





## Coal Ash Program Overview

- A detailed program review was conducted
- We have ash / groundwater interfaces at almost all coal sites
  - 24 sites
  - 61 ponds
  - 58 structural/landfills
- Large number of experts have dedicated years to managing program
- Coal ash is impacting the environment
- Duke is in compliance with State and Federal standards
- Duke has a strong coal ash program and has opportunity to proactively become the industry leader



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Reviewed groundwater and coal ash conditions at all Duke power plants

Respective SME's for each region provided background and data

Duke experts have been working on coal ash issue for years, are very knowledgeable, and have program well underway

- Environmental scientist familiar with each region, regulatory SME's, Strategic Engineering group, Power Generation

- After a deep dive review I am very comfortable with the current status of our program

Need to be very clear that our coal ash is impacting the groundwater at all locations

This is not an overnight event, ash has been managed in this fashion for decades and it will take decades to close the ponds

All this said, we are compliant with all regulations and in many locations do far more that regulations require through our voluntary programs

I see our coal ash program as a huge opportunity to launch a public education program, invest considerable capital in our plants, and be an environmental leader when it comes to coal ash

# Groundwater Regulation Overview and Results

Retired station, decommissioning is underway, detailed ash pond

characterization work will begin in the first quarter of 2014

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Expect considerable attention from environmental groups when we submit  
closure plan

Also likely to have considerable media coverage due to proximity of City of  
Charlotte drinking water intakes about 5 miles downstream of site

## Complexities of Groundwater Monitoring

- Requirements vary by State (See Appendix A for details)
  - Sampling frequency
  - Sampling parameters
  - Sampling locations
- Remedial actions vary by State
  - Minimal groundwater regulations in place currently
  - Federal EPA guidance (CCR, ELG) a minimum of 12 months away
- As a general rule, mitigation equates to removing the source and allowing natural attenuation to occur



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The question of compliance is a very difficult one

Groundwater standards are very different in each state we operate

- specific standards are different

- compliance location is different

Reporting and remediation requirements also vary drastically

In general we monitor for the federal 2L groundwater standards at all sites and then report to the regulatory agencies as required

## Groundwater Monitoring Methodology

- Install monitoring wells
  - Upgradient (Background wells - 43)
  - Downgradient (Compliance Monitoring wells - 258)
- Sample and report results as required
- Remediate concern if results are verified
- Expand sample area as needed if results indicate potential impact on receptor
  - Primary standard indication at compliance well
  - Install additional monitoring well if possible
  - Receptor located downstream of compliance well indication
  - Perform additional testing at receptor location



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Regardless of state requirements Duke monitors groundwater around ash storage areas at all sites (all active ponds and ash storage started after 19??)

All sites have background wells upgradient of ash ponds to provide baseline information on groundwater conditions in the area

- this is very important because there are several locations where certain standards are above the 2L limit prior to being impacted by our coal ash

Downgradient compliance monitoring wells then monitor any impacts our coal ash is having on the GW flow and ensures we are not impacting any receptors

If a monitoring wells shows a GW exceedence and a receptor could be impacted based on expected GW flow we take action to remediate

- depending on site this could include installation of additional monitoring wells

- testing the receptor well

- moving receptor to an alternate water source



# Generating Station Ash Pond Groundwater Sampling Overview

Plant	2L Groundwater Standards Exceeded																					
	Antimony	Arsenic	Barium	Boron	Cadmium	Chloride	Chromium	Copper	Iron	Lead	Mn	Mercury	Nickel	Nitrate	Nitrite	Selenium	Silver	Sulfate	Thallium	Zinc	TDS	pH
Asheville				X		X	X		X	X	X			X		X		X	X		X	X
Sutton	X	X		X	X				X	X	X					X		X	X		X	X
Cape Fear	X	X		X	X				X	X					X		X				X	X
Dan River Steam Station	X	X		X					X	X	X						X				X	X
Gibson		X		X		X			X	X							X				X	X
Lee Plant (NC)		X		X			X		X	X	X										X	X
Buck Steam Station				X			X		X	X							X				X	X
Gallagher		X		X					X	X	X						X				X	X
Marshall Steam Station				X					X	X							X				X	X
Mayo					X		X		X	X									X		X	X
Miami Fort		X				X			X	X							X				X	X
Beckjord									X	X					X		X				X	X
Cliffside Steam Station							X		X	X							X				X	X
Roxboro							X		X	X							X				X	X
Allen Steam Station				X					X	X			X									X
Belews Creek							X		X	X									X			X
East Bend						X			X	X								X				X
Robinson		X					X										X				X	X
Cavuga				X											X		X					X
Riverbend	X								X	X												X
Weatherspoon									X	X									X			X
WS Lee Steam Station				X					X	X												X
Wabash River									X	X												X
Crystal River		X																				
Edwardsport																						
Edwardsport IGCC																						
Zimmer																						

Table summarizes where we are exceeding the federal 2L GW standards at our



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- At compliance boundary (500' in NC, or at state approved monitoring well location)

- may or may not have similar state guidelines

- many of the background wells show same exceededence (i.e. Fe and Mn) so likely naturally occurring issues

Primary standard violation are in downgradient wells that does not have a receptor between the well location and any drinking water receptors

All results are communicated as required to state agencies and no remedial actions are currently outstanding

# Coal Ash Program Examples

Asheville  
Riverbend  
Cayuga

(See Appendix B for additional information)

Retired station, decommissioning is underway, detailed ash pond

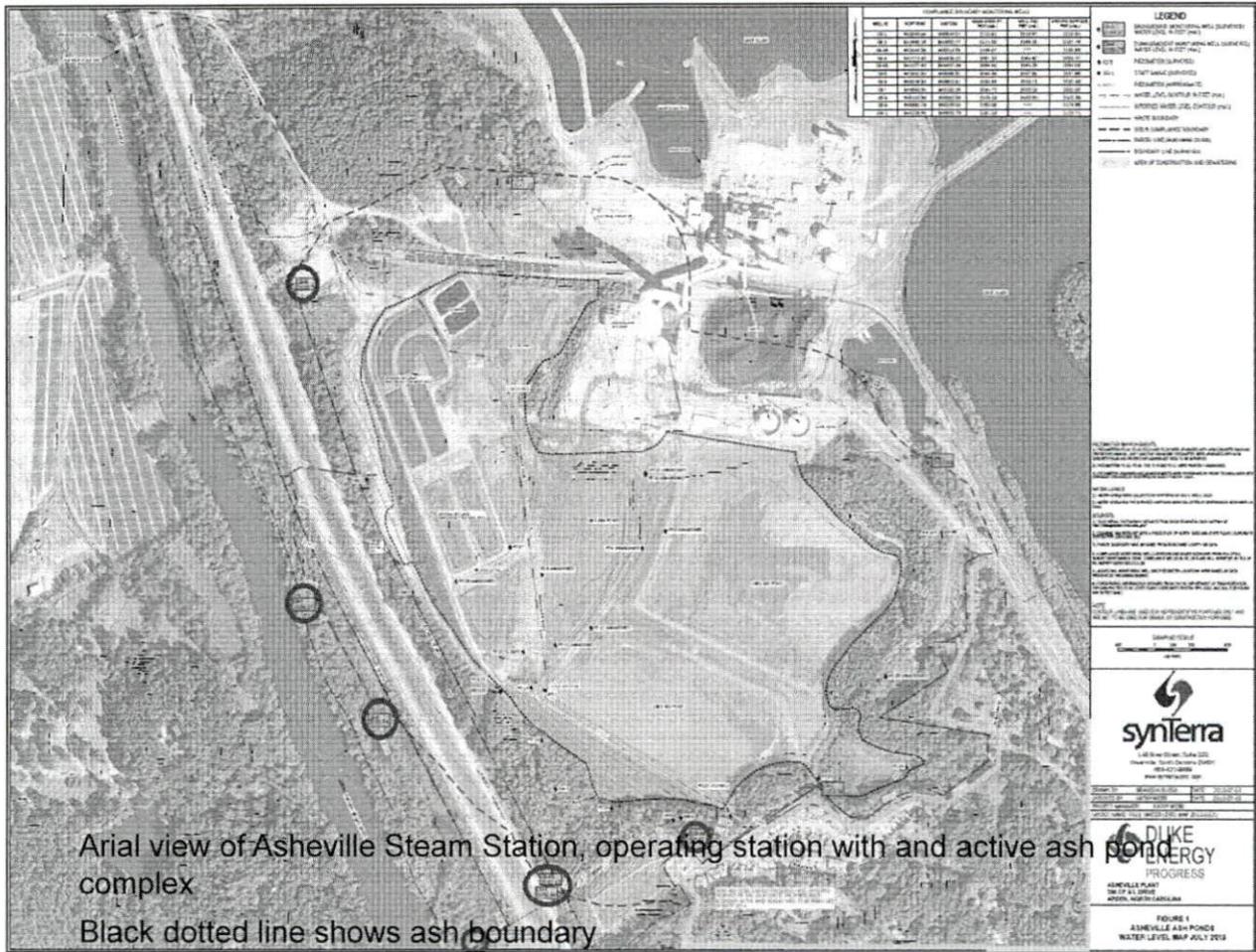
characterization work will begin in the first quarter of 2014

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Expect considerable attention from environmental groups when we submit closure plan

Also likely to have considerable media coverage due to proximity of City of Charlotte drinking water intakes about 5 miles downstream of site





Aerial view of Asheville Steam Station, operating station with and active ash pond complex  
 Black dotted line shows ash boundary

- Red line is compliance boundary (500' or property line whichever is closer)
- Background (3 – yellow blocks) and compliance (8 – green blocks) well network is shown with groundwater flow contours (blue and green lines) (we will see in a couple slides how GW flow is determined)
- Groundwater flow is toward the ash ponds and then toward the French Broad River
- Boron and Thallium indication at Monitoring Well CB-3R (decreasing) (circled in red) side gradient of ash pond – near Bear Leah Trail receptors
- Boron at monitoring well CB-4 CB-5 and CB-6 (decreasing) – no receptors between ahs pond and French Broad River
- Boron and Selenium (decreasing) at Monitoring Well CB-7 and CB-8 down gradient of ash pond – no receptors between ahs pond and French Broad River
- Levels of boron, selenium, and thallium have been decreasing since water level in pond decreased, dewatering key driver to improved results
- Boron is not linked to health issues, but is an early indicator for other heavy metals such as arsenic, selenium, etc











# Riverbend Station

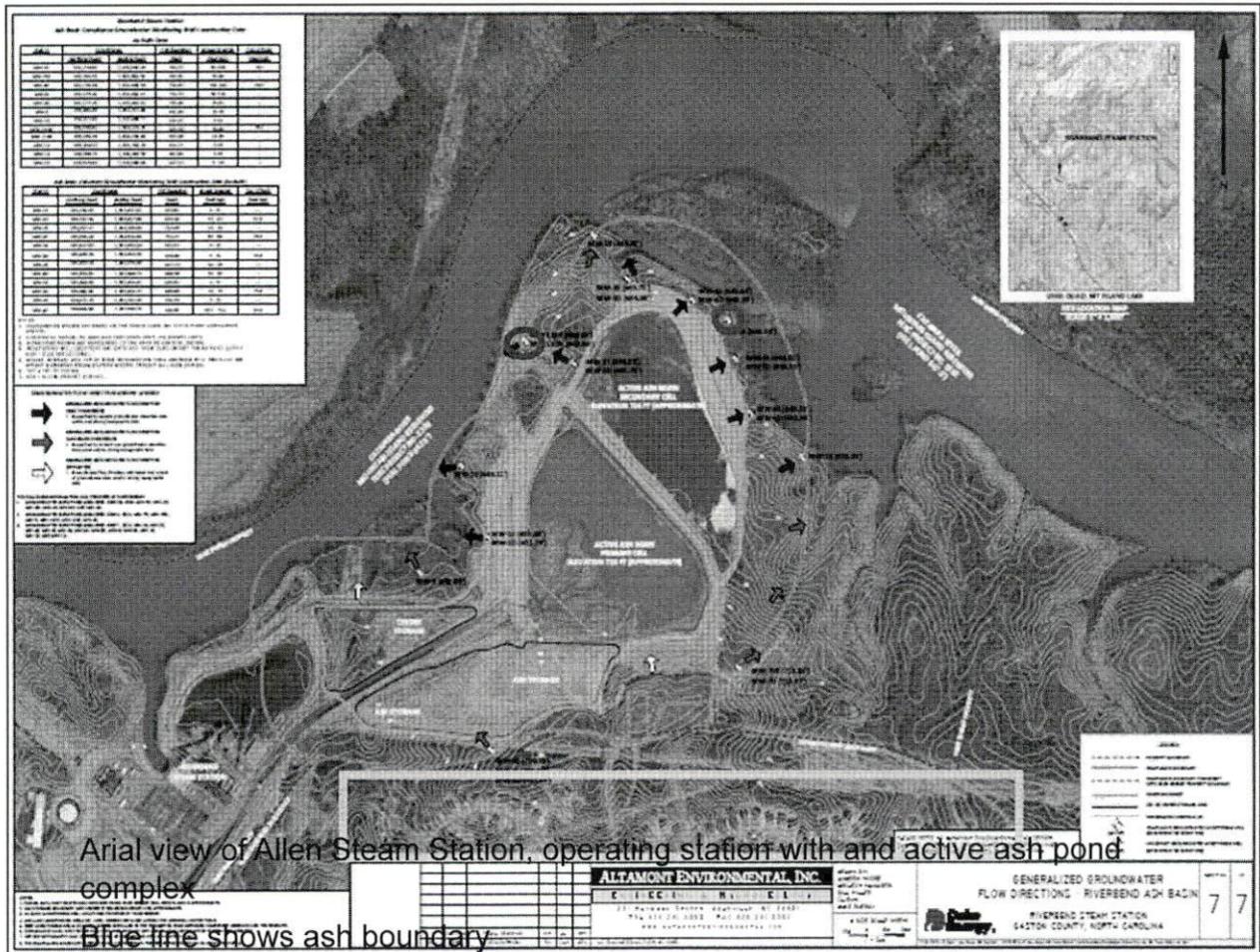
Retired station, decommissioning is underway, detailed ash pond

characterization work will begin in the first quarter of 2014

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Expect considerable attention from environmental groups when we submit closure plan

Also likely to have considerable media coverage due to proximity of City of Charlotte drinking water intakes about 5 miles downstream of site



Aerial view of Allen Steam Station, operating station with and active ash pond complex

Blue line shows ash boundary

Red line is property boundary

Green line is compliance boundary (500' or property line whichever is closer)

Background (2) and compliance (12) well network is shown with groundwater flow indications (we will see in a couple slides how GW flow is determined)

Groundwater flow is toward the Catawba River

Highest GW indications (Fe, Mn) are at well (MW- 13 - circled in red) Boron starting the show up in MW-11 downstream of ash pond just before GW enters Catawba River – no receptors

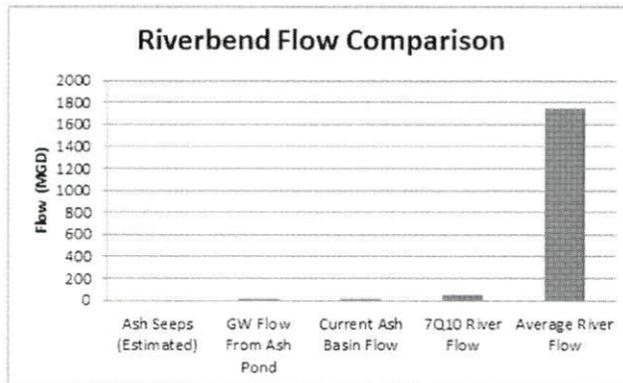
All receptors (approx 300) in pink box and are all upgradient of ash pond, GW flow makes it very difficult for us to impact these locations





## What is a Hydraulic Break?

- A large body of water
  - The relative low point for ground water flow
  - Significantly greater flow than groundwater contribution
  - Acts as a sink for all surrounding groundwater
  - Receptors located across a hydraulic break are unaffected, regardless of distance from ash pond



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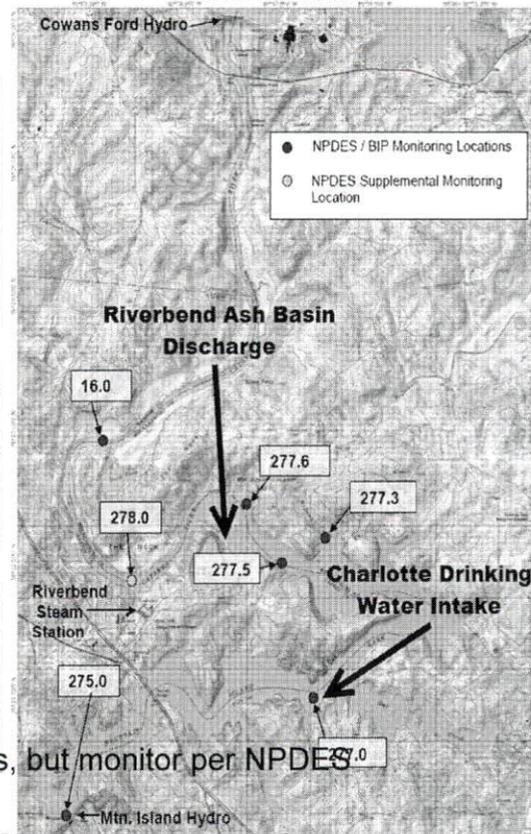
The dilution factor when water reaches a large receiving body is generally overwhelming

	Belews Creek	
Riverbend		
Ash Seep flow estimate MGD	= 0.303409	0.001
GW Flow from ash ponds MGD	= 0.9	0.5
Ash basin flow (NPDES Outfall) MGD	= 9	4.9
7Q10 river flow MGD	= 51.7	51.7
Current river flow MGD	= 371.0	1750



## Riverbend Station River Impact Monitoring

Upstream 278	As, (µg/L)	< Cd, (µg/L)	< Cr, (µg/L)	< Cu, (µg/L)	< Hg, USEP (µg/L)	< Pb, (µg/L)	< Se, (µg/L)	< TDS (mg/L)
Riverbend SS	< 1.00	NA	NA	NA	NA	NA	< 1.00	NA
Riverbend SS	< 1.00	< 1.00	< 1.00	1.02	< 0.05	< 1.00	< 1.00	51.00
Riverbend SS	< 1.00	< 1.00	< 1.00	< 1.00	< 0.05	< 1.00	< 1.00	52.00
Riverbend SS	< 1.00	< 1.00	< 1.00	1.22	< 0.05	< 1.00	< 1.00	42.00
Riverbend SS	< 1.00	< 1.00	< 1.00	1.25	< 0.05	< 1.00	< 1.00	51.00
Riverbend SS	< 1.00	< 1.00	< 1.00	1.66	< 0.05	< 1.00	< 1.00	< 25.00
Mean	1.00	1.00	1.00	1.23	0.05	1.00	1.00	44.20
Downstream 277.5								
Riverbend SS	< 1.00	< 1.00	< 1.00	1.38	< 0.05	< 1.00	< 1.00	47.00
Riverbend SS	1.12	< 1.00	< 1.00	1.42	< 0.05	< 1.00	< 1.00	54.00
Riverbend SS	< 1.00	< 1.00	< 1.00	< 1.00	< 0.05	< 1.00	< 1.00	49.00
Riverbend SS	< 1.00	< 1.00	< 1.00	1.30	< 0.05	< 1.00	< 1.00	42.00
Riverbend SS	< 1.00	< 1.00	< 1.00	1.11	< 0.05	< 1.00	< 1.00	51.00
Riverbend SS	< 1.00	< 1.00	< 1.00	1.67	< 0.05	< 1.00	< 1.00	31.00
Mean	1.02	1.00	1.00	1.31	0.05	1.00	1.00	45.67
CLT DW Intake 277								
Riverbend SS	< 1.00	< 1.00	< 1.00	1.58	< 0.05	< 1.00	< 1.00	52.00
Riverbend SS	< 1.00	< 1.00	< 1.00	3.22	< 0.05	< 1.00	< 1.00	55.00
Riverbend SS	< 1.00	< 1.00	< 1.00	< 1.00	< 0.05	< 1.00	< 1.00	53.00
Riverbend SS	< 1.00	< 1.00	< 1.00	1.83	< 0.05	< 1.00	< 1.00	47.00
Riverbend SS	< 1.00	< 1.00	< 1.00	1.21	< 0.05	< 1.00	< 1.00	56.00
Riverbend SS	< 1.00	< 1.00	< 1.00	1.65	< 0.05	< 1.00	< 1.00	< 25.00
Mean								



