the two ash samples and the soil directly beneath the pond, chromium data were insufficient to get a full profile with pH.

The chromium concentrations in the downgradient soil sample (core LC-12) appear to follow the line for pure $Cr(OH)_3(A)$ rather than the solid solution. This result is quite unexpected given the amount of amorphous iron oxides in the soil. In any event, the solubility control would occur only at pHs well