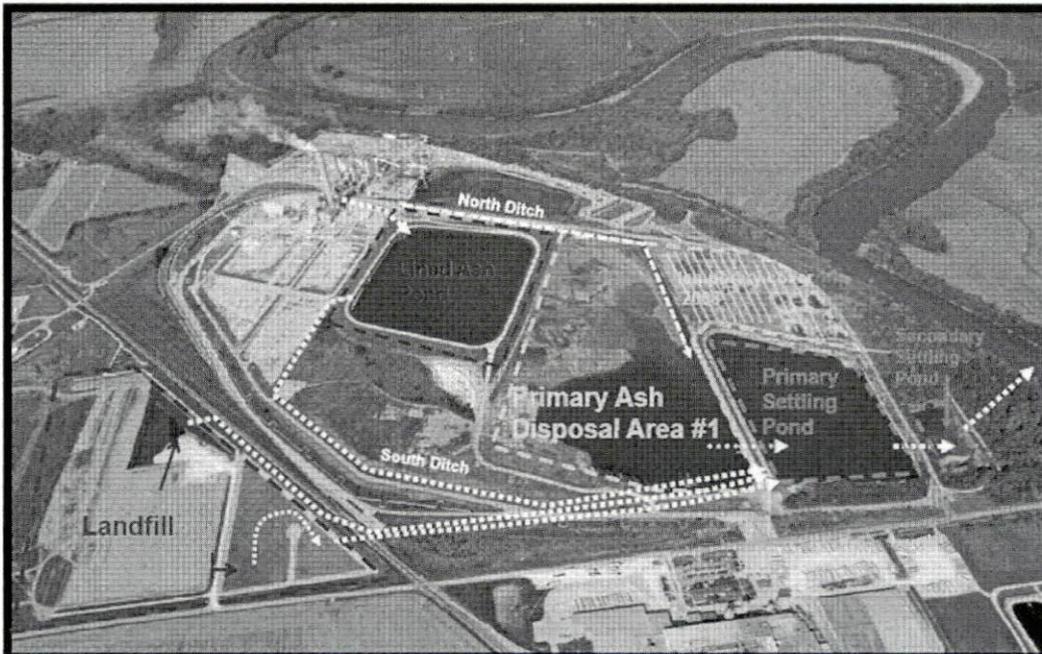
Duke monitors rivers and lakes around plants, but monitor per NPDES requirements or surface water standards

This often means we can't directly compare GW standards to surface water standards – we monitor different parameters

However, we do have comparable results for some stations

- Above the monitoring points around Riverbend are shown on the map on the right (upstream marker 278, Downstream of plant marker 277.5, at CLT drinking water intake marker 277)
- Results are essentially the same at all three locations over the past 3 years and all are below GW and surface water standards
- And impacts are reducing

## Cayuga Station – Site Lay-out



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Finally, I would like to review the Cayuga site

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We are going to flip through several slides quickly, but you will get a very good view of what impact remediation efforts are having and the benefits of a strong relationship with the state regulators

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This site was selected based on the fact it is a very advanced coal ash remediation site that continues to operate as a coal plant and has significant impacts on GW

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From this view you can see a new lined ash pond that is in service and was constructed in 2005. this is the only lined ash pond in the Duke fleet

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The lined ash pond is built over an old existing ash pond and is acting as a synthetic cap for this pond

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The primary ash disposal area #1 is in the process of being closed with the cap in place method

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The Primary and secondary settling basins will remain in service

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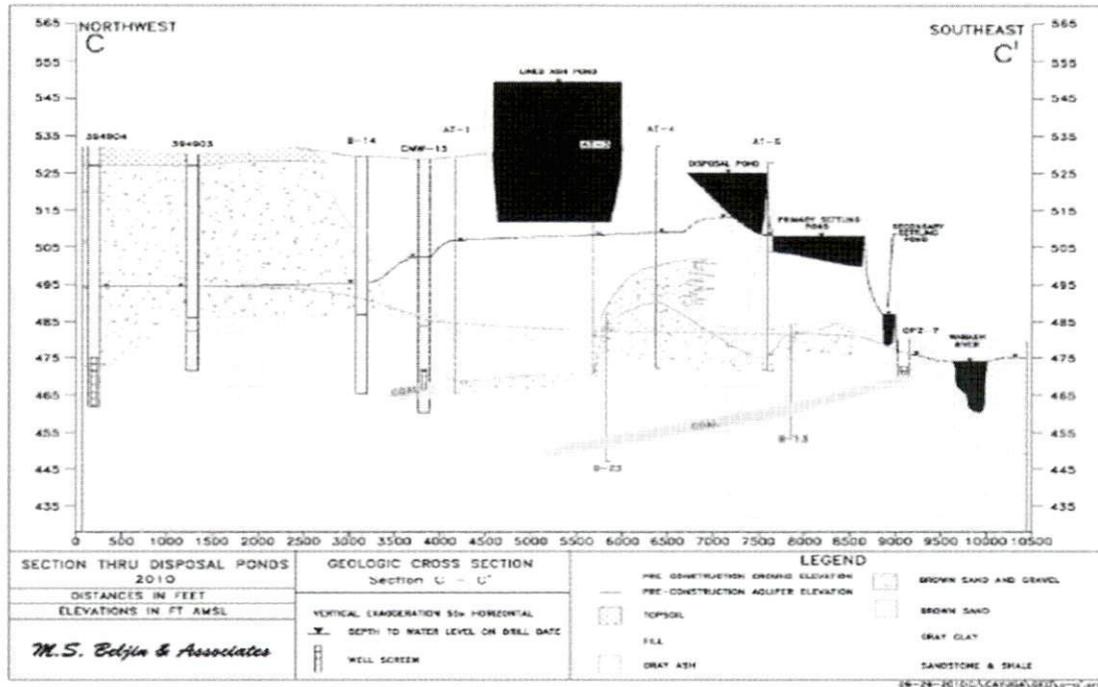
The site lined landfill is in the bottom left

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# Cayuga Station Groundwater Cross Section



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This cut-away view the Cayuga site shows very porous soil condition immediately below the plant that is made up of sand and gravel and the old existing ash pond

Another unique feature is the shale sandstone base the exits the ground right at river level

Like water above ground, groundwater flows downhill and travels from higher GW levels to lower lever

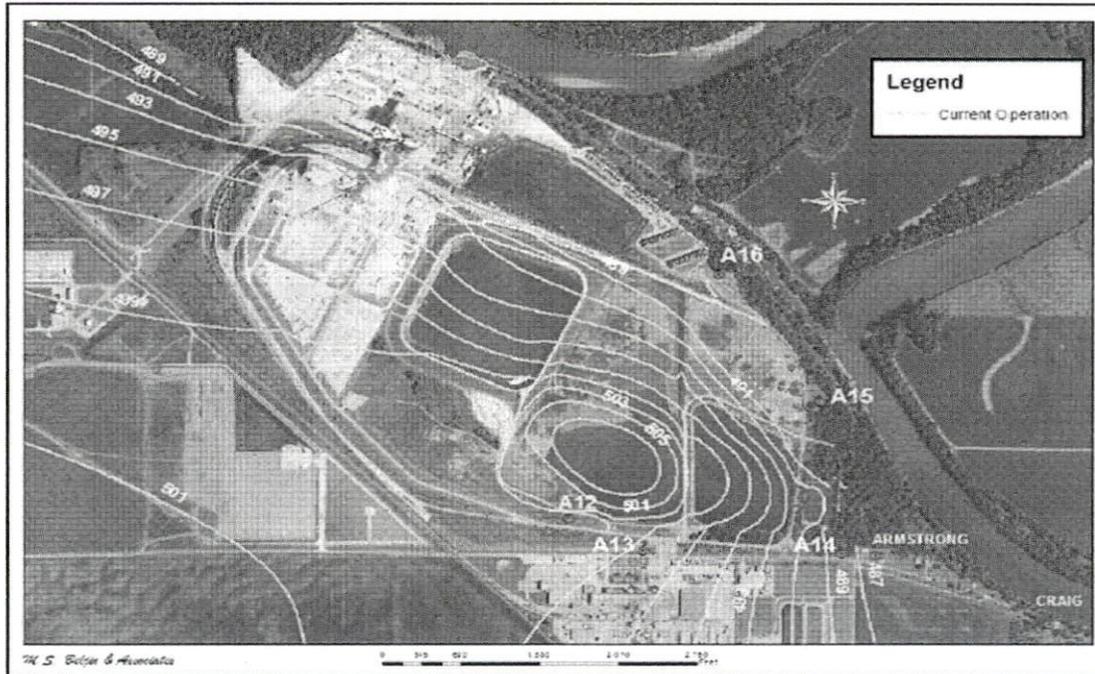
As you can see the Wabash River is the hydraulic break receiving body and is the low point, all GW flows to it

Our primary ash pond is the high point of ground water and influences the flow in the immediate area, with water flowing out in all directions

Due to the porous soil this site has some of the highest water loss of all sites (approx 6MGD into ash pond, 2MGD loss)

Seeps have been incorporated into the site NPDES permit during recent renewal process

## Cayuga Station – Current Operations



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Here is a different view of the GW elevations

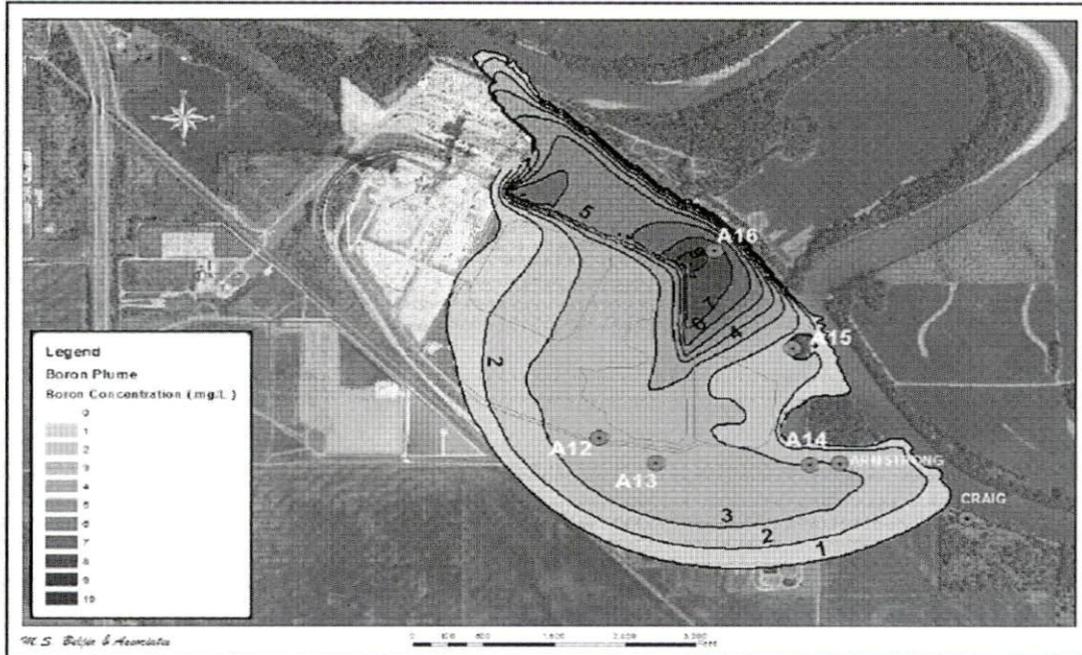
Generally the flow is toward the Wabash River as you saw on the cut away view

The primary ash pond influences this somewhat as water flows in all directions from this pond, but quickly turns back to the river

Note on the drawing that the lined ash pond has no impact on GW flow



## Cayuga Station – Current Boron Plume



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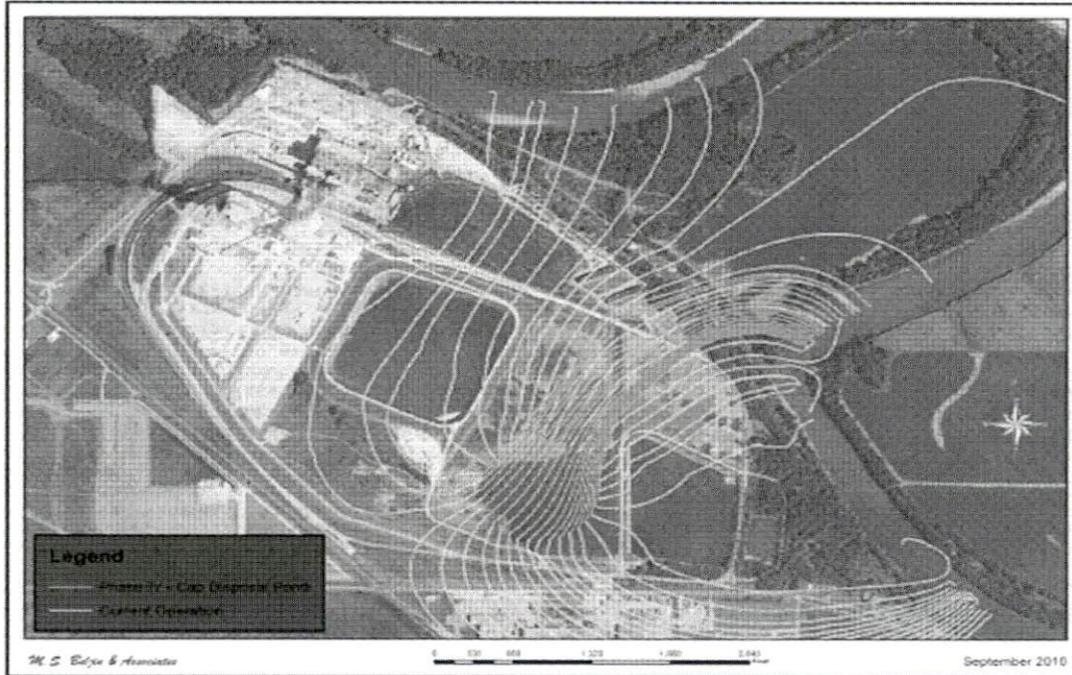
A similar view showing the boron plume currently seen at the site

Remember that boron is only an early indicator of other elements and is not a health related standard

When this was first investigated there were 3 downgradient residences, one was purchased and demolished and two were moved to municipal water

Only 5 residences remain, all are upgradient away from the plume and on municipal water

## Cayuga Station – Groundwater Flow After Ash Pond Close



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The primary ash pond is in the process of being closed with the cap in place method  
Voluntary ash pond closure underway and was coordinated with the State

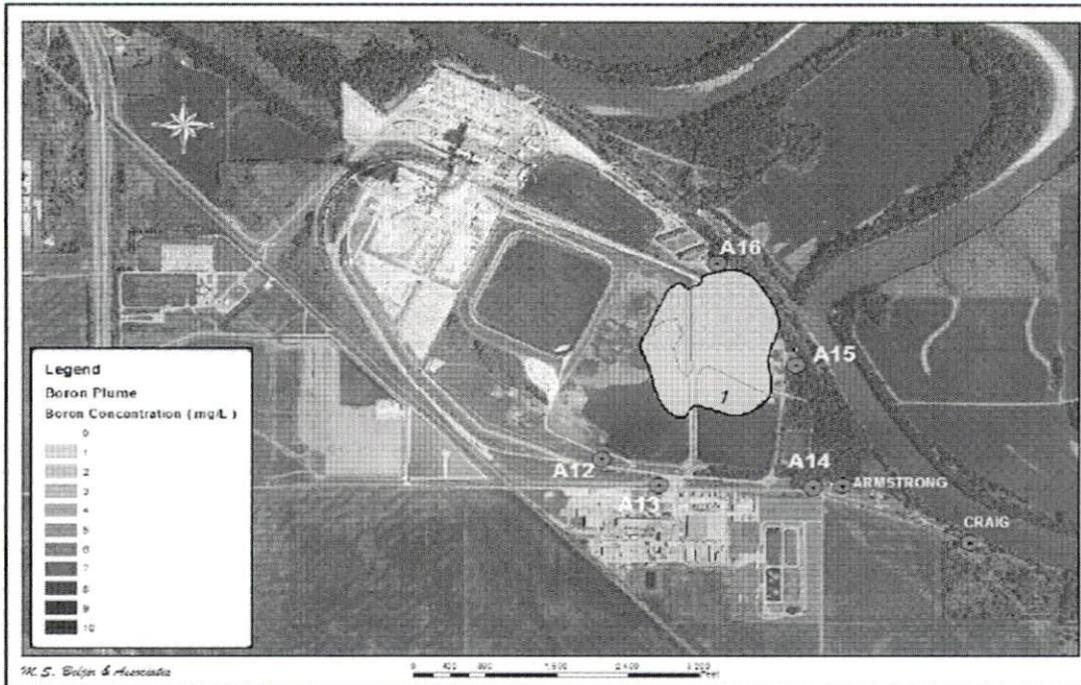
They are using plant ash and gypsum as fill as it is produced to create 5% grade, plan  
for 2025 completion, end with clay or synthetic cap

Could close faster if State did not allow us to use plant byproducts to close as they are  
produced

Minimal environmental impact and large cost savings

The blue lines show the new expected GW flow once the pond is capped

## Cayuga Station – Forecasted Boron Plume 2022



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This graphic shows the expected remaining Boron plume in 2022 once the pond is dewatered and capped

There will likely be a minimal impact on GW from the coal ash based on the fact that the very bottom of the old existing ash pond will remain in the GW table

The State is aware of this and approved the closure plan based on the minimal impact and the high dilution rate

Again, this shows the dramatic effect that ash basin dewatering can have. Groundwater impacts decrease quickly

Capping the pond then prevents future impacts from surface water leaching through the ash



## Receptors – Who is at Risk?

- Receptors are those in the path of groundwater flow – i.e., downgradient
- Where groundwater flows into a water body, it is a barrier to distant receptors
- Receptors are residential/industrial groundwater drinking water wells in the path of migrating groundwater
- Most drinking water is provided by municipal systems
- Individuals up-gradient are not at risk



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As discussed earlier, receptors are locations that use groundwater (via wells) and could be impacted by our coal ash

Significant work has been done to date to ensure we are not impacting receptors

Over the next few years we will be completing detailed receptor surveys at all locations to verify GW flow expectation and what receptor water sources are

# Receptor Summary

Plant	Background Wells	Compliance Wells	Groundwater Standard Exceedences	Secondary Standard Exceedences	Residences Within 1/2 Mile	Down Gradient Receptors	Side Gradient Receptors	Up Gradient Receptors
Crystal River	1	6	2	5	~0	0	0	0
Cayuga	2	10	2	2	~10	0	0	5
Edwardsport	0	0	0	0	~100	0	0	0
Edwardsport IGCC	0	0	0	0	~100	0	0	0
Gallagher	0	2/7	2	5	~50	0	1	0
Gibson	4	58	2	6	~15	0	5	0
Wabash River	0	5	0	3	~10	0	0	0
Beckjord	2	18	1	5	~10*	0	8*	2
East Bend	1	6	0	4	~5	0	0	0
Miami Fort	1	5	1	6	~0	0	0	0
Zimmer	2	8	0	0	~0	0	0	0
Allen Steam Station	2	11	2	3	~250	0	0	250
Asheville	3	8	4	8	~2500	0	3	3
Belews Creek	2	7	2	3	~50	0	1	40
Buck Steam Station	2	12	2	5	~150	0	0	150
Cape Fear	2	11	4	6	~100	0	0	20
Cliffside Steam Station	2	7	1	5	~25	0	5	10
Dan River Steam Station	1	6	3	5	~50	0	0	1
Lee Plant (NC)	3	10	3	5	~100	0	0	10
WS Lee Steam Station	2	13	1	3	~75	0	25	50
Marshall Steam Station	2	10	1	5	~100	0	0	3
Mayo	2	8	3	4	~20	0	5	10
Riverbend	2	12	1	3	~300	0	0	5
Robinson	1	2	2	3	~250	0	25	100
Roxboro	1	7	1	5	~20	0	0	20
Sutton	2	15	7	5	~200	0	0*	0
Weatherspoon	1	3	1	3	~100	0	80	0
<b>Total</b>	<b>43</b>	<b>258</b>	<b>48</b>	<b>66</b>	<b>407</b>	<b>0</b>	<b>150</b>	<b>670</b>

Indicate larger populations could be affected due to proximity of municipal wells



This table shows receptor information for all sites

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- Residences located within 1/2 mile of ash storage areas (include all locations regardless if on wells, cisterns, municipal water)
- Downgradient receptors – note that all downgradient receptors have been eliminated
- Side gradient and upgradient receptors
- Monitoring wells are in place to ensure that side and up gradient receptors are not being impacted

## Potentially Impacted Receptors: Action Taken to Date

Station	Constituent	Response
Asheville	Iron, manganese, thallium	Provided alternate water supply; more investigation
Sutton	Boron	Agreement to provide municipal connection to CFPWA
Allen	No impacts identified	NCDENR sampled neighbor's wells; results showed no 2L impacts
Cayuga	Boron	Provided municipal water connection; closing ash basin
Gibson	Boron	Provided municipal water connection; closing ash basin
Beckjord	Sulfate	Installed "interceptor" well

See Appendix C for detailed list of receptor work by station



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Preemptive actions taken to date are shown on this table

These issues have been monitored for years and when issues were identified action was taken

Could have been more proactive in the recent Sutton and Asheville cases, but both situations were being monitored

It is important that we continue to monitor GW samples and take actions proactively if any indications are seen

No current concerns at any sites where specific receptor testing should be done - **VERIFY**

Sutton and Asheville remediation work is currently in progress

# Ash Pond Closure Status

Retired station, decommissioning is underway, detailed ash pond

characterization work will begin in the first quarter of 2014

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ENERGY

Expect considerable attention from environmental groups when we submit closure plan

Also likely to have considerable media coverage due to proximity of City of Charlotte drinking water intakes about 5 miles downstream of site

## Ash Pond Closure Methodology (See Appendix D for Ash Pond Closure Details)

- Have begun site characterization and conceptual closure design at several retired sites
- Closure process for operating sites will be considered when regulatory risk of CCR and Effluent Limitations Guidelines (ELG) rules is manageable
- Detailed engineering reviews ensure we understand all factors
- Default strategy is cap-in-place/hybrid
- Excavation and removal reviewed further if default strategy does not ensure groundwater quality
- Throughout process, reuse options will be evaluated considering prudent cost, time to close and other factors
- The selected closure plan will be implemented when cost effective reuse options do not exist (including other factors)

 **Our current hybrid strategy v. excavation and removal is:** Confidential, For Planning Purposes Only

Protective of groundwater – more so if one considers timeliness

Faster – benefits flow much sooner – decades in most cases

More cost effective

Reduced impact to customers, responsible cost management and recovery issues



## Ash Pond Closure Methodology Continued

- Decommissioned Site – Perform Site Characterization
  - Identify ash locations
  - Identify ash depth
  - Map expected groundwater flow and level
  - Locate potential receptors
  - Develop State approved closure plan
- Operating Site – Active Ash Pond(s)
  - Capital upgrades
    - Dry flyash and dry bottom ash, redundancy
    - Waste water pond(s)
    - Additional water treatment
  - Site Characterization – same as above



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Pond closure work has been underway for some time

Work is accelerating due to the current decommissioning work at several sites

However, work has either been completed or is underway at 13 ash ponds

Our plan for properly closing the ash ponds at the decommissioned sites is well defined

If we decide to proceed, the work to close the ponds at the active sites is very similar to the decommissioned sites, but capital investments at the plant must be completed first

This work is estimated to cost about \$XX over X years

This work will involve system upgrades, additional redundancy, and new equipment to handle waste water processing

## Ash Pond Current Closure Plans

Plant	Excavation Complete	Excavation In Progress	Excavation Planned	Hybrid Cap in Place Complete	Hybrid Cap in Place In Progress	Hybrid Cap in Place Planned	Eco-Evaporation Planned	Unknown	Active Unlined In Service	Active Lined In Service
Crystal River	1								1	
Coyuga					1					
Edwardsport	2									
Gallagher					1	1				
Gibson					2				1	
Wabash River						3		1		1
Beckjord			2			2		5	1	
East Bend									1	
Miami Fort						2			1	
Zimmer										
Allen Steam Station					1	3			1	
Asheville		1				1			1	
Belews Creek						2			1	
Buck Steam Station						3		1		
Cape Fear						2	3			
Cliffside Steam Station			1			1			1	
Dan River Steam Station			2			2				
Lee Plant (NC)						1	2			
WS Lee Steam Station						4		1	1	
Marshall Steam Station					1	1			1	
Mayo						1			1	
Riverbend						4		1		
Robinson						2				
Roxboro				1	1	2			1	
Sutton			1			2				
Weatherspoon				1		1				
Total	3	1	6	2	7	40	5	9	13	1

This table shows the wide variety of work being done or planned for our ash ponds

The general preference is to use the hybrid cap in place methodology to close the ponds since it is the lowest cost and when done properly can provide the same amount of environmental protection as excavation

Based on the site specific information we have currently, all forms of pond closure are expected to be used

As detailed characterizations are completed, closure plans will be modified to address new details identified

Regardless of the best information and engineering review there will always be the possibility of follow-up closure work

As an example, GW levels may not receded to the levels expected keeping the lower levels of ash in the GW table

In this case we may need to come back in at a later date an install additional hydraulic breaks

# Coal Ash Dam Overview

Retired station, decommissioning is underway, detailed ash pond

characterization work will begin in the first quarter of 2014

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Expect considerable attention from environmental groups when we submit closure plan

Also likely to have considerable media coverage due to proximity of City of Charlotte drinking water intakes about 5 miles downstream of site

## Ash Dam Stability Review Process

- Initial dam construction based on detailed structural design plan
  - Soil conditions
  - Groundwater levels
  - Site conditions
  - Expected ash pond usage
- Routine inspection plan approved by State
- Perform routine inspections and report results as required
  - Vegetation management
  - Physical condition
  - Groundwater level
- Remediate all identified concerns



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All ash pond dams are inspected routinely based on plans approved by the state

This included vegetation management, physical condition, and GW levels

Any issues are noted, submitted to the state along with repair plans, review and completed once approved

## Components of the Duke Energy Dam Management Program

Location	Dam Totals
DEC	29
DEP	29
Midwest	24*
DEF	0

- **Dam Inspections** (See Appendix E for detailed inspection results and recommendations)
  - Internal monthly visual inspections & annual document review
  - Inspected after unusual events ( seismic activity or rain fall >2" )
  - Regulatory or third-party engineering firm inspections every 2 – 5 years
- **Operation and Maintenance Procedures**
- **Routine Engineering Studies**
  - Slope Analysis, Hydraulic Analysis, Breach Analysis

\*Coal ash dams in Indiana are not regulated, 8 Midwest dams in Ohio and



Kentucky are  
Dam inspections are both time and event based

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Internal and external engineering SME's are used

External engineering studies completed every 2 – 5 years based on regulatory requirements

EAPs include communication methods (primary and backup), perform inundation studies, inundation maps, share internal and external, conduct drills



## Areas of Focus - Ash Basins and Dams

- General
  - Eco-evaporative closure method is going to be difficult to obtain approval
- Asheville
  - Need to provide alternate water supply to 3 residences on Bear Leah Drive
  - GW exceedences in downgradient monitoring wells improving with lower water levels
  - Very high profile ash remediation location, need to finalize long term plans for generation assets so that ash strategy can be finalized
  - This is first active ash pond that should be addressed
- Roxboro Ash Basin
  - Hyco Lake starting to trend up due to low turnover, likely need to move to ZLD like Mayo
  - Dry ash system needs additional redundancy before ash pond can be closed

Eco-evaporative closure method planned for 5 – 6 ponds currently, old ponds

with significant cover growth

 ENERGY

May cause more impact if we clear and install a synthetic cap

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Geosyntech is the engineering firm performing the closure analysis and has used this method at other locations in the Northeast

### Asheville

Working to mitigate GW impacts at three side gradient residences currently

Very high profile site

Need to finalize long term generation strategy before deciding on ash pond closure methodology

### Roxboro

Hyco Lake has relatively low volume turnover, dry flayash system in place, still sluice bottom ash

May need to move to ZLD like Mayo due to scrubber waste water impact on lake

Would need more redundancy in dry ash system, currently sluicing to ash pond is emergency back-up system

## Areas of Focus - Ash Basins and Dams Continued

- Beckjord Ash Basins

- Relatively steep slopes on C ash pond with history of shallow slope failure
- Implemented a monitor and repair program to promptly address these shallow failures
- Regulatory agency approved this program with the understanding the basin will be decommissioned in the near future
- Several unstable old ash storage areas near landfill (~\$50M to excavate)
- We provided land North of A ash pond for municipal wells – avoid at all locations in future
- Ash basins located over high yield aquifer (~\$50 - \$300M to remediate)

- Robinson Ash Basin

- Ash pond may contain low level radioactive material
- It will be very difficult to move ash
- Conceptual closure engineering to begin in 2014

### Beckjord Ash Basin C Pond



Relatively steep slopes and history of shallow slope failures.

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Slope stability analyses indicates continued failure without improving the dams

If left unaddressed, shallow failures can be progressive and lead to a breach.

Geotechnical group has implemented a monitor and repair program to quickly address these shallow failures.

Regulatory agency has approved this plan despite the decommissioning of this pond in the near future.

The condition appears to be a medium risk.

All ash ponds are above high yield aquifer and no new ash storage project are approved in these locations even if lined

### Robinson Ash Basin

Unit 1 and the associated ash basin are planned for decommissioning.

Experienced an event where ash may have been contaminated by materials from Unit 2. Due to incident where Unit 1 and Unit 2 shared a condensate storage tank

Tank drained and cleaned out into a waste water settling pond, this pond was



## Areas of Focus - Ash Basins and Dams Continued

- Sutton Ash Basin
  - Small release of ash during Sept 2010 hurricane
  - Repairs were made, but additional ash placement has increased the pool height
  - The ash ponds are very full and some ash will need to be moved
  - Must complete municipal water connection to replace Cape Fear Municipal wells
  - Industrial wells are influencing GW flow and boron plume
  - Environmental groups focused on Sutton Lake which is not classified as waters of the State

### Sutton Ash Basin



Had a release of ash caused by overtopping due to hurricane conditions. Planning Purposes Only

Repairs were made, but additional ash placement has increased the pool height, decreasing the freeboard (distance from pool level to dam crest).

Risk of additional overtopping during severe storm conditions.

Scheduled for decommissioning and it is expected this issue will be addressed through the decommissioning process.

Ash ponds very full, can't cap in place as is, need to move some ash. Interstate project needs a lot of fill, this would be great result if they use our ash (they are reluctant currently pending CCR ruling)

This condition appears to be a moderate risk.

## Other Site Groundwater Concerns

- Future impacts are not completely solved by closing ash ponds
- Scrubber waste water next major issue, could be address as capital investments are made at operating sites to close ash ponds
- Groundwater conditions (level, spring) likely to change closure plans
- Gibson zero discharge pond
  - Water loss will continue after ash ponds closed
  - Impact to plant equipment as water cycles up
- Will face still opposition from environmental groups
- Zimmer has GW issues related to FGD runoff issues



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Expect vigorous SELC pushback when the plan is filed.

Scrutiny will only increase while reasonable efforts to close basins are not underway.

Concern over influence on judge in current consent decree and tie to recent Santee Cooper and SCANA decisions to excavate

Scrubber waste water is creating chloride, bromide, and TDs groundwater issues

## Recommendations

- Internal

- Aggressively pursue closure of ash ponds at all decommissioned sites
- Ensure characterization work identifies all areas of concerns
- Present all forms of closure methodologies to regulatory agencies to ensure there is alignment (hybrid, excavate, eco-evaporate)
- Coordinate closure strategy with other utilities
- Develop capital investment plan for coal plant upgrades – dry fly ash, dry bottom ash, redundancy, scrubber waste water (growth capital)
- Close **all** active ash ponds (COR accounts)

- External

- Launch a large scale stakeholder education program
- Consider engaging environmental groups regarding closure plans

See Appendix F for capital and closure plan cost summaries



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Close ash ponds at decommissioned plants to establish a closure process with regulators and test acceptance of various closure methods

I would like to see Duke adopt the strategy if closing all ash ponds

Incorporate a capital investment program to allow for closure of active ponds and mitigate impacts of scrubber waste water

We should then launch a large media campaign to educate the public on the closure science and costs to gain support for this plan once vetted with regulatory agencies and other utilities

Is there a benefit to engaging environmental groups directly, they would likely want to be linked to a "close all ash ponds" announcement, but do we think it is possible for them to accept alternate closure methods to excavation?

Duke philosophy is to not create any new unprotected ash storage footprints



# Groundwater Standards by State

Show Federal standards – then individual states, clarify summaries

2L Groundwater Standards																							
North Carolina	Parameter	Antimony	Arsenic	Barium	Boron	Cadmium	Chloride	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Nitrate	Nitrite	Selenium	Silver	Sulfate	Thallium	Zinc	TDS	pH
	Limit	1 µg/L	10 µg/L	700 µg/L	700 µg/L	2 µg/L	250 mg/l	10 µg/L	1 mg/l	300 µg/l	15 µg/L	50 µg/L	1 µg/L	100 µg/L	10 mg/l	1 mg/l	20 µg/L	20 µg/L	250 mg/l	0.2 µg/L	1 mg/l	500 mg/l	SU
			Primary			Primary		Primary	Secondary										Secondary		Secondary	Secondary	
South Carolina	Parameter	Antimony	Arsenic	Barium	Boron	Cadmium	Chloride	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Nitrate	Nitrite	Selenium	Silver	Sulfate	Thallium	Zinc	TDS	pH
	Limit		10 µg/L			5 µg/L		100 µg/L	1 mg/l										300 mg/l		5 mg/l	500 mg/l	
	Do not report results to State under voluntary plan																						
Indiana	Parameter	Antimony	Arsenic	Barium	Boron	Cadmium	Chloride	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Nitrate	Nitrite	Selenium	Silver	Sulfate	Thallium	Zinc	TDS	pH
	Limit																						
2L Groundwater Standards - Voluntary																							
Ohio	Parameter	Antimony	Arsenic	Barium	Boron	Cadmium	Chloride	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Nitrate	Nitrite	Selenium	Silver	Sulfate	Thallium	Zinc	TDS	pH
	Limit	1 µg/L	10 µg/L	700 µg/L	700 µg/L	2 µg/L	250 mg/l	10 µg/L	1 mg/l	300 µg/l	15 µg/L	50 µg/L	1 µg/L	100 µg/L	10 mg/l	1 mg/l	20 µg/L	20 µg/L	250 mg/l	0.2 µg/L	1 mg/l	500 mg/l	SU
2L Groundwater Standards - Voluntary																							
Kentucky	Parameter	Antimony	Arsenic	Barium	Boron	Cadmium	Chloride	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Nitrate	Nitrite	Selenium	Silver	Sulfate	Thallium	Zinc	TDS	pH
	Limit	1 µg/L	10 µg/L	700 µg/L	700 µg/L	2 µg/L	250 mg/l	10 µg/L	1 mg/l	300 µg/l	15 µg/L	50 µg/L	1 µg/L	100 µg/L	10 mg/l	1 mg/l	20 µg/L	20 µg/L	250 mg/l	0.2 µg/L	1 mg/l	500 mg/l	SU
Federal 2L Groundwater Standards - Secondary Standards Guidance Only																							
Florida	Parameter	Antimony	Arsenic	Barium	Boron	Cadmium	Chloride	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Nitrate	Nitrite	Selenium	Silver	Sulfate	Thallium	Zinc	TDS	pH
	Limit	1 µg/L	10 µg/L	700 µg/L	700 µg/L	2 µg/L	250 mg/l	10 µg/L	1 mg/l	300 µg/l	15 µg/L	50 µg/L	1 µg/L	100 µg/L	10 mg/l	1 mg/l	20 µg/L	20 µg/L	250 mg/l	0.2 µg/L	1 mg/l	500 mg/l	SU



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This chart shows the incredible variation state to state in groundwater monitoring standards

- Need to verify OH, KY, and FL standards

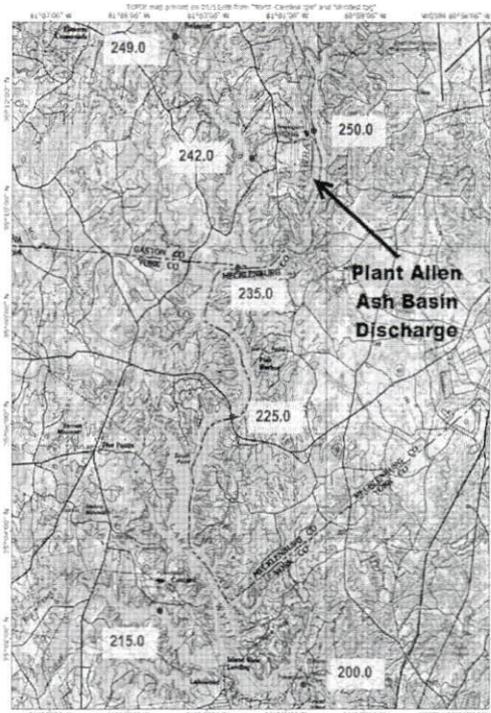






# Allen Steam Station River Impact Monitoring

Location	As (µg/l)	Cd (µg/l)	Cr (µg/l)	Cu (µg/l)	Hg (µg/l)	Pb (µg/l)	Se (µg/l)	Zn (µg/l)	TDS (mg/L)
250.0 (Upstream)	< 1.00	< 1.00	< 1.00	1.89	< 0.05	< 1.00	< 1.00	< 2.00	62
250.0 (Upstream)	< 1.00	< 1.00	< 1.00	2.57	< 0.05	< 1.00	< 1.00	< 2.10	56
250.0 (Upstream)	< 1.00	< 1.00	< 1.00	1.28	< 0.05	< 1.00	< 1.00	< 1.28	53
250.0 (Upstream)	< 1.00	< 1.00	< 1.00	2.23	< 0.05	< 1.00	< 1.00	< 1.00	51
250.0 (Upstream)	< 1.00	< 1.00	< 1.00	1.52	< 0.05	< 1.00	< 1.00	< 1.62	57
250.0 (Upstream)	< 1.00	< 1.00	< 1.00	1.92	< 0.05	< 1.00	< 1.00	< 1.28	29
Average- 100% RL	1.00	1.00	1.00	1.90	0.05	1.00	1.00	1.55	51
Average- 50% RL	0.50	0.50	0.50	1.90	0.03	0.50	0.50	1.30	51
235.0 (Downstream)	< 1.00	< 1.00	1.58	6.45	< 0.05	< 1.00	< 1.00	5.18	79
235.0 (Downstream)	< 1.00	< 1.00	< 1.00	6.62	< 0.05	< 1.00	< 1.00	2.53	71
235.0 (Downstream)	< 1.00	< 1.00	< 1.00	2.35	< 0.05	< 1.00	< 1.00	1.57	54
235.0 (Downstream)	< 1.00	< 1.00	< 1.00	6.03	< 0.05	< 1.00	< 1.00	1.82	54
235.0 (Downstream)	< 1.00	< 1.00	1.43	1.94	< 0.05	< 1.00	< 1.00	2.68	72
235.0 (Downstream)	< 1.00	< 1.00	< 1.00	6.37	< 0.05	< 1.00	< 1.00	1.92	44
Average- 100% RL	1.00	1.00	1.17	4.96	0.05	1.00	1.00	2.62	62
Average- 50% RL	0.50	0.50	0.84	4.96	0.03	0.50	0.50	2.62	62



Duke monitors rivers and lakes around plants, but monitor per NPDES

requirements or surface water standards



This often means we can't directly compare GW standards to surface water standards – we monitor different parameters

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However, we do have comparable results for some stations

- Above the monitoring points around Riverbend are shown on the map on the right (upstream marker 278, Downstream of plant marker 277.5, at CLT drinking water intake marker 277)
- Results are essentially the same at all three locations over the past 3 years and all are below GW and surface water standards
- And impacts are reducing





WP 1-3-1

WP 1-3-2



WP 1-3-1

WP 1-3-2





# Potentially Impacted Receptors: Detailed Summary

Plant	Corrective Actions	Existing Concerns
Cayuga	One residence demolished, two residences moved to municipal water supply, industrial facility does not use for drinking water	None
Edwardsport	Legacy ash ponds cleaned out as part of IGCC conversion, liner installed and now used as water treatment pond for IGCC	None
Edwardsport IGCC	Likely need to fulfill IDEM ash pond closure requirements for water treatment pond if IGCC stops using pond as water treatment location	None
Gallagher		None
Gibson	Residential receptors with elevated boron in wells were connected to municipal water supplies	None
Wabash River		None
Beckjord	Interceptor well installed North of A ash pond in the 80's to mitigate the sulfate indication that was found in neighboring public drinking water wells. All test post installation of the interceptor well have been below the sulfate limit	None
East Bend	One well has shown an upward trend for Chloride and sulfate, there are no potential receptors, but work is underway to address the trend	None
Miami Fort	The As indication in one well has been linked to a site condition and not the ash pond	None
Allen Steam Station	Potential receptors exist to the West of the ash ponds, but are upgradient and it is not believed they will see any impacts from the ash ponds. The State recently sampled several wells in this area, results are pending	None
Asheville	Five private wells are side-gradient to the ash pond, two of these wells were put on bottled drinking water per the States request due Fe and Mn results. A groundwater receptor survey within 1/2 mile of the ash pond compliance boundary and a groundwater site conceptual model have been completed and results submitted to NCDENR. Long term mitigation efforts are	Yes
Belews Creek		None
Buck Steam Station	Potential receptors exist to the southeast of the ash ponds, but are upgradient and it is not believed they will see any impacts from the ash ponds.	None
Cape Fear		None
Cliffside Steam Station		None
Dan River Steam Station		None
Lee	One well (CMW-6) consistently have high As readings, additional land was purchased to allow Duke to have a full 500' compliance boundary in this area. Another well was installed in this area further from the ash basis. As readings are lower, but still above the GW limits	None
WS Lee Steam Station		None
Marshall Steam Station		None
Mayo		None
Riverbend	There has only been one sample event where Antimony was detected. The reading was 1.04µg/L and the lab detection limit is 1.00 µg/L	None
Robinson	Chromium exceedence has only been observed in a background well	None
Roxboro		None
Sutton	Two Cape Fear Public Utility Authority drinking water wells will be removed from service with future service coming from the Wilmington, NC drinking water system. Other industrial receptors utilize non-potable wells.	Yes
Weatherspoon	Only Thallium exceedence was in a background well	None

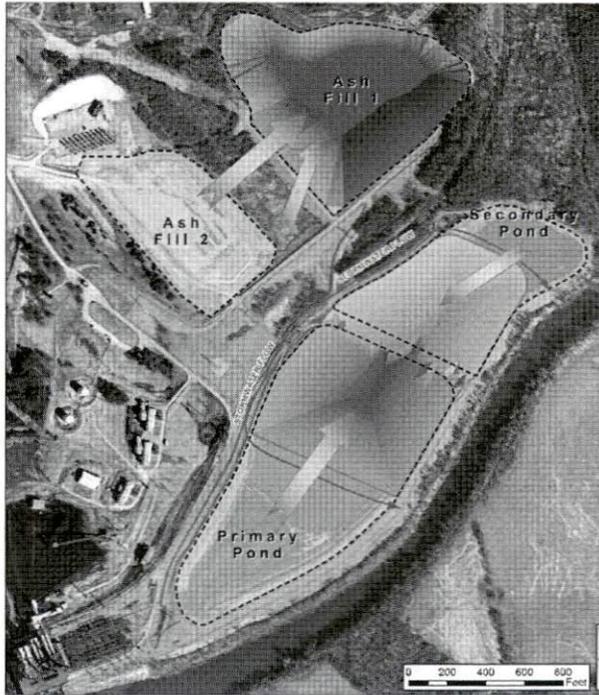


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# Ash Basin Closure Conceptual Design



Current Characterization & Design Work		
Station	Contractor	Complete
Weatherspoon	S&ME	Completed
Dan River	AMEC	1/17/2014
Buck	HDR	2/28/2014
Lee (NC)	Geosyntec	1/1/2014
Cape Fear	Geosyntec	1/1/2014

Scheduled for 2014		
Station	Start	Complete
Riverbend	Feb.	Aug.
Sutton	Feb.	Aug.
Robinson	April	Oct.
Wabash River	April	Oct.
Beckjord (Budget)	May	Nov.



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Accelerate the timing of closure – very limited ability; Already falling behind original retired plant schedule and dependent on state agency approval

Hybrid Closure might be considered in order to minimize the surface area of an engineered cover system or to minimize the amount of borrow material from other sources.

## Duke Energy Inventory of Unclosed Ash Ponds and Fills

	Ash Ponds (acres)	Total Fill (acres)	Total Acres	Ash Ponds (MM tons)	Total Fill (MM tons)	Total MM Tons
DEP	804	515	1,319	28.1	19.2	47.3
DEC	1,428	453	1,881	59.9	13.3	73.2
DEF	28	154	182	0.1	4.7	4.8
DEI	372	468	840	7.8	22.9	30.7
DEO & DEK	350	396	746	7.4	36.9	44.3
	<b>Total Acres:</b>		<b>4,969</b>	<b>Total Tons:</b>		<b>200,411,361</b>

- Total coal ash sites/structures- 24 sites/ 61 ponds; 58 structural/landfills
- Ash currently added to ponds- less than 1 million tons/year and decreasing
- Ponds serve multiple purposes (e.g., stormwater retention)



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Total Fill= Landfill is disposal while structural fill has a beneficial use (e.g., plant staging area, parking lot, warehouse, etc.)

New ash added to ponds is about 50/50 fly and bottom ash; most dry fly ash is being reused or disposed in lined landfills.

For example, MSS burns more than a unit train per day – a unit train is 120 cars, 10% ash

= 18,792 tons of coal/day and 1880 tons of ash/day

MSS 1-4 summer rating is 2087 MW (less than Belews Creek 1&2, Roxboro 1-4 and Crystal River 1, 2, 4, 5)

2014 estimate is about 4.5 MM tons produced with about 1 MM to ponds, 2.4 MM to landfills and 1.2 MM sold (rest is intra-station activity e.g., EBS and WHZ)

Ponds serve other functions – stormwater control, boiler chemical cleaning waste; other waste streams are treated and diluted in the ponds; ponds continue to operate after station is retired.

## Ash Ponds and Fills Closure Costs

	Non-Hazardous Cap In Place	Non-Hazardous Excavation	Hazardous Excavation	Comments
<b>Tons Excavated</b>	27.4M	146.5M	189.5M	Additional 40M tons already lined and/or capped would require excavation under hazardous classification (e.g., 20M tons in Gibson East Ash Pond)
<b>Rate to Excavate, Load, Haul &amp; Place</b>	\$5.66 to \$7.05/ton	\$8.44/ton	\$60 to \$104/ton	Hazardous handling estimates derived from EPRI study. Increased cost for certified drivers/operators, double-lined trucks, hazmat suits, cleaning, spill management, etc. Hazardous reclassification requires all off-site landfills for certain stations.
<b>Acres of Additional Landfill</b>	0	1,174	1,516	
<b>Acres Capped (ponds &amp; landfills)</b>	3,327	1,591	1,945	
<b>10-year Capital</b>	\$1.5B	\$3.3B	\$11.5B	
<b>Capital to Completion</b>	\$1.5B	\$7.1B	\$23.0B	Excavation options extend beyond 10 years. Excavating 750,000 tons/year/station assumed.



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Cap-in-place cost would not be lost if had to excavate & remove some (all) later since characterization studies, ash consolidation and other measures have value even for excavate and remove.

Typically look 10 years ahead for presentations. In previous presentation only the 10-year figure was provided. Total costs are over a 36-year period.

### Assumptions & Risks:

Ash tonnages calculated using limited information. Due to age of the facilities, ash basin documentation is incomplete or does not exist, resulting in engineering estimates that are based upon some assumptions. Conceptual engineering studies will refine the ash tonnages.

Landfills were sited for each station and in many cases were offsite; selected by looking for open greenfields as close to the station as possible. No environmental, cultural, or public impacts were investigated; property values are unknown. If assumed locations are not available, costs will increase as the landfill location has to move outward, lengthening the haul distance.

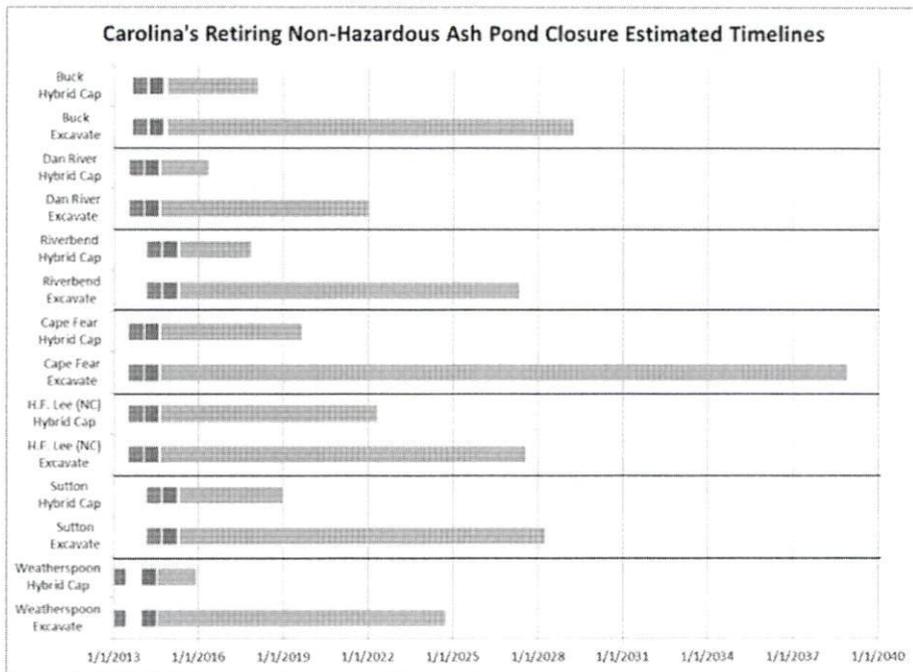
Availability of qualified engineering firms to design, permit, and provide support during construction across the entire fleet during the same timeframe would be difficult and will increase costs. This is not factored into the estimates.

Availability and/or lack of qualified earthwork contractors and equipment to perform





**Carolina's Retiring Non-Hazardous Ash Pond Closure Estimated Timelines**



**Legend**  
 Conceptual Design    Final Design    Construction

**Under current plans we anticipate closing all ponds at retiring units using cap-in-place or hybrid by 2022 to 2023 (HF Lee; Beckjord)** E4 | Confidential, For Planning Purposes Only

Litigation regarding the landfill permitting and construction could delay this schedule even longer.

Explain why Riverbend and Sutton not first in order and get date we plan to start study- 1<sup>st</sup> quarter next year – expectation is March. We will need to get out a RFQ in January so that the contractor could begin work around that time.

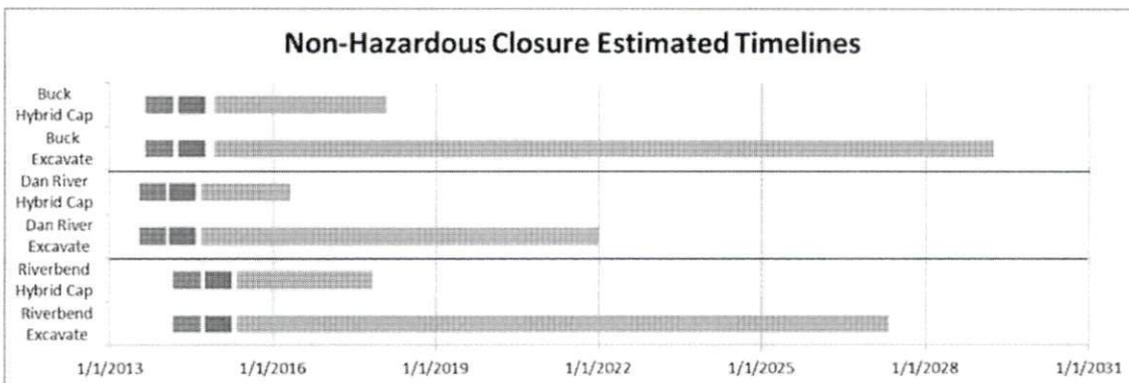
Landfill construction 5 to 7 years (additional 1 to 3 years if litigated)

### Duke Energy Carolinas Retired Ash Ponds

Station	Non-Hazardous Hybrid Cap (-10%,+20%)	Non-Hazardous Excavating (-10%,+40%)	Hazardous Excavating (-10%,+50%)
Buck	\$ 41,160,030	\$ 222,153,709	\$ 520,247,681
Dan River	\$ 21,680,223	\$ 49,245,450	\$ 74,136,450
Riverbend	\$ 34,764,370	\$ 180,110,921	\$ 537,037,838

Legend	
	Conceptual Design
	Final Design
	Construction

### Non-Hazardous Closure Estimated Timelines



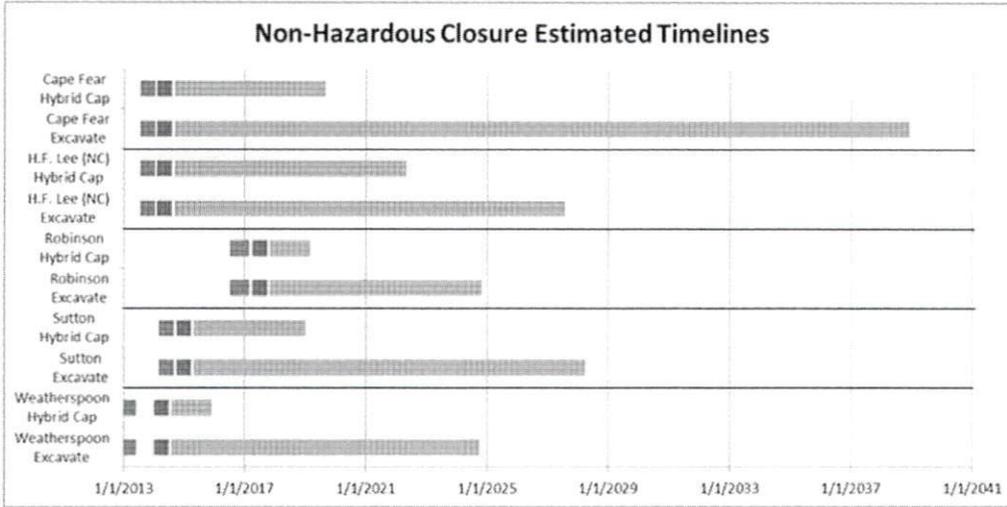
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### Duke Energy Progress Retired Ash Ponds

Station	Non-Hazardous Hybrid Cap (-10%,+20%)	Non-Hazardous Excavating (-10%,+40%)	Hazardous Excavating (-10%,+50%)
Cape Fear	\$ 79,301,092	\$ 557,413,424	\$ 1,242,461,739
H.F. Lee (NC)	\$ 64,791,241	\$ 201,479,526	\$ 475,915,193
Robinson	\$ 30,062,445	\$ 32,477,571	\$ 55,332,632
Sutton	\$ 59,452,176	\$ 185,641,409	\$ 476,781,193
Weatherspoon	\$ 31,166,512	\$ 111,809,658	\$ 263,368,159

Legend	
	Conceptual Design
	Final Design
	Construction

### Non-Hazardous Closure Estimated Timelines

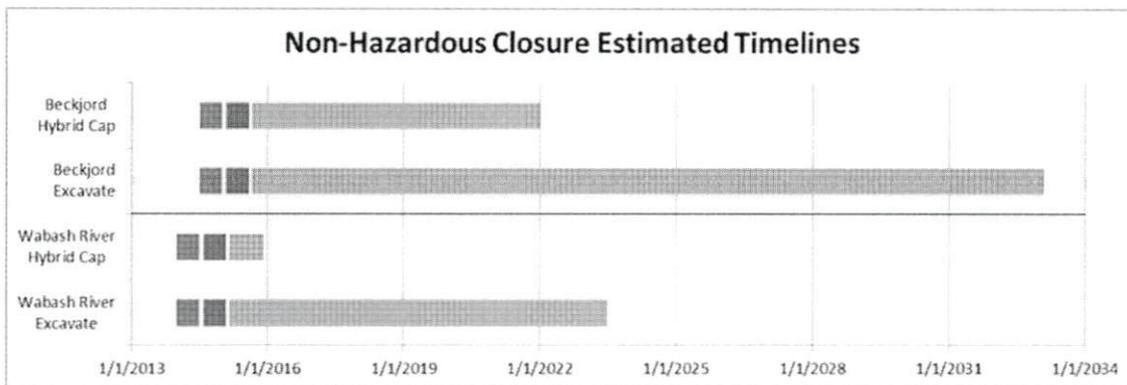


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### Duke Energy Ohio & Indiana Retired Ash Ponds

Station	Non-Hazardous Hybrid Cap (-10%,+20%)	Non-Hazardous Excavating (-10%,+40%)	Hazardous Excavating (-10%,+50%)
Beckjord	\$ 41,873,319	\$ 317,288,305	\$ 596,845,396
Wabash River	\$ 48,004,780	\$ 61,805,344	\$ 440,338,625

Legend	
	Conceptual Design
	Final Design
	Construction



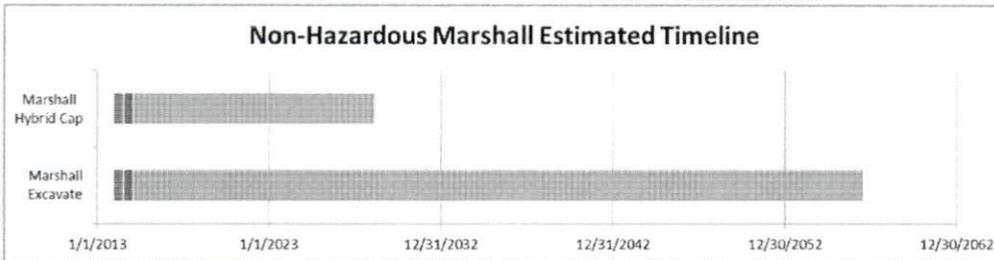
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### Duke Energy Operating Ash Ponds

Station	Non-Hazardous Hybrid Cap (-10%,+20%)	Non-Hazardous Excavating (-10%,+40%)	Hazardous Excavating (-10%,+50%)
Allen	\$ 95,446,399	\$ 497,485,022	\$ 899,414,442
Asheville	\$ 18,562,209	\$ 60,987,762	\$ 440,928,344
Belews Creek	\$ 125,423,443	\$ 564,761,515	\$ 1,323,903,631
Cayuga	\$ 52,444,779	\$ 133,673,275	\$ 648,318,307
Cliffside	\$ 58,702,947	\$ 228,776,058	\$ 577,152,430
Crystal River	\$ 33,186,482	\$ 194,503,065	\$ 343,961,931
East Bend	\$ 17,252,091	\$ 36,683,367	\$ 116,673,722
Gallagher	\$ 49,342,935	\$ 165,216,969	\$ 895,416,662
Gibson	\$ 133,232,459	\$ 190,124,858	\$ 8,286,368,453
Lee (S.C.)	\$ 29,801,516	\$ 80,329,551	\$ 205,768,454
Marshall	\$ 203,566,551	\$ 2,388,606,224	\$ 2,731,780,088
Mayo	\$ 63,406,161	\$ 204,931,251	\$ 579,539,991
Miami Fort	\$ 12,839,993	\$ 40,701,643	\$ 195,581,562
Roxboro	\$ 86,614,407	\$ 366,670,125	\$ 787,346,647

Legend	
	Conceptual Design
	Final Design
	Construction

### Non-Hazardous Marshall Estimated Timeline



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## List of CCR Impoundments in the Dam Safety Program

	Station	Dam Name	Current Status	Hazard Classification	Last Regulatory Inspection	Hydraulic Height (ft)	Slope (#/1)	Impoundment Capacity (acre-ft)
DUKE ENERGY CAROLINAS	Allen	Retired Ash Basin Dam	DRAINED	High	Dec-12	70	2	5,915
		Active Ash Basin Dam	ACTIVE	High	Dec-12	50	2	1,870
	Belew's Creek	Ash Pond	ACTIVE	High	Apr-13	115	2.5	190,000
	Buck	Main Dam	ACTIVE	High	Jan-13	80	3	12,564
		New (Additional Primary) Dam	ACTIVE	High	Jan-13	70	2.5	2,844
		Basin 1 to Basin 2 Dam	ACTIVE	High	Jan-13	80	2.5	N/A
		Basin 2 to Basin 3 Dam	ACTIVE	High	Jan-13	80	2.5	801
		Intermediate Dam	ACTIVE	High	Jan-13	14	2.5	N/A
	Cliffside	Inactive Ash Basin #5 Main Dam	ACTIVE	High	Feb-13	97	2.5	685
		Inactive Ash Basin 1-4 Main Dam	ACTIVE	High	Feb-13	38	2.5	266
		Active Ash Basin Dam	ACTIVE	High	Feb-13	120	2.5	5,025
	Dan River	Active Primary Ash Basin	ACTIVE	High	Jan-13	37	2	477
		Active Secondary Ash Basin	ACTIVE	High	Jan-13	27	2	187
	Lee	Primary Ash Basin	ACTIVE	High	Jun-10	75	2	779
		Secondary Ash Basin	ACTIVE	High	Jun-10	75	2	391
	Marshall	Active Ash Basin Dam	ACTIVE	High	Jan-13	90	2	6,885
	Riverbend	Active Ash Basin Dam 1 (Primary)	ACTIVE	High	Dec-12	80	2.5	1,640
		Ash Basin Dam 2 (Secondary)	ACTIVE	High	Dec-12	70	2.5	987
		Ash Basin Intermediate Dam	ACTIVE	High	Dec-12	8	3	N/A

- Hazard Classification - Classification given by the state based on the possible effects of a dam failure
- Slope - (#) Horizontal : (1) Vertical



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## List of CCR Impoundments in the Dam Safety Program

	Station	Dam Name	Current Status	Hazard Classification	Last Regulatory Inspection	Hydraulic Height (ft)	Slope (#/1)	Impoundment Capacity (acre-ft)
DUKE ENERGY PROGRESS & DUKE ENERGY FLORIDA	Asheville	1982 Ash Pond Dam	ACTIVE	High	Apr-13	95	2	1,400
		1964 Ash Pond Dam	ACTIVE	High	Apr-13	90	2.5	N/A
	Cape Fear	1956 Ash Pond Dam (Inactive)	DRAINED	High	Mar-10	20	1.1 - 1.5	N/A
		1963 Ash Pond Dam (Inactive)	DRAINED	High	Mar-10	22	1.5	N/A
		1970 Ash Pond Dam (Inactive)	DRAINED	High	Mar-10	27	2	N/A
		1978 Ash Pond Dam	ACTIVE	High	Mar-10	27	2	N/A
		1985 Ash Pond Dam	ACTIVE	High	Mar-10	28	2.0 - 4.0	1,764
	HF Lee	Active Ash Pond	ACTIVE	High	Jan-12	20	3.3	1,980
		Ash Pond 1 (Inactive)	EXEMPT	Low	Feb-10	7	2	231
		Ash Pond 2 (Inactive)	EXEMPT	Low	Feb-10	15	3	795
		Ash Pond 3 (Inactive)	EXEMPT	Low	Feb-10	10	2	850
	Mayo	Ash Pond Dam	ACTIVE	High	Mar-13	90	2.5	4,100
		FGD Settling Pond	ACTIVE	Low	Mar-13	20	3	103
		FGD Flush Pond	ACTIVE	Low	Mar-13	20	3	7
	Robinson	Ash Pond	ACTIVE	Low	Feb-11	20	2.5	410
	Roxboro	West Ash Pond Dam	ACTIVE	High	Mar-13	70	2	4,800
		West Ash Pond South Rock Filter	ACTIVE	Intermediate	Mar-13	51	1.3	4,800
		West FGD Settling Pond	DRAINED	High	Mar-13	36	2.75	442
		East FGD Settling Pond	ACTIVE	High	Mar-13	36	2.75	132
		FGD Forward Flush Pond	ACTIVE	High	Mar-13	36	2.75	51
		East Ash Pond	ACTIVE	Low	Mar-13	38	3	N/A
		Sutton	1972 Cooling Pond	ACTIVE	Low	Feb-12	12	2
	Crystal River	1971 Ash Pond	ACTIVE	Low	Feb-12	24	3	248
		1984 Ash Pond	ACTIVE	Low	Feb-13	32	2.5	1,364
	Weatherspoon	1979 Ash Pond	ACTIVE	Intermediate	Nov-12	28	1.5	425
	Crystal River	FGD Settling Pond 6	ACTIVE	No Ranking for Florida	Internal Jan-13	22	3	66
		FGD Settling Pond 7	ACTIVE	No Ranking for Florida	Internal Jan-13	16	3	16

Exempt - This dam is not under the jurisdictional authority of the regulatory agency due to size and/or hazard classification.



## List of CCR Impoundments in the Dam Safety Program

	Station	Dam Name	Current Status	Hazard Classification	Last Regulatory Inspection	Dam Height (ft)	Slope (#/1)	Impoundment Capacity (acre-ft)
DUKE ENERGY INDIANA, KENTUCKY, & OHIO	Zimmer	Active Wastewater Pond	ACTIVE	Low	Exempt - No Dam	N/A	N/A	N/A
		Active Clearwater Pond	ACTIVE	Low	Exempt - No Dam			N/A
		Active Settling Basin D	ACTIVE	Low	Exempt - No Dam			N/A
	Beckjord	Inactive Ash Pond A	RETIRED	Significant	Mar-12	20	2	N/A
		Active Ash Pond B	ACTIVE	Significant	Mar-12	20	3	280
		Active Ash Pond C	ACTIVE	Significant	Mar-12	50	1.5	1,400
		Active Ash Pond C Extension	ACTIVE	Significant	Mar-12	40	3	1,300
	Edwardsport	Primary	CONVERTED to wastewater ponds	Significant	Mar-12	15	2	N/A
		Secondary		Significant	Mar-12	15	2	N/A
	Gallagher	Ash Pond A	ACTIVE	Significant	Mar-12	29	2	936
		Secondary Pond	ACTIVE	Low	Mar-12	19	2	63
	East Bend	Active Wastewater Pond	ACTIVE	Significant	Mar-12	60	2	1,844
	Gibson	Inactive East Ash Pond 1	Closure underway	Low	Mar-12	20	3	1,733
		Inactive East Ash Pond 2	Closure underway	Low	Mar-12	20	3	1,733
		Inactive East Ash Pond 3	Closure underway	Low	Mar-12	20	3	3,325
		Active East Ash Pond Settling Basin	ACTIVE	Low	Mar-12	20	3	743
		Active North Ash Pond	ACTIVE	Low	Mar-12	20	3	350
		Active North Ash Pond Settling Basin	ACTIVE	Low	Mar-12	20	2	150
	Wabash River	Active Primary Pond A	ACTIVE	Significant	Mar-12	19	2	1,350
		Active Primary Pond B	ACTIVE	Significant	Mar-12	19	2	538
		Active Secondary Pond A	ACTIVE	Significant	Mar-12	20	2	73
		Active Secondary Pond B	ACTIVE	Significant	Mar-12	20	2	N/A
	Miami Fort	Active South Pond	ACTIVE	Significant	Mar-12	22	2	1,450
		Active Ash Pond A	ACTIVE	Significant	Mar-12	40	2	803
	Cayuga	Active Ash Pond B	ACTIVE	Significant	Mar-12	40	3	515
		Active Lined Disposal Cell 1	ACTIVE	Significant	Mar-12	32	3	1,400
		Active Ash Disposal Area 1	ACTIVE	Significant	Mar-12	42	2	260
Active Primary Settling Pond		ACTIVE	Significant	Mar-12	55	2	225	
Active Secondary Settling Pond		ACTIVE	Low	Mar-12	24	2	36	
		Retired Ash Pond	RETIRED	Significant	Mar-12	40	2	N/A





## Cost Recovery Issues

\$s in millions

	Total Cost of Removal Reserve (as of 6/30/13)	Steam Cost of Removal Reserve (as of 6/30/13)	Non-Hazardous Cap In Place	Non-Hazardous Excavation & Disposal	Hazardous Excavation & Disposal
DEC	\$1,600	\$224	\$610	\$1,300	\$4,200
DEP	1,100	138	430	1,000	2,800
DEI	731	367	280	500	3,000
DEO	231	-	100	250	820
DEK	61	12	20	35	140
DEF	488	71	30	190	340
Total 10 year	\$4,211	\$812	~\$1,500	~3,300	~11,500

- Total cost to completion for nonhazardous excavation is \$7.1B and for hazardous excavation is \$23.0B
- The company could potentially reallocate portions of the "total" COR to cover the cap-in-place ash pond costs
  - Regulatory approval likely to be required to do this



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This table shows the various 10 year scenarios and the COR reserve balances. The second column shows the portion reserved for the steam assets. Just because the "steam" reserve is lower than the planned costs does not mean we could not use some of the other "total" COR reserve to cover the ash pond costs.

There are different points of view as to what type of approval would be required to access the COR funds not specifically allocated to steam currently. One point of view is that no approval is needed and the other is that we would have to notify regulators of the usage. As mentioned earlier, the next depreciation study would likely show that you would need to replenish these reserves at the next rate case; especially anything beyond the steam COR.

# Remaining Dry Ash Conversion Capital Project Cost Estimates (Non-Hazardous)

Project	Facility	Sum of 2013	Sum of 2014	Sum of 2015	Sum of 2016	Sum of 2017	Sum of 2018	Sum of 2019	TOTAL COSTS	
Dry Flyash Collection	Asheville	\$0	\$0	\$53,045	\$79,568	\$5,941,040	\$9,335,920	\$0	\$15,409,573	
	Cayuga	\$11,386,085	\$25,890,333	\$6,973,736	\$0	\$0	\$0	\$0	\$44,250,154	
	Cliffside	\$0	\$0	\$0	\$2,377,075	\$8,589,354	\$13,365,744	\$519,499	\$24,831,672	
	Killen	\$0	\$0	\$0	\$1,321,134	\$4,762,687	\$7,428,431	\$288,728	\$13,800,980	
	Mayo	\$335,346	\$129,415	\$307,010	\$4,657,710	\$0	\$0	\$0	\$5,429,481	
	Roxboro	\$3,005,204	\$16,298,109	\$28,073,660	\$1,465,458	\$2,500,000	\$0	\$0	\$51,342,431	
	Stuart	\$0	\$0	\$559,875	\$3,171,692	\$7,602,835	\$8,259,174	\$4,537,039	\$24,130,615	
	<b>TOTAL</b>	<b>\$14,726,635</b>	<b>\$42,317,857</b>	<b>\$35,967,326</b>	<b>\$13,072,638</b>	<b>\$29,375,916</b>	<b>\$38,389,269</b>	<b>\$5,345,265</b>	<b>\$179,194,906</b>	
	Dry Bottom Ash Collection	Allen	\$0	\$0	\$0	\$2,837,134	\$11,688,995	\$24,079,327	\$21,701,495	\$80,306,951
		Asheville	\$0	\$0	\$625,912	\$3,808,931	\$9,747,014	\$11,704,635	\$268,849	\$26,155,341
Belews Creek		\$0	\$0	\$0	\$6,678,768	\$25,223,481	\$43,930,133	\$18,001,907	\$93,834,289	
Cayuga		\$0	\$0	\$0	\$3,277,056	\$12,380,089	\$21,575,892	\$8,886,888	\$46,119,925	
Cliffside		\$0	\$0	\$0	\$4,486,122	\$16,172,471	\$25,224,434	\$980,421	\$46,863,448	
Conesville		\$0	\$0	\$0	\$673,130	\$2,381,294	\$4,884,266	\$4,383,920	\$12,182,610	
East Bend		\$0	\$0	\$0	\$1,651,782	\$6,846,540	\$14,103,873	\$12,711,116	\$35,323,311	
Gallagher		\$0	\$0	\$0	\$1,036,588	\$4,270,744	\$8,797,730	\$7,928,956	\$22,034,018	
Gibson		\$0	\$0	\$609,699	\$10,128,637	\$33,945,801	\$54,793,619	\$20,609,502	\$120,087,258	
Killen		\$0	\$0	\$0	\$1,576,187	\$5,682,155	\$8,862,538	\$344,469	\$16,465,348	
Marshall		\$0	\$0	\$0	\$5,507,386	\$21,171,342	\$38,293,106	\$20,208,672	\$85,180,506	
Mayo		\$8,706,400	\$0	\$0	\$0	\$0	\$0	\$0	\$8,706,400	
Miami Fort		\$0	\$0	\$1,230,463	\$5,703,196	\$11,487,503	\$7,395,080	\$276,979	\$26,093,221	
Roxboro		\$0	\$0	\$2,490,772	\$12,717,206	\$28,697,546	\$28,331,717	\$18,377,794	\$90,615,034	
Stuart		\$0	\$0	\$916,672	\$5,192,949	\$12,447,971	\$13,522,581	\$7,428,404	\$39,506,578	
<b>TOTAL</b>	<b>\$6,706,400</b>	<b>\$0</b>	<b>\$5,873,518</b>	<b>\$65,185,071</b>	<b>\$202,122,947</b>	<b>\$305,478,932</b>	<b>\$142,109,372</b>	<b>\$727,476,239</b>		
Dry Flyash Collection and Fixation	Gibson	\$2,511,230	\$103,885	\$0	\$0	\$0	\$0	\$0	\$2,615,115	
	<b>TOTAL</b>	<b>\$2,511,230</b>	<b>\$103,885</b>	<b>\$0</b>	<b>\$0</b>	<b>\$0</b>	<b>\$0</b>	<b>\$0</b>	<b>\$2,615,115</b>	
<b>GRAND TOTAL</b>	<b>\$23,944,265</b>	<b>\$42,421,742</b>	<b>\$41,840,843</b>	<b>\$78,257,708</b>	<b>\$231,496,863</b>	<b>\$343,868,201</b>	<b>\$147,454,637</b>	<b>\$909,286,260</b>		



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## Duke Energy Steam Facility Data (As of 9/30/13)

Structure	Operating state	Jurisdiction	Steam unit facility	Owned capacity - summer rating (MW)	Fuel type	Current cooling method	Air Emissions controls	Ash handling (flyash, bottom ash)	Ash ponds on site (3)
Regulated	In Operation	DE Carolinas	Allen	1,127	Coal	Once-Through	Scrubber	Dry, Wet Sludge	Active and Inactive
Regulated	In Operation	DE Carolinas	Bellevue Creek	2,220	Coal	Once-Through	Scrubber and SCR	Dry, Wet Sludge	Active and Inactive
Regulated	In Operation	DE Carolinas	Cliffside 5	569	Coal	Closed Cycle	Scrubber and SCR	Wet Sludge, Wet Sludge	Active and Inactive
Regulated	In Operation	DE Carolinas	Cliffside 6	625	Coal	Closed Cycle	Scrubber and SCR	Dry, Dry	Active and Inactive
Regulated	In Operation (1)	DE Carolinas	Lee	370	Coal	Once-Through		Wet Sludge, Wet Sludge	Active and Inactive
Regulated	In Operation	DE Carolinas	Marshall	2,078	Coal	Once-Through	558MW with Scrubber and SCR; 1420MW with Scrubber	Dry, Wet Sludge	Active and Inactive
Regulated	In Operation	DE Carolinas	Buck CC	620	Gas	Closed Cycle	SCR		Inactive
Regulated	In Operation	DE Carolinas	Dan River CC	620	Gas	Closed Cycle	SCR		Inactive
Regulated	In Operation	DE Carolinas	Catawba	435	Nuclear	Closed Cycle			
Regulated	In Operation	DE Carolinas	McGuire	2,200	Nuclear	Once-Through			
Regulated	In Operation	DE Carolinas	Doonsee	2,538	Nuclear	Once-Through			
Regulated	In Operation	DE Progress	Asheville	378	Coal	Once-Through	Scrubber and SCR	Wet Sludge, Wet Sludge	Active and Inactive
Regulated	In Operation	DE Progress	Mayo	604	Coal	Cooling Lake	Scrubber and SCR	Dry, Dry	Inactive
Regulated	In Operation	DE Progress	Roanoke 1-4	2,327	Coal	Once-Through (1-3), Closed Cycle (4)	Scrubber and SCR	Dry, Wet Sludge	Active and Inactive
Regulated	In Operation (1)	DE Progress	Sutton 1-3	575	Coal	Cooling Lake		Wet Sludge, Wet Sludge	Active and Inactive
Regulated	In Operation	DE Progress	Smith 4-6	1,122	Gas	Closed Cycle	SCR		
Regulated	In Operation	DE Progress	Wayne County CC	920	Gas	Closed Cycle	SCR		Inactive
Regulated	In Operation	DE Progress	Brunswick	1,517	Nuclear	Once-Through			
Regulated	In Operation	DE Progress	Harris	742	Nuclear	Cooling Lake			
Regulated	In Operation	DE Progress	Robinson	724	Nuclear	Once-Through			Inactive
Regulated	In Operation	DE Florida	Andros	1,011	Gas	Once-Through			
Regulated	In Operation	DE Florida	Bartow CC	1,133	Gas	Once-Through	SCR		
Regulated	In Operation (2)	DE Florida	Crystal River 1-2	873	Coal	Once-Through		Dry, Dry	Active
Regulated	In Operation	DE Florida	Crystal River 4-5	1,422	Coal	Closed Cycle	Scrubber and SCR	Dry, Dry	
Regulated	In Operation	DE Florida	Hess CC	1,912	Gas	Cooling Lake	SCR		
Regulated	In Operation	DE Florida	Sarasota River	129	Gas/Oil	Once-Through			
Regulated	In Operation	DE Florida	Tiger Bay	295	Gas	Closed Cycle			

(1) Potential retirements include DEC Lee Units 1-2, Sutton Units 1-3, Wabash River Units 2-5, Mears For Unit 6, and Backport Units 4-6. Reflects already completed retirement of Edgewater 5-6 (100 MW), Buck 3-6 (385 MW), Cliffside 1-4 (198 MW), Dan River 1-3 (278MW), Riverbend 4-7 (454MW), Galaghis 1-3 (288MW) per Consent Decree, Seepford 1 (94MW), Weatherproof 1-3 (177 MW), DEP Lee 1-3 (261 MW), Bartow 1-3 (440 MW), Robinson 1 (177 MW), Cape Fear 5-6 (316 MW), Crystal River 3 (783 MW) and Backport 2-3 (222MW) which retired 10/1/2013. Wabash River Unit 6 (320 MW) potential to be converted to gas or retired. DEC Lee Unit 3 (110MW) to be converted to gas.

(2) Crystal River 1-2 (875 MW) potential to be retired. MATS compliance options are being reviewed.

(3) "Inactive" means that the storage facility is not currently receiving ash.



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## Duke Energy Steam Facility Data, cont. (As of 9/30/13)

Structure	Operating state	Jurisdiction	Stream unit facility	Owned capacity— summer rating (MW)	Fuel type	Current cooling method	Air Emissions controls	Ash handling (fresh, bottom ash)	Ash ponds on site (3,4)
Regulated	In Operation	DE Indiana	Coryca	1,005	Coal	Once-Through	Scrubber; SCR Under Construction	Wet Sluice (Dry Under Construction); Wet Sluice	Active and Inactive
Regulated	In Operation	DE Indiana	Gibson	2,822	Coal	Cooling Lake, No NPDES Permit	Scrubber and SCR	Dry, Wet Sluice	Active and Inactive
Regulated	In Operation (1)	DE Indiana	Wabash River	698	Coal	Once-Through		318MW Dry, Wet 350MW Wet, Wet	Active and Inactive
Regulated	In Operation	DE Indiana	Gallagher 264	280	Coal	Once-Through	Baghouse	Dry, Wet Sluice	Active and Inactive
Regulated	In Operation	DE Indiana	Edwardsport IGCC	918	Coal	Closed Cycle - No Intake	Scrubber and SCR	Dry Slag Handling	
Regulated	In Operation	DE Indiana	Hobbesville CC	310	Gas	Closed Cycle			
Regulated	In Operation	DE Kentucky	East Bend	414	Coal	Closed Cycle	Scrubber and SCR	Dry, Wet Sluice	Active
Regulated	In Operation (1)	DE Kentucky	Miami Fort 6	163	Coal	Once-Through		Wet Sluice, Wet Sluice	Active
Non-Regulated	In Operation	DE Ohio	Gooseville 4	312	Coal	Closed Cycle	Scrubber and SCR	Dry, Wet Sluice	Active
Non-Regulated	In Operation	DE Ohio	Stuart 1-3	675	Coal	Once-Through	Scrubber and SCR	Wet Sluice, Wet Sluice	Active
Non-Regulated	In Operation	DE Ohio	Stuart 4	225	Coal	Closed Cycle	Scrubber and SCR	Wet Sluice, Wet Sluice	Active
Non-Regulated	In Operation	DE Ohio	Kilen	198	Coal	Closed Cycle	Scrubber and SCR	Wet Sluice, Wet Sluice	Active
Non-Regulated	In Operation (1)	DE Ohio	Beckford	543	Coal	Once-Through		150 MW Dry, Wet 393MW Wet, Wet	Active and Inactive
Non-Regulated	In Operation	DE Ohio	Miami Fort 7-8	640	Coal	Closed Cycle	Scrubber and SCR	Dry, Wet Sluice	Active
Non-Regulated	In Operation	DE Ohio	Zimmer	605	Coal	Closed Cycle	Scrubber and SCR	Dry, Dry	Active
Non-Regulated	In Operation	Duke Energy	Fayette CC	833	Gas	Closed Cycle	SCR		
Non-Regulated	In Operation	Duke Energy	Hanging Rock CC	1,262	Gas	Closed Cycle	SCR		
Non-Regulated	In Operation	Duke Energy	Washington CC	639	Gas	Closed Cycle	SCR		
Regulated	Under Construction	DE Progress	Sutton CC	625	Gas	Closed Cycle	SCR		

- (1) Potential retirements include DEC Lee Units 1-2, Sutton Units 1-3, Wabash River Units 2-5, Miami Fort Unit 6, and Beckford Units 4-6. Reflects already completed retirements of Edwardsport 6-8 (180 MW), Buck 3-6 (388 MW), Calfade 1-4 (158 MW), Doe River 1-3 (275 MW), Riverbend 4-7 (454 MW), Galagher 1-3 (280 MW) per Consent Decree, Beckford 1 (84 MW), Watherspoon 1-3 (177 MW), DEP Lee 1-3 (261 MW), Bentow 1-3 (440 MW), Robinson 1 (177 MW), Cape Fear 5-8 (318 MW), Crystal River 3 (78 MW) and Beckford 2-3 (222 MW) which retired 10/1/2013. Wabash River Unit 8 (320 MW) potential to be converted to gas or retired. DEC Lee Unit 3 (170 MW) to be converted to gas.
- (2) Crystal River 1-2 (875 MW) potential to be retired. MATS compliance options are being reviewed.
- (3) "Inactive" means that the storage facility is not currently receiving ash.
- (4) Other locations with inactive ash ponds include the retired Riverbend, Cape Fear, and Watherspoon Stations.



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# Guidance for Comanagement of Mill Rejects at Coal-Fired Power Plants

**TR-108994**

Final Report, June 1999

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# REPORT SUMMARY

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Traditionally, utilities have comanaged some or all of their low-volume wastes with their high-volume combustion by-products in disposal facilities. This report presents guidance on comanagement of coal combustion by-products and mill rejects containing pyrites at coal-fired power plants. The report specifically addresses the issue of environmental protection from leachates due to oxidation of pyrites under certain conditions. Included is a discussion of acid-base accounting and neutralization capacity of alkaline coal ash to assist in appropriate comanagement of mill rejects in landfills and impoundments.

## **Background**

The electric utility industry annually generates more than 100 million tons of high-volume coal combustion by-products (CCBs) consisting of fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) sludge. Historically, about 25% of high-volume by-products have been used for construction materials and other applications; most of the remaining 75% have been disposed of in landfills or impoundments. Utilities also generate a number of low-volume wastes as a result of coal fuel preparation, equipment maintenance, water purification, and materials storage and handling practices associated with fossil fuel combustion. This study was part of an EPRI multiyear effort, performed in cooperation with the Utility Solid Waste Activities Group (USWAG) and individual utility companies. The study was designed to characterize utility comanagement practices as well as collect and analyze a comprehensive set of data pertinent to environmental effects and best management practices.

## **Objectives**

To characterize mill rejects generated as a by-product of coal processing; to assess environmental effects from comanagement of high-volume CCBs and coal mill rejects; to develop guidance for environmentally effective comanagement practices for mill rejects containing pyrites.

## **Approach**

Investigators conducted a survey of 40 power plants in 1996 to obtain information on power plant equipment, coal types burned, coal mill rejects generation rates, and handling/disposal methods. They next performed limited sampling and laboratory analyses to establish chemical composition and mineralogy of mill rejects. In addition, they researched literature and completed laboratory tests to develop an understanding of acid-base accounting and neutralization potential for CCBs as well as comanagement systems for mill rejects. Finally, they developed alternatives for coal mill rejects management/comanagement and modified the EPA's draft Industrial D guidance material on performing closure and postclosure operations (included here).

## Results

This report summarizes six case studies developed as a result of the 1996 EPRI survey. These studies revealed the following:

- From 55-75% of the coal-fired power plants comanage mill rejects and CCBs in landfills or impoundments. Because many plants do not record mill rejects production, limited data were available on the amount of mill rejects generated. Based on available data, mill rejects generation ranged from 0.15 lbs/hr to 2800 lbs/hr.
- Analysis of mill reject samples revealed that quartz, pyrite, calcite, dolomite, kaolinite, siderite, marcasite and two types of feldspars were the minerals most often present. Pyritic sulfur ranged from less than 0.01% to 20.85%.
- Three of the six case studies showed the presence of leachates formed by pyrite oxidation. These acidic leachates were characterized by elevated concentrations of sulfate and metals such as iron, nickel, and arsenic.
- Tests on regrinding and coburning of coal mill rejects showed that coburning in utility boilers is a technically feasible management option. The study provides guidelines for comanagement of rejects with coal ash in an impoundment or landfill.

## EPRI Perspective

Previous EPRI research provided technical inputs to the EPA, leading to its 1993 determination that regulation of high-volume fossil fuel combustion by-products as hazardous waste was unwarranted. At that time, the EPA deferred its determination on low-volume wastes as well as the comanagement of high-volume by-products with low-volume wastes, pending further study. In its March 1999 Report to Congress, the EPA noted its limited concern for the comanagement of pyritic materials and indicated the Agency had engaged the utility industry in a program to appropriately manage these wastes. EPRI developed this technical guidance manual in close consultation with the EPA Office of Solid Waste, in particular with the staff of the Industrial and Extractive Waste Branch. The manual fulfills the need for industrywide technical guidance on appropriate management/comanagement of mill rejects containing pyrites.

## TR-108994

### Keywords

Pyrite

Mill rejects

Comanagement

Groundwater quality

Coal combustion by-products

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## EXECUTIVE SUMMARY

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Some coal-fired power plants generate rejects when they mill fuel coal, particularly for burning in PC boilers. Depending on the type of coal and the type of mill, the quantity of mill rejects generated varies. Because of relatively small amounts of mill rejects, they are often comanaged with fly ash and bottom ash. Mill rejects can be defined as the dense material found in fuel coal that cannot be ground by the mills at a power plant to the desired size for burning in the boilers. This material may include hard coal, rocks with quartz, and the iron sulfide minerals such as pyrite and marcasite. However, some mill rejects may contain only a small percentage of these sulfide minerals. There are also power plants where no mill rejects are generated.

One of the objectives of this research was to obtain information on the generation rate, the mineralogic and chemical characteristics and the management practices for mill rejects. A second objective of this research was to identify practical alternatives for the sound comanagement of mill rejects generated at coal-fired power plants. As suggested by the U.S. EPA staff, this report also contains information for closure and post-closure considerations for the comanagement of mill rejects and coal ash in landfills and impoundments. Technical information on the comanagement of mill rejects was provided to the U.S. EPA for use in the part 2 Bevill determination on the “remaining wastes” in 1999.

In 1995, EPRI surveyed coal-fired power plants and found that 55 percent of the 264 plants included in the survey comanaged mill rejects with coal combustion by-products (CCBs) in landfills or impoundments. A second focused but limited survey of 24 utilities representing 40 power plants completed in 1996, found that 75 percent of these plants comanaged mill rejects in landfills or impoundments. Five plants and an additional three units at other plants did not generate mill rejects. Limited data were found on the amount of mill rejects generated because many plants do not record mill rejects production. The quantity of mill rejects generated at plants surveyed for this project ranged from 0.15 lbs/hr to 2,800 lbs/hr, with an average of 350 lbs/hr for the 16 plants with data. In contrast, the rate of ash production at these plants ranged from 3,200 lbs/hr to 90 thousand lbs/hr. The mill rejects typically represent 0.003 to 0.043 percent of the total ash produced.

The composition of mill rejects varies due to differences in the input coal and mining methods. Nineteen samples of mill rejects were analyzed for mineralogy and chemical composition to augment the similar information obtained from published literature. These mill reject samples were derived from all types of coals, with total sulfur content of the coal ranging from 0.33 to 2.4 percent and ash content in the coal ranging from 4.5 to 15 percent. The major minerals found in the mill reject samples were quartz, pyrite, calcite, dolomite, kaolinite, siderite, marcasite, and two feldspars—albite and microcline. Pyrite was identified by X-ray diffraction in 13 of the 19 samples, but was the dominant mineral in only three samples from high-sulfur bituminous coals. The forms of pyrite vary from crystalline to microcrystalline to framboidal.

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Mill reject samples were analyzed for sulfur, major alkali cations, and 13 trace elements. The total sulfur in the mill reject samples ranged from 0.01 to 30 percent. Pyritic sulfur ranged from less than 0.01 to 20.85 percent, with a mean and median of 5.4 and 3.4 percent, respectively. The organic sulfur ranged from less than 0.01 to 8.95 percent, with a mean and median of 2.35 and 0.85 percent, respectively. Both the pyritic and organic sulfur were higher in mill rejects from bituminous coals than in mill rejects from subbituminous coals or lignite.

The chemical concentrations of analyzed constituents in mill rejects were compared to those of coal fly ash and bottom ash. Elements higher in mill rejects included iron, sulfur, arsenic, nickel, and selenium. Except for selenium, these elements are commonly associated with pyrites. TCLP leachates from mill rejects were lower in concentration for arsenic, barium, cadmium, chromium, and lead than in TCLP leachates from coal ash. Selenium was low in all leachate types. Silver and thallium concentrations were below detection levels in most TCLP tests for mill rejects.

This report contains a summary of six case studies of mill rejects comanagement in landfills and impoundments under different hydrogeologic settings. Four of these case studies involve comanagement of mill rejects in impoundments, and the other two involve landfill disposal. Three of these sites showed the presence of leachates formed by the oxidation of pyrites. These leachates are typically acidic, with elevated concentrations of iron and sulfate. The other three sites did not show the presence of such leachates, indicating that oxidation of pyrites was either absent or very minimal, or that no pyrites were present in the mill rejects.

The observations from the case studies indicate that when mill rejects contain pyrites, potential exists for the oxidation of the pyrites and the generation of acidic leachates with elevated concentrations of sulfate and metals. Sulfide in pyrites, in the presence of water and oxygen, biologically and chemically converts to sulfuric acid, with the concomitant release of iron, arsenic, nickel, and other metals. Even small amounts of pyrites can produce acidic leachates when exposed to oxygen over a sustained period of time in the presence of moisture. Therefore, it is necessary to manage mill rejects containing pyrites so that either the oxidation of pyrites is avoided, or the acidic leachates are neutralized, to control the migration of metals and sulfate into the groundwater. Alternatively, mill rejects containing pyrites can be reground and coburned in utility boilers completely eliminating the need for comanagement of mill rejects in landfills and impoundments.

Three alternatives for the management of mill rejects are presented in this report: (1) comanagement with coal ash in an impoundment or in a landfill; (2) management of mill rejects separately in an engineered land disposal unit; and (3) elimination of the need for disposal by regrinding and coburning with coal in the utility boilers. Guidance on how to evaluate and select from these alternative management methods is provided in this report. Acid-base accounting methods are also presented for use in this context. It is recognized that the amount of pyrites in mill rejects and potential for net acidity generation will influence the option selected for use at a specific site. Methods are also discussed for reducing the potential for pyrite oxidation following closure of the landfills and impoundments, along with postclosure monitoring needs.

Tests on coburning of mill rejects were conducted in a 600,000 lbs/hr fuel evaluation facility in 1995. Both screening and detailed tests were conducted to evaluate the effect of a mixture of coal and mill rejects on boiler efficiency, fouling and slagging potential, and nitrogen and sulfur emissions. These fuel evaluation tests showed that coburning is a technically feasible

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management option for mill rejects for some power plants. Therefore, all three options for management of mill rejects are feasible, although comanagement of mill rejects with ash in an impoundment or a landfill is the alternative most commonly used by the utilities.

The U.S. EPA, in its recently completed Report to Congress on Wastes from Fossil Fuel Combustion, has expressed some concern about the risks from leachates generated by pyrite oxidation. The Agency indicated that it has engaged the utility industry in a program for ensuring that management of pyrite-containing mill rejects will minimize any potential risks. This technical guidance manual was developed in cooperation with the U.S. EPA Office of Solid Waste as a result of this concern.



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# 1

## INTRODUCTION

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### Overview of Comanagement

The electric utility industry generates more than 100 million tons of fly ash, bottom ash, boiler slag, and flue-gas desulfurization (FGD) sludge each year from the combustion of coal (ACAA, 1998). Collectively, these are referred to as “high-volume” coal combustion by-products (CCBs). Historically, about 25 percent of the high-volume by-products have been used for construction materials and other beneficial use applications, while most of the remaining 75 percent have been disposed in utility-owned and non-utility-owned landfills or impoundments.

Utilities also generate other wastes associated with fossil fuel combustion, in conjunction with equipment maintenance, water purification, and materials storage and handling. Examples are boiler cleaning liquids, wastewater treatment sludges, demineralizer reagents, boiler and cooling tower blowdown, coal pile runoff, and mill rejects. These wastes are commonly referred to as “low-volume” wastes, although in some cases their liquid volumes may be substantial (greater than one million gallons per year per generating station). Most utilities have historically comanaged some or all of these low-volume wastes with their high-volume by-products in land disposal facilities.

EPRI, in cooperation with the Utility Solid Waste Activities Group (USWAG) and individual utility companies, has completed a multiyear research effort to generate field-scale information to evaluate environmental effects arising from comanagement of low-volume wastes with high-volume combustion by-products. The findings from this research are key technical inputs to a rescheduled 1999 regulatory determination by the United States Environmental Protection Agency (EPA) on “remaining wastes.”

### Regulatory Background

In 1980, Representative Thomas Bevill of Alabama sponsored an amendment to the Resource Conservation and Recovery Act (RCRA) that temporarily excluded three broad types of waste from Subtitle C hazardous waste disposal regulations: fossil fuel combustion waste, certain mining wastes, and cement kiln dust (Public Law 96-482, 1980). The rationale for the exclusion was that the wastes were generated in large volumes, there was little existing information regarding their characteristics and environmental behavior, and the potential hazards posed by the wastes were believed to be low based on the limited available data. The exclusion from hazardous waste regulations would remain in effect for these “Bevill Wastes” until completion of a comprehensive study of the wastes by the EPA as defined in RCRA Section 8002, and a subsequent determination on how to regulate them, if warranted.

In the case of fossil fuel combustion wastes, the exclusion referred to "fly ash waste, bottom ash waste, slag waste, and flue gas emission control waste generated primarily from the combustion of coal or other fossil fuels" (RCRA Sec. 3001 (b) (3) (A)). In 1981, Gary Dietrich, then the EPA Associate Deputy Assistant Administrator for Solid Waste, clarified the EPA's interpretation of the scope of the fossil fuel combustion waste exclusion in a letter to USWAG. The Dietrich letter stated that the exclusion applied to the following:

- fly ash, bottom ash, boiler slag, and flue gas emission control wastes resulting from (1) the combustion solely of coal, oil, or natural gas; (2) the combustion of any mixture of these fossil fuels; or (3) the combustion of any mixtures of coal and other fuels, up to a 50 percent mixture of such other fuels; and
- wastes produced in conjunction with the combustion of fossil fuels, which are necessarily associated with the production of energy, and which traditionally have been, and which actually are, mixed with and codisposed or cotreated with fly ash, bottom ash, boiler slag, or flue gas emission control wastes from coal combustion.

In 1988, the EPA completed its study of coal combustion wastes from electric generating power plants and issued a Report to Congress (RTC) finding that high-volume coal combustion by-products do not warrant regulation as hazardous waste under RCRA. When the EPA did not complete the required regulatory determination within six months of the RTC, a lawsuit filed in 1991 by the Bull Run Coalition led EPA to enter into a Consent Decree with a new schedule for completing the determination. The Consent Decree, formally entered on June 30, 1992, divided fossil fuel combustion wastes into two categories with different schedules: high-volume wastes from combustion of coal by electric utilities, and "remaining wastes." Remaining wastes were defined as:

- fly ash, bottom ash, boiler slag, and flue gas emission control wastes from the combustion of coal by electric utility power plants when such wastes are mixed with, codisposed, cotreated or otherwise comanaged with other wastes generated in conjunction with the combustion of coal or other fossil fuels; and
- any other wastes subject to Section 8002(n) of RCRA (except fly ash, bottom ash, boiler slag, and flue gas emission wastes from coal combustion by electric utilities).

Remaining wastes therefore include all wastes generated from the combustion of any mixture of coal and other fuels up to 50 percent mixtures of such other fuel; all combustion wastes when the primary fuel is a fossil fuel other than coal; and high-volume by-products from coal combustion when they are comanaged with other wastes generated in conjunction with the combustion of fossil fuels.

In accordance with the 1992 Consent Decree schedule, EPA published a final regulatory determination on high-volume coal combustion by-products in the Federal Register on August 9, 1993. The determination stated that, "Based on all of the available information, EPA has concluded that regulation of the four large-volume fossil fuel combustion wastes as hazardous waste under RCRA Subtitle C is unwarranted" (58 FR 42472). However, the determination was strictly limited to the management of the four high-volume coal combustion by-products. Comanagement of any other waste, regardless of volume or character, with the four high-volume by-products was not covered under the 1993 determination.

## **Purpose of This Report**

In 1995, EPRI completed a survey of the utility industry to establish the extent to which high-volume by-products are comanaged with other combustion wastes (EPRI, 1997). The survey results indicate that approximately 80 percent of disposal facilities serving coal-fired power plants comanage at least one low-volume waste with the high-volume CCBs. Comanagement was most prevalent at impoundments, many of which comanage more than six low-volume wastes.

To ensure that the appropriate information is available to EPA for the 1999 regulatory determination on remaining wastes, electric utilities, through EPRI and in conjunction with USWAG, have completed research to develop and synthesize information on the spectrum of utility waste comanagement practices; determine the composition of remaining, or comanaged wastes; and evaluate the nature and extent of actual environmental releases, and the subsequent fate of the releases from comanagement facilities. A series of reports on these CCB comanagement investigations for the Bevill Study have been published by EPRI. As part of this intensive effort, a study was designed to characterize mill rejects and determine utility comanagement practices for these wastes. As a result of detailed comments from EPA's Office of Solid Waste on the scope of the report and on earlier drafts, this guidance for the comanagement of mill rejects containing pyrites was developed.

Mill rejects, generated as a by-product of processing coal for combustion, are sometimes referred to as pyrites, but pyrites are not always present in mill rejects, and when present, they generally comprise only a small percentage of the total quantity of the mill rejects. However, when pyrites are present and allowed to undergo oxidation, the resulting acidity and other constituents in the leachates have the potential for impacting land and water resources. This guidance document includes a discussion of acid-base accounting and neutralization capacity of alkaline coal ash to assist in the appropriate comanagement in landfills and impoundments. Information is also provided on the closure and postclosure operations of the comanagement facilities.



# 2

## GENERATION AND CHARACTERISTICS OF MILL REJECTS

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### Generation of Mill Rejects

A survey of 40 power plants with 78 units operated by 24 utilities was conducted in 1996 for this study, to obtain information on power plant equipment, coal type burned, the mill rejects generation rate, and handling/disposal methods. Information pertaining to coal type and plant equipment is summarized in Table 2-1. The surveyed plants burned a variety of coals including bituminous, subbituminous, and lignite. The most common type of coal used was eastern bituminous (62.5 percent of the 40 plants).

Mill rejects are produced when the grinding of input coal encounters dense material that cannot be reduced to the desired size. The size required depends on the type of boiler used at the plant and the tendency of a coal to agglomerate. For example, pulverized coal boilers need milled coal with 70 to 80 percent passing a 200 mesh screen (less than 74 microns in diameter) and 98 percent passing a 50 mesh screen (less than 300 microns in diameter) (Shannon, 1982). A higher proportion of finer material is needed when burning bituminous coals than when burning subbituminous coals or lignite. Stoker boilers with traveling grates can accept coal up to 2 inches in diameter (Berkowitz, 1994). Cyclone furnaces can accept coal up to 0.24 inches in diameter, as well as slurried fuel.

There are several types of mills used to produce pulverized coal for boilers, including rolling mills, bowl mills, ball and tube mills, ball and race mills, and attrition-type mills. Ball and race mills, rolling mills, and bowl mills operate at medium speeds and primarily crush the coal. Ball and tube mills are suitable for coals that are abrasive and hard to grind. These mills operate at slow speeds and use impact processes to break the particles. Attrition mills operate at high speeds and are not suitable for highly abrasive coals. Three common types of mills are described in more detail below.

Bowl mills have a grinding ring around the edges of a ceramic-lined rotating bowl. Centrifugal force moves the coal toward the outer portion of the bowl, where it is ground. A hot-air stream across the top of the bowl removes the ground coal, while larger pieces are forced back into the bowl. The ground coal then goes to a classifier where it can be recycled to the mills if not fine enough. Unground materials including pyrites fall to the bottom of the mill, where scrapers remove them from the bowl. Bowl mills can be further separated into those with deep or shallow bowls. The multiple passes of bowl mills make them suitable for high-moisture coals. The capacity of bowl mills is a function of desired fineness, grindability of coal as measured by the Hargrove index, and initial moisture content. The capacity of the bowl mill decreases at higher moisture content or for finer grind. Base capacities of standard size bowl mills range from 14,000 to 200,000 lbs/hr (CE, 1996). For example, standard Raymond bowl mills can pulverize coal to 70 to 90 percent less than 200 mesh for a wide range of coal types. The moisture content in coal can be a maximum of 15 percent for bituminous coals and 40 percent for lignites.

Generation and Characteristics of Mill Rejects

Table 2-1  
List of Equipment Types Used by the Power Plants Surveyed

Sample No.	Utility	Plant	State	Type of Boiler	Type of Pulverizer	Coal Type	Coal Feed Rate	Sulfur Content	Ash Content
NA	1	AA	AZ	Tangential Fired (CE)	Raymond Bowl Mill (CE)	W Subbit	3 M tons/hr	>0.5 %	15.00%
NA	1	BB - Unit #1	AZ	Drum Type (RS)	Ball Mill (RS)	W Subbit	NA	7%	25.00%
NA	1	BB - Unit #2	AZ	Natural Circulation (FW)	Ball Mill (RS)	W Subbit	NA	7%	25.00%
NA	1	BB - Unit #3	AZ	Super Critical (BW)	Roller Mill (BW MPS-89)	W Subbit	NA	7%	25.00%
R-1	2	CC	CO	Carolina Boiler (BW)	Roller Mill (BW)	W Subbit	200 tons/hr	0.33%	8.11%
NA	2	DD	CO	Atm. Circ. Fluidized Bed	NA	W Subbit	55 tons/hr	0.8 - 1 %	19-22 %
R-4	3	E - Unit #1	FL	Tangential Fired (CE)	Raymond Bowl Mill (CE)	Reclaimed	16 tons/hr	<2 %	7 - 10 %
R-15	4	F	GA	Wall Type (FW)	Ball Mills (BW)	Bituminous	NA	1.01%	10.35%
R-17	4	G - Units #1 & 2	GA	Tangential Fired (CE)	Raymond Bowl Mill (CE)	Bituminous	NA	0.63%	8.50%
R-16	4	G - Units #3 & 4	GA	Tangential Fired (CE)	Raymond Bowl Mill (CE)	Subbituminous	NA	0.36%	5.15%
NA	5	H Unit #3	IL	Tangential Fired (CE)	Raymond Bowl Mill (CE)	IL Bitum	NA	2.93%	10.49%
NA	5	H Units #1 and 2	IL	Cyclone Fired (BW)	NA	IL Bitum	NA	2.93%	10.49%
NA	5	HA	IL	Drum Type (BW)	Raymond Bowl Mill (CE)	Bituminous	200 tons/hr	0.70%	8-10 %
NA	5	HN - Units #1 & 2	IL	Tangential Fired (CE)	Raymond Bowl Mill (CE)	Bituminous	420 tons/hr	2.94%	NA
NA	6	J - Unit #3	MD	Wall Fired (CE)	Roll on Race - bowl (CE)	E Bituminous	NA	1%	14.00%
NA	6	J - Unit #4	MD	Tangential Fired (CE)	Roll on Race - bowl (CE)	E Bituminous	NA	1%	14.00%
R-12	7	K	MO	Tangential Fired (CE)	Raymond Bowl Mill (CE)	Subbit (30 %)	4.2 M tons/yr	0.22%	4.56%
R-12	7	K	MO	Tangential Fired (CE)	Raymond Bowl Mill (CE)	Subbit (70 %)	1.8 M tons/yr	2.86%	10.54%
R-19	7	M	MO	Tangential Fired (CE)	Raymond Bowl Mill (CE)	Subbituminous	NA	1.10%	7.10%
R-18	7	N	MO	Tangential Fired (CE)	Raymond Bowl Mill (CE)	IL Subbit(80 %)	NA	1.10%	7.10%
R-18	7	N	MO	Tangential Fired (CE)	Raymond Bowl Mill (CE)	PR Subbit(20 %)	NA	0.37%	5.60%
R-6	8	P	NC	Drum Type (CE)	Raymond Bowl Mill (CE)	E Bitumin	NA	1.21%	10.08%
R-7	8	P	NC	Super Critical (CE)	Raymond Bowl Mill (CE)	E Bitum	NA	1.25%	10.91%
NA	9	Q - Units #1 & 2	NM	Foster Wheeler	Vertical Mill (FW MPS-23)	W Subbit	6.5 M tons/yr	0.85%	24.00%
NA	9	Q - Units #3&4	NM	Babcock and Wilcox	Roller Mill (BW MPS-89)	W Subbit	6.5 M tons/yr	0.85%	24.00%
NA	10	B	NY	NA	Raymond Bowl Mill (CE)	Spot Coal	NA	2.10%	16.20%
NA	10	C - Unit #1	NY	NA	Raymond Bowl Mill (CE)	PA & WV Bitum	NA	2.60%	8.90%
NA	11	D - Units #63,64,65,66	NY	NA	Ball and Race Pulverizer (BW)	PA & WV Bitum	NA	1.50%	9.40%
NA	11	D - Units #67 & 68	NY	Tangential Fired (CE)	Raymond Bowl Mill (CE)	PA & WV Bitum	NA	1.50%	9.40%
R-8, R-9, R-10	12	R - Unit #12	NY	Tangential Fired (CE)	Raymond Bowl Mill (CE)	Bituminous	NA	NA	7.50%
NA	12	A - Units #1,2,3,&4	NY	NA	Raymond Bowl Mill (CE)	PA & WV Bitum	400 tons/hr	2.40%	10.40%
R-2	13	S Unit #2	OH	Universal Pressure (BW)	Roller Mill (BW MPS-89)	OH Bituminous	50 tons/hr	1%	12.30%
R-3	14	T Unit #1	OH	Universal Pressure (BW)	Roller Mill (BW MPS-89)	PA Bituminous	35 tons/hr	2.40%	10.80%
NA	15	U	OK	Tangential Fired (CE)	Raymond Bowl Mill (CE)	WY Subit	NA	0.50%	5.00%
NA	6	V - Units #1&2	PA	Wall Fired (FW)	Ball in Tube (FW)	E Bituminous	NA	2.20%	14.00%
NA	6	W - Units #1,2,&3	PA	Wall Fired (BW)	Roll on Race - bowl (BW)	E Bituminous	NA	2.40%	11.00%
NA	6	I - Unit #33	PA	Tangential Fired (CE)	Roll on Race - bowl (CE)	E Bituminous	NA	4%	14.00%
R-5	16	BR - Unit #1	PA	Pulverized Coal	Roller Mill	PA Bituminous	115 tons/hr	1.70%	8.50%
NA	16	BR - Unit #2	PA	Pulverized Coal	Roller Mill	PA Bituminous	140 tons/hr	1.70%	8.50%
R-11	17	X	TX	Tangential Fired (CE)	Raymond Bowl Mill (CE)	CO Bituminous	6000 tons/gy	NA	5.00%
R-13	18	Y	TX	Babcock and Wilcox	Roller Mill (BW MPS-89)	TX Lignite	NA	0.8-1.75 %	15.00%
R-14	18	Z	TX	Babcock and Wilcox	Roller Mill (BW MPS-89)	PR Subbit	NA	0.38%	4.46%
NA	6	EE - Unit #3	WV	Tangential Fired (CE)	Roll on Race - bowl (CE)	E Bituminous	NA	1.80%	14%
NA	6	EE - Units #1&2	WV	Wall Fired (RS)	Hammer Attrition (RS)	E Bituminous	NA	1-2.1 %	14.00%
NA	6	FF - Unit #1	WV	Tangential Fired (CE)	Roll on Race - bowl (CE)	E Bituminous	NA	1-2.1 %	14.00%
NA	6	FF - Unit #2	WV	Wall Fired (BW)	Roll on Race - bowl (BW)	E Bituminous	NA	1-2.1 %	14.00%
NA	6	GG - Units #1,2,&3	WV	Wall Fired (FW)	Ball in Tube (FW)	E Bituminous	NA	4%	14.00%
NA	6	HH - Units #1&2	WV	Wall Fired (FW)	Ball in Tube (FW)	E Bituminous	NA	4.50%	14.00%
NA	6	II - Unit #5	WV	Top Fired (FW)	Ball in Tube (FW)	E Bituminous	NA	1.10%	14.00%
NA	6	II - Unit #6	WV	Top Fired (BW)	Ball on Race (BW)	E Bituminous	NA	1.60%	13.00%
NA	6	JJ - Unit #1	WV	Top Fired (BW)	Ball on Race (BW)	E Bituminous	NA	1.60%	13.00%
NA	6	JJ - Unit #2	WV	Cyclone Fired (BW)	Crusher (BW)	E Bituminous	NA	1.60%	13.00%
NA	19	KK	NV	NA	NA	W Slag Coal	NA	NA	NA
NA	20	LL	TX	NA	NA	PR Subbit	NA	NA	NA

NA - Not available or applicable; PR=Powder River; Subbit=Subbituminous; Bitum=Bituminous  
 CE - Combustion Engineering  
 FW - Foster Wheeler  
 BW - Babcock & Wilcox  
 RS - Riley Stoker

Ball mills have a large rotating drum containing 3/4 inch to 2 inch diameter forged steel balls in the lower part. The balls are tumbled with the coal at low speed. Oversize coal particles are returned via gravity and centrifugal separation to be reground with the incoming coal. Capacities of standard size ball mills range from 24,000 lbs/hr to 183,000 lbs/hr for eastern bituminous coals (FW, 1996). This type of mill can easily mix different types of coals, and can handle abrasive coals. Fineness can be adjusted by changing the residence time of the coal in the mill or the loading rate.

Ball and race mills have a row of balls with a rotating race above and a stationary one below. Pyrites and dense material drop to the bottom of the mill after one pass, because this material cannot be picked up by the air. After being ground several times, the coal is sent to a classifier, where coal that is too large in size is returned to the grinding mill.

The particle sizes of the mill rejects depend on the coal type, moisture content, type and age of mill, and coal loading rate. The size of rejects at three plants where measurements were available ranged from less than 2 mm to greater than 19 mm (Fellman and Horzempa, 1988). The amount of particles of less than 2 mm is usually less than 10 percent. Most of the particles in the mill rejects are between 2 and 4.8 mm in size. The particle size distribution varies considerably from one day to the next and over a given day. In some cases, larger rocks of one inch or more in diameter can be found in mill rejects.

For the 16 plants with data, the mill rejects generation rate varied from 0.15 lbs/hr to 2,800 lbs/hr for the plant as a whole. The average rate for the 16 plants was 350 lbs/hr. In general, the generation rate was higher for coals with higher sulfur content, but the correlation was not strong. For example, some plants may not generate mill rejects even though high-sulfur coal is burned, because the coal is processed off-site. The plants that burn subbituminous coals tended to have lower mill reject generation rates. The generation rate is influenced by the type, input size, and hardness of the coal; presence of impurities (e.g., siliceous rock); percent pyrites; type and age of mill; and requirements of the specific boiler used at the power plant.

The quantity of mill rejects generated is not usually measured at power plants. Compared to fly ash, mill rejects represent a much smaller volume (tons per day for fly ash versus tons per year for mill rejects). The actual quantity of mill rejects requiring disposal also depends on whether a dry or wet system is used for removing the mill rejects from the hoppers or pulverizers.

## **Characteristics of Mill Rejects**

Mill rejects are derived from coal. Therefore, understanding the general physical and chemical characteristics of coal is important to understand the nature of mill rejects and their variability. Accordingly, this section begins with a discussion of coal composition. Next, the mineralogy and chemical composition of mill rejects are presented, with comparisons to input coal and coal ash. Then, mill reject leachate composition is compared to coal ash leachate composition.

## **Composition of Input Coal**

Coal is a heterogeneous mixture of organic and inorganic components. The primary component of coal is carbonaceous material resulting from the accumulation and decay of plant matter in marine or freshwater seas and marshes (Hessley et al., 1986). As the plant matter is transformed and consolidated, the carbon content increases and the rank, or degree of metamorphism, of the coal also increases (Table 2-2). Physical properties and chemical composition of typical bituminous coals are shown in Figure 2-1.

Sulfur occurs in three major forms in coal—pyritic, organic, and soluble sulfate (Figure 2-2). Elemental sulfur can occur, but is rare (Shimp et al., 1975). Bituminous coals have more pyritic sulfur than most subbituminous coals or lignites, because of the increased metamorphism necessary to produce bituminous coals and the potential for hydrothermal solutions to deposit sulfur. A typical range for pyritic sulfur in coal is 0.4 to 4 percent. Organic sulfur is usually from 0.3 to 2 percent (Valkovic, 1983). The organic sulfur fraction is higher in coals formed in marine conditions than in coals formed in freshwater conditions. The organic sulfur is considered to be tied up in heterocyclic organic compounds that are distributed throughout the coal. Sulfate sulfur is generally less than 0.1 percent. The sulfate is thought to be present mostly as gypsum ( $\text{CaSO}_4$ ) and as jarosite ( $\text{FeSO}_4$  with sodium and potassium) (Hessley et al., 1986).

Most of the pyritic sulfur is contained in two minerals, pyrite and its dimorph marcasite. The chemical formula for both is  $\text{FeS}_2$ , but the crystal structure differs. Pyrite has a cubic crystalline structure, while marcasite has an orthorhombic structure. Both minerals can occur in massive, cryptocrystalline, and crystalline forms (e.g., cubes, octahedrons, or pyritohedrons). The poorly crystalline forms are generally found in lower grade coals, where pyrite can be formed diagenetically in clayey sediments of shallow seas where reducing conditions typically occur, or in hydrothermal deposits (Deer et al., 1966). The most reactive form of pyrite in coal, the framboidal type with its large surface area, is thought to be formed by colloidal deposition. Trace elements such as nickel, cobalt, and manganese can substitute for a small portion of the iron in the pyrite. Other sulfides such as arsenopyrite, sphalerite, chalcopyrite, and galena can be present in association with the pyrite or as impurities in it. These sulfides can contain a wide variety of trace elements including arsenic, copper, cadmium, lead, nickel, and zinc (Table 2-3). Other elements such as antimony, beryllium, boron, chromium, and vanadium are more likely to be associated with the organic fraction (Gluskoter, 1977). Certain other elements, such as selenium, can be found in both the organic and inorganic fractions. The reason for the occurrence in both fractions is thought to be the uptake of selenium by plants prior to the formation of the coal.

Because of its plant origin and subsequent burial by sediments, coal can contain remnants of plants (e.g., wood, bark, roots, and leaves) and rocks (e.g., shale and sandstone). Other noncoal material can be incorporated during the mining process, particularly when the coal is present in thin beds. The noncoal inorganic material is likely to be harder than the coal, and hence included in the mill rejects (e.g., quartz, which was identified by X-ray diffraction in many of the samples analyzed). Because much of the inorganic material is hard to grind, it becomes part of the mill rejects (see Table 2-4).

**Table 2-2  
Classification of Coals by Rank (ASTM D388)**

Class	Group	Heating Value <sup>b</sup>				Agglomerating Character
		Fixed-carbon limits <sup>a</sup>	Volatile-matter limits <sup>a</sup>	Btu/pound	kcal/g	
Anthracitic	Meta-anthracite	+98	<2			
	Anthracite	92-98	2-8		7.2-7.8	Nonagglomerating
	Semianthracite	86-92	8-14			
Bituminous	Low-volatile bituminous coal	78-86	14-22	>14,000		
	Medium-volatile bituminous coal	69-78	22-31	13,000-14,000	>7.8	Commonly agglomerating
	High-volatile A bituminous coal	<69	*31	11,500-13,000	6.4-7.2	Agglomerating
	High-volatile B bituminous coal			10,500-11,500	5.9-6.4	
Subbituminous	Subbituminous A coal			10,500-11,500	5.9-6.4	
	Subbituminous B coal			9500-10,500	5.3-5.9	Nonagglomerating
	Subbituminous C coal			8300-9500	4.6-5.3	
Lignite	Lignite A (lignite)			6300-8300	3.5-4.6	
	Lignite B (brown coal)			<6300	<3.5	
<b>Features</b>						
<b>Class</b>	<b>Physical Appearance</b>	<b>Characteristics</b>				
Anthracite	Black, hard, usually with glassy luster	Very hard and brittle; burns with almost no smoke				
Bituminous	Black, dense, brittle	Is moderately resistant to weathering; plant structures visible with microscope; burns with short blue flame				
Subbituminous	Black; dull or waxy luster	Weathers easily; plant residues faintly shown				
Lignite	Brown to brownish black	Poorly to moderately consolidated; weathers rapidly; plant residues apparent				

Source: Valkovic, 1983.

<sup>a</sup> Dry, mineral-matter-free basis.

<sup>b</sup> Moist, mineral-matter-free basis.

# BITUMINOUS COAL CHARACTERISTICS

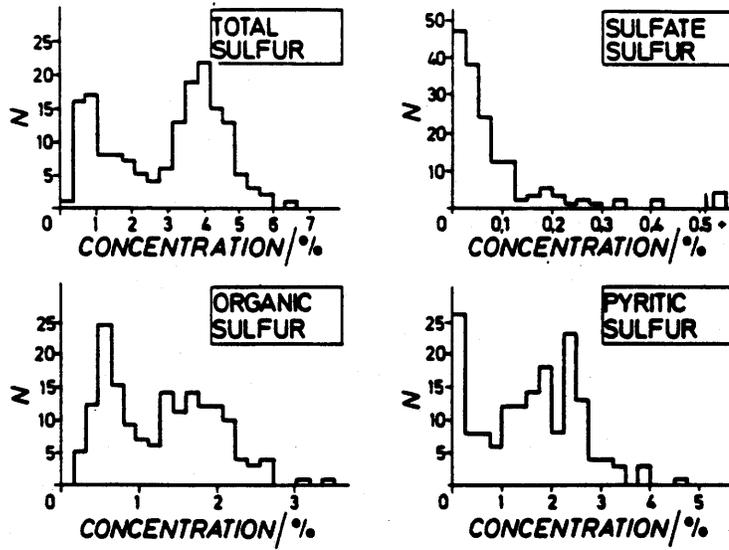
## RANGES & TYPICAL VALUES

	<u>MEAN</u>	<u>RANGE</u>
Caloric Value	6.5 kcal/g (11640 BTU/Lb)	5.0–7.8 kcal/g (9,000–14,000 BTU/Lb)
Ash Content	14% (wt)	4.6–17.7% (wt)
Percent Moisture	10% (wt)	5.0–25% (wt)
Total Sulfur	2% (wt)	0.5–6% (wt)
Pyritic Sulfur	1% (wt)	0.4–2% (wt)
Bulk Density, Packed	60 Lbs/Ft. <sup>3</sup>	40–80 (Lbs/ft. <sup>3</sup> )
Particle Size-Shipped	~0.5" to 5"	
Pulverized Feed Coal Size	~200 MESH	
Volatile Matter	25% (wt)	10–45% (wt)
Heteroatoms	N~1.5% (wt);	0~5–10% (wt)
Structure=fused rings, methylene linkages aliphatic fragments		
→ Metamorphic Conversions % C ↑ %; O decreasing, order: methoxy ↓, carboxyl ↓, carbonyl ↓, hydroxyl ↓		



Figure 2-1 Summary of bituminous coal characteristics.

a) forms of sulfur



b) relationships between pyrites and sulfur

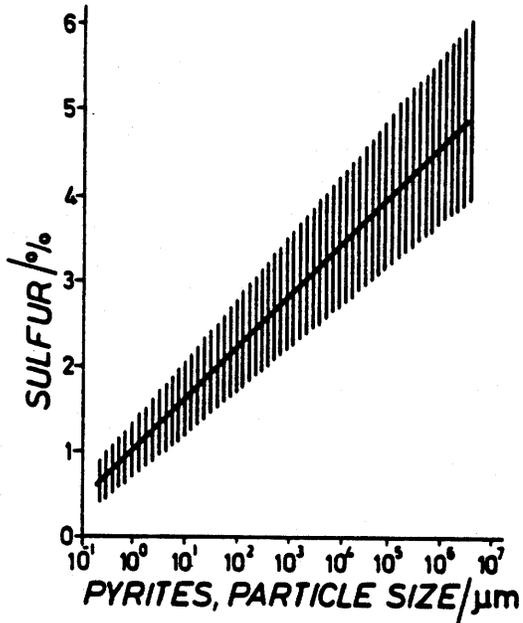


Figure 2-2  
Sulfur in U.S. coals a) forms of sulfur and b) relationships between pyrites and sulfur (Valkovic, 1983).

**Table 2-3**  
**Mineral Association of Trace Elements in Coal**

Element	Mineral Association
Arsenic	Arsenopyrite (FeAsS)
Barium	Barite (BaSO <sub>4</sub> )
Boron	Illite and tourmaline (complex aluminum silicates)
Calcium	Gypsum (CaSO <sub>4</sub> ·2H <sub>2</sub> O), Calcite (CaCO <sub>3</sub> )
Cadmium	Sphalerite (Zn, Cd)S
Cobalt	Linnaeite (CO <sub>3</sub> S <sub>4</sub> )
Copper	Chalcopyrite (CuFeS <sub>2</sub> )
Fluorine	Fluorapatite Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (F,OH)
Iron	Pyrite (FeS <sub>2</sub> ), marcasite (FeS <sub>2</sub> ), hematite (Fe <sub>2</sub> O <sub>3</sub> ), siderite (FeCO <sub>3</sub> )
Lead	Galena (PbS)
Manganese	Siderite (FeMn)CO <sub>3</sub> and calcite (CaMn)CO <sub>3</sub>
Molybdenum	Molybdenite (MoS <sub>2</sub> )
Nickel	Millerite (NiS)
Phosphorus	Fluorapatite Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (F,OH)
Silica	Quartz (SiO <sub>2</sub> )
Strontium	Goyazite group (hydrous strontium aluminum phosphates)
Titanium	Oxide (TiO <sub>2</sub> )
Zinc	Sphalerite (ZnS)
Zirconium	Zircon (ZrSiO <sub>4</sub> )

**Average Organic Affinity of Some Elements**

Element	Percent	
	Ref. A	Ref. B
Germanium	100	87
Beryllium	75-100	82
Gallium	75-100	79
Titanium	75-100	78
Boron	75-100	77
Vanadium	100	76
Nickel	0-75	59
Chromium	0-100	55
Cobalt	25-50	53
Yttrium		53
Molybdenum	50-75	40
Copper	25-50	34
Tin	0	27
Lanthanum		3
Zinc	50	0

Source: Ref A is Zubovic et al., 1960, Ref B is Tyrkian and Wedepohl, 1964 in Valkovic, 1983.

**Table 2-4**  
**Components of Mill Rejects for Example Plant**

**Sulfur Content in Coal and Mill Rejects**

Total S in coal is 2.1 percent (58 percent is pyrites)

Total S in rejects is 28.7 percent (85 percent is pyrites)

<b>Composition of Rejects</b>	<b>Percent by Volume</b>	<b>Percent by Weight</b>
Pyrite	29.4	44.8
Coal	15.2	6.0
Carbonaceous shale	12.8	9.0
Siltstone	12.2	9.3
Marcasite	10.2	15.5
Shale	8.4	6.4
Bone	6.4	3.5
Calcite	3.8	3.1
Iron Oxides	1.4	2.2
Clay	0.2	0.2
	100.0	100.0

<b>Pyrite Forms</b>	<b>Percent by Volume</b>
Irregular porous structures	32.0
Irregular dense structures	30.8
Semifusinite	13.8
Replacement (e.g., fusinite)	11.8
Euhedral crystals	5.0
Cleat and Crack fillings	3.6
Framboids	3.0
	100.0

Data are from Fellman and Horzempa, 1988.

## **Mineralogy of Mill Rejects**

Little information on the composition of mill rejects is available in the literature, as most of the emphasis has been on characterizing the input coal, or on the resulting fly ash and bottom ash. To supplement the available data, a limited sampling and analysis program was conducted for this project to establish the chemical composition and the mineralogy of mill rejects. Mill rejects were obtained from eleven utilities in ten states, covering a range of coal types and locations. The coal types included lignite, as well as subbituminous and bituminous coals from eastern and western mines (see Table 2-1). The total sulfur content of the input coals at these plants ranged from 0.33 to 2.4 percent. Ash content of input coals ranged from 4.5 to 15 percent. Percent ash is an indication of the mineral matter present in the coal, but not an exact measure of it.

Mineralogy was determined on 19 samples of mill rejects. The mill reject samples were first crushed in an Iler Rock Crusher. A 2 g subsample was then ground with an agate mortar and pestle to less than 62  $\mu\text{m}$ . The finely ground material was then placed in a Plexiglass sample holder for X-ray analysis. The major minerals were determined using a Scintag XDS-2000 X-ray diffraction system. Samples were scanned using  $\text{CuK}\alpha$  radiation at 45 KV and 40 MA from  $10^\circ$  to  $70^\circ 2\phi$ , at a scan rate of  $1^\circ$  per minute. The spectra were then analyzed using Scintag software on a Digital Microvax 3100 to determine the relative abundance of minerals present in the samples, based on relative peak intensity. A qualitative estimate of the amount of a given mineral was made using the following classification: **abundant**—distinct, high-intensity peaks relative to other minerals; **present**—distinct peaks of moderate intensity; and **minor**—identifiable peaks of low intensity. The mineral content of the samples varied from very low to over 90 percent. The samples with more mineral matter had higher intensities on the diffractograms.

The major minerals found by X-ray diffraction were quartz, pyrite, calcite, dolomite, kaolinite, siderite, marcasite, and the feldspars albite and microcline (Table 2-5). The crystalline component of the mill rejects was dominated by silicate minerals, followed by carbonate minerals and then sulfide minerals. The most common mineral was quartz in 13 out of 19 samples. As seen in this table, not all mill rejects had pyrite. Thus, while "pyrites" is sometimes used synonymously with "mill rejects," this is not appropriate. In these samples, pyrite and marcasite were abundant only in 3 out of 19 samples. The mill rejects sample with the clearest diffractogram for pyrite (R-3) was from eastern bituminous coal mill rejects with 2.4 percent total sulfur (Figure 2-3a). These mill rejects had 30 percent total sulfur, of which 20.85 percent was pyritic sulfur. The ash content in the rejects, representing predominantly mineral matter, was 72.3 percent. This sample had crystalline pyrite visible to the eye. Marcasite was found only in one sample (R-7) in eastern bituminous coal mill rejects having a total sulfur content of 1.25 percent. The total sulfur in the mill rejects was 19.3 percent, of which 13.5 percent was pyritic sulfur. The ash content of the rejects was 45 percent. This sample (R-7) also had other identifiable minerals including quartz, kaolinite, and calcite (Figure 2-3b).

**Table 2-5  
Major Minerals Present in Mill Reject Samples**

Sample	Carbonate Minerals			Sulfide Minerals			Silicate Minerals		
	Calcite	Dolomite	Siderite	Pyrite	Marcasite	Kaolinite	Quartz	Albite	Microcline
R-1	M	M		M		P	A		
R-2	A	P		A			A		
R-3				M		P	A		
R-4				P			A		
R-5	P			P		P	A		
R-6	P			P		M	A		
R-7	M			P	P		A		
R-8	P	P		P			A		
R-9	P	A		P			A		
R-10	P	A		A			A		
R-11			M	A			P		
R-12	M			A			A		
R-13	M			P			A		
R-15				M			A		
R-16	M		A			P	A	M	
R-17	A	M				M	A		
R-18	A	M					P		
R-19	A	M					M		

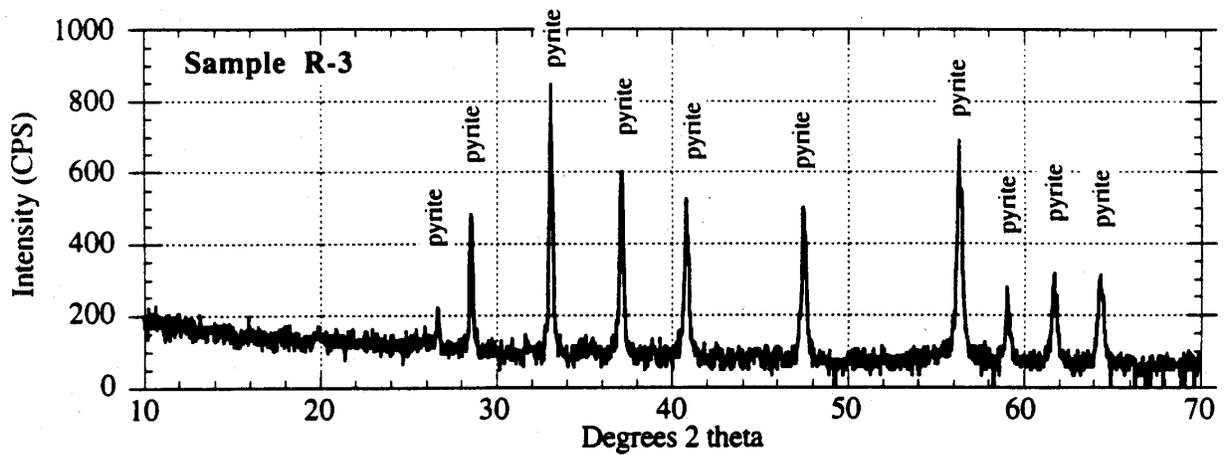
A = Abundant.

P = Present.

M = Minor constituent.

No minerals were detected in sample R-14 by x-ray diffusion.

a) X-ray diffractogram for sample R-3 containing only pyrite



b) X-ray diffractogram for sample R-7 containing marcasite

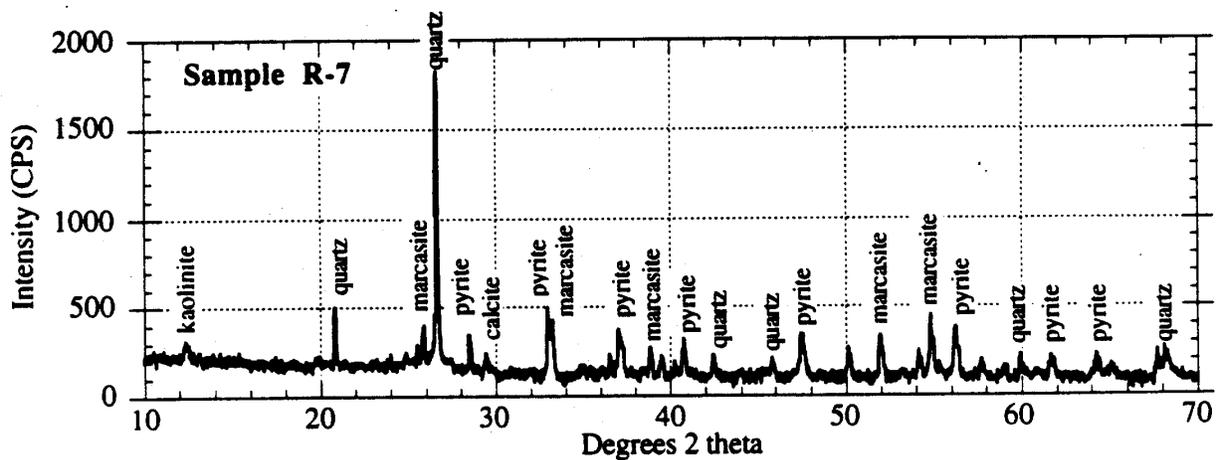


Figure 2-3  
X-ray results showing a) pyrite and b) marcasite.

Carbonate minerals occurred in 15 out of the 19 samples. Calcite was the most common carbonate mineral, with dolomite present in four samples (e.g., R-2, from bituminous coal with 1.0 percent total sulfur—(see Figure 2-4a)) and siderite, an iron carbonate, present in two samples (R-16, from a subbituminous coal with 0.4 percent total sulfur, and R-11, a western bituminous coal with low total sulfur—(see Figure 2-4b)). Other silicate minerals found included the clay mineral kaolinite and two alkali feldspars, microcline (a potassium feldspar) and albite (a sodium feldspar) (e.g., R-15, from a bituminous coal with 1 percent total sulfur—

(see Figure 2-4c)). Diffractograms for the remaining samples are included in Appendix A to this report. The minerals found in these samples are consistent with those expected from published literature (Berkowitz, 1994).

Minerals not found from the x-ray diffraction analyses in these samples that have been identified in coal (Table 2-6) include the following:

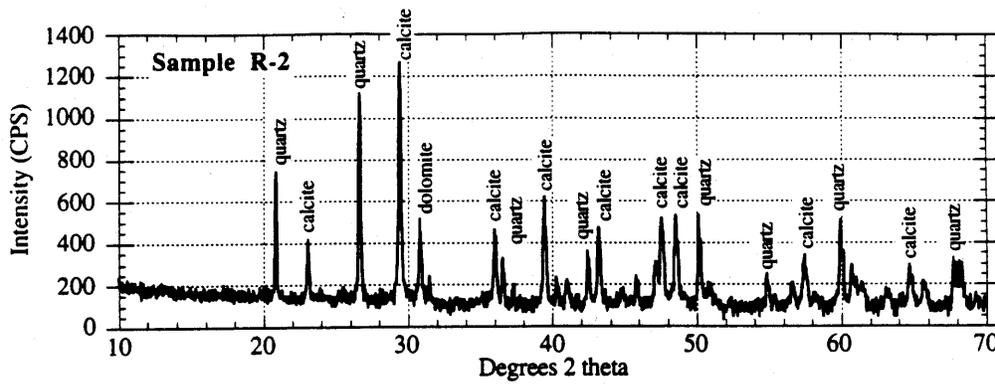
- Clay minerals - illite, montmorillonite, mixed illite-montmorillonite, chlorite
- Carbonates - ankarite ( $2\text{CaCO}_3 \cdot \text{MgCO}_3 \cdot \text{FeCO}_3$ ) and occasionally magnesite ( $\text{MgCO}_3$ ), rhodochrosite ( $\text{MnCO}_3$ ), and strontianite ( $\text{SrCO}_3$ )
- Sulfides - small amounts of pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ), galena, sphalerite ( $\text{ZnS}$ ), and chalcopyrite ( $\text{CuS}$ )
- Sulfates - gypsum ( $\text{CaSO}_4$ ), barite ( $\text{BaSO}_4$ ), and various iron sulfates
- Oxides - magnetite and hematite ( $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ ), rutile and anatase ( $\text{TiO}_2$ )
- Others - goethite/limonite ( $\text{FeOOH}$ ), zircon ( $\text{ZrSiO}_4$ ), apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$ ), and halite ( $\text{NaCl}$ )

### **Chemical Composition of Mill Rejects**

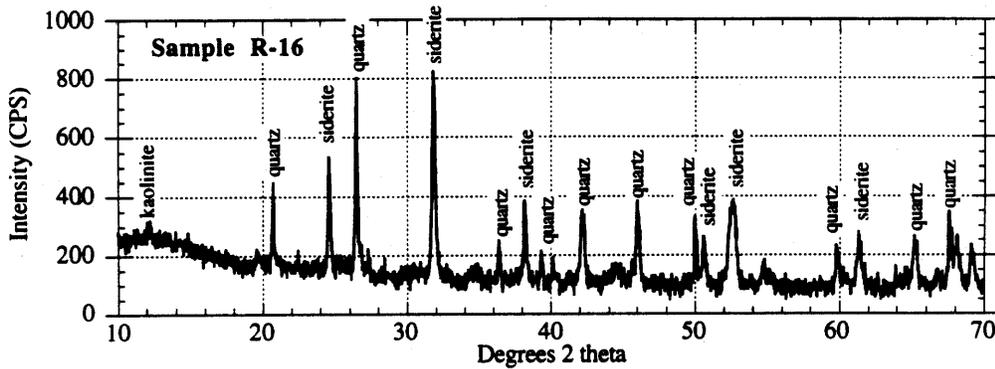
Chemical analyses were also conducted on the 19 mill reject samples described above. The parameters analyzed were sulfur forms, four major alkali cations, and thirteen minor and trace elements. The laboratory analytical methods are shown in Table 2-7. The amounts of sulfur, ash, and moisture content found in the samples are shown in Table 2-8. The total sulfur ranged from 0.01 percent in the mill reject sample from a bituminous coal with 1 percent sulfur (R-2) to 30 percent in the mill reject sample from a bituminous coal with 2.4 percent total sulfur (R-3). The pyritic sulfur was also highest in this latter sample (20.85 percent). The mean and median pyritic sulfur, 5.4 and 3.4 percent respectively, were considerably less than this maximum value. The bituminous mill reject samples had higher total sulfur, and higher amounts of pyritic and organic sulfur (Figure 2-5).

The results of the above mill reject samples were compared to those from the Fellman and Horzempa (1988) study. The parameters measured in these latter samples (sulfur forms, ten elements, coal characteristics) and the analytical methods are shown in Table 2-9. The total sulfur for the plants in the Fellman and Horzempa study spanned a narrower range (16.5 to 39.3 percent) because only eastern bituminous coals were included (Table 2-10). The pyritic sulfur for these samples was also higher (11.0 to 29.3 percent).

a) X-ray diffractogram for sample R-2 containing quartz, calcite, and dolomite.



b) X-ray diffractogram for sample R-16 containing quartz, and the Fe carbonate siderite together with minor amounts of kaolinite



c) X-ray diffractogram for sample R-15 containing silicate minerals; quartz, microcline, albite, and kaolinite. Pyrite occurs as a minor constituent

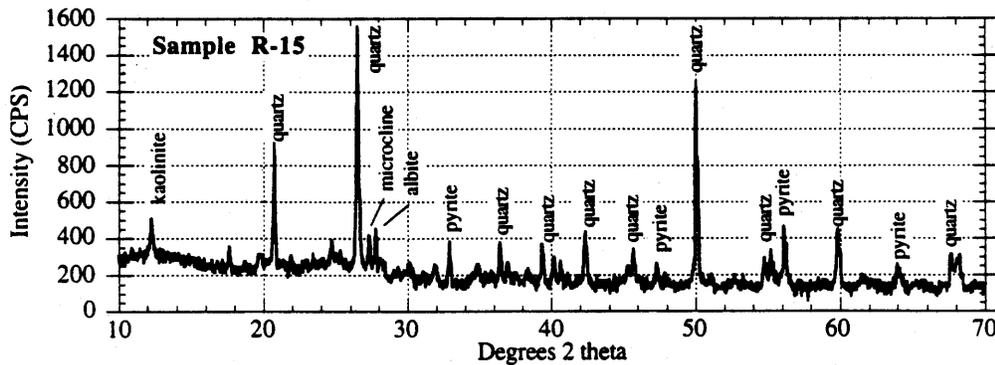


Figure 2-4  
X-ray results showing a) quartz, calcite, and dolomite; b) siderite; and c) silicate minerals.

**Table 2-6  
Minerals Found in Coals and Their Abundance**

Mineral	Composition	Common Minor and Trace Element Associations	Frequency of Occurrence in Coal Seams	Concentration in Mineral Matter
<b>Clay minerals</b>				
illite (sericite)	$KAl_2(AlSi_3O_{10})(OH)_2$		Common	Abundant
smectite (including mixed layered)	$Al_2Si_4O_{10}(OH)_2 \cdot H_2O$	Na, Ca, Fe, Li, Ti, Mn, F & other lithophile elements	Common	Abundant
kaolinite group	$Al_2Si_2O_5(OH)_4$		Common	Abundant
Chlorite	$Mg_2Al(AlSi_3O_{10})(OH)_8$		Rare	Moderate
<b>Sulfides</b>				
pyrite	$FeS_2$ (isometric)		Rare-common	Variable
marcasite	$FeS_2$ (orthorhombic)	As, Co, Cu, & other chalcophile elements	Rare-moderate	Trace
pyrrhotite	$Fe_{1-x}S$		Rare	Trace
sphalerite	Zn S		Rare	Minor-trace
galena/chalcocopyrite	$PbS/CuFeS_2$			
<b>Carbonates</b>				
calcite	$CaCO_3$		Rare-common	Abundant
dolomite (ankerite)	$CaMg(CO_3)_2$	Mn, Zn, Sr	Moderate	Trace
siderite	$FeCO_3$		Rare	Minor
<b>Oxides</b>				
quartz	$SiO_2$	-	Common	Abundant
magnetite/hematite	$Fe_3O_4/Fe_2O_3$	Mn, Ti	Common	Minor-trace
rutile & anatase	$TiO_2$	-	Common	Trace
<b>Others</b>				
goethite/limonite	$FeOOH$	Mn, Ti	Common	Trace
feldspar	$K(Na)AlSi_3O_8$	Ca	Moderate	Trace
zircon	$ZrSiO_4$	-	Moderate	Trace
sulfates: gypsum	$CaSO_4 \cdot 2H_2O$	-	Moderate	Minor
barite	$BaSO_4$	Na, Sr, Pb	Rare	Minor
szomolnokite	$FeSO_4 \cdot H_2O$	-	Rare	Trace
apatite	$Ca_5(PO_4)_3(F, Cl, OH)$	Mn, Ce, Sr, U	Moderate	Trace
halite	NaCl	K, Mg	Rare	Trace

Source: Harvey and Ruch, 1986 in Vorres, 1986.

**Table 2-7**  
**Laboratory Analytical Methods Used for Mill Reject Chemical Analyses**

Forms of Sulfur	Method	Det. Limits*
Total	ASTM D4239-C	0.1, wt %
Pyritic	ASTM D2492	0.1, wt %
Organic	ASTM D2492	0.1, wt %
Sulfate	ASTM D2492	0.1, wt %
As	ASTM D4606 AA/HG or GF	1 mg/Kg
Ba	ASTM D3683 ICP	5 mg/Kg
Cd	ASTM D3683	1 mg/Kg
Cr	ASTM D3683	5 mg/Kg
Cu	ASTM D3683	5 mg/Kg
Fe	ASTM D3683	5 mg/Kg
Pb	ASTM D3682 AA/GF	1 mg/Kg
Hg	ASTM D3684 CVAA	1 mg/Kg
Ni	ASTM D3683	5 mg/Kg
Se	ASTM D4606 AA/HG or GF	1 mg/Kg
Ag	ASTM D3683	5 mg/Kg
Zn	ASTM D3683	5 mg/Kg
Mn	ASTM D3683	5 mg/Kg
Ca	ASTM D3682	5 mg/Kg
Mg	ASTM D3682	5 mg/Kg
K	ASTM D3682	5 mg/Kg
Na	ASTM D3682 AA emission	5 mg/Kg

Note: For metals listed in D3682 and D3683 actual analyses were performed on the ashed sample, then calculated back to a whole coal basis. For As, Se, Pb, and Hg, the coal was combusted by oxygen bomb and then the vapors were collected and analyzed.

\*Actual detection limits vary slightly due to dilutions and volume of coal actually ashed.

**Table 2-8  
Sulfur, Ash, and Moisture Content in Mill Reject Samples Collected for This Project**

Compound	Units	R-1	R-1 Split	R-2	R-3	R-4	R-5	R-6	R-7	R-7 Split	R-8	R-8 Split	R-9	R-9 Split	R-10	R-10 Split
Sulfate-S	wt%	0.01	0.03	<0.01	0.2	<0.01	0.03	0.07	0.17	0.19	0.06	0.04	<0.01	<0.01	<0.01	<0.01
Pyritic-S	wt%	3.49	3.31	<0.01	20.85	4.71	11.8	10.12	13.53	12.22	3.41	3.89	<0.01	<0.01	<0.01	<0.01
Organic-S	wt%	0.16	0.29	0.01	8.95	2.05	5.39	5.74	5.56	8.6	0.7	0.31	0.06	0.03	0.01	0.01
Total Sulfur	wt%	3.66	3.63	0.01	30	6.77	17.22	15.93	19.26	21.01	4.17	4.24	0.06	0.03	0.01	0.01
Moisture	wt%	3.7	-	0.49	0.26	1.2	0.82	1.15	0.95	-	0.4	-	0.55	-	0.77	-
Ash	wt%	63.88	-	72.2	72.27	46.2	55.11	47.94	45	-	68.91	-	77.93	-	67.18	-

Compound	Units	R-11	R-12	R-13	R-14	R-15	R-16	R-17	R-18	R-18 Split	R-19	Min.	Max.	Mean	Median	Std. Deviation
Sulfate-S	wt%	15.1	0.22	0.47	0.1	0.03	0.08	0.02	<0.01	<0.01	0.02	0.005	0.47	0.07	0.03	0.11
Pyritic-S	wt%	17.09	15.1	9.05	0.01	4.94	1.89	0.15	0.06	0.06	0.2	0.005	20.85	5.44	3.41	6.36
Organic-S	wt%	2.08	5.16	2.68	1.07	0.85	2.11	6.21	0.3	0.3	<0.01	0.005	8.95	2.35	0.85	2.87
Total Sulfur	wt%	19.21	20.48	12.2	1.18	5.82	4.08	6.38	0.37	0.37	0.22	0.01	30	7.85	4.17	8.80
Moisture	wt%	5.82	0.64	2.28	0.36	-	-	-	-	-	-	0.26	5.82	1.39	0.80	1.57
Ash	wt%	44.57	79.01	67.64	99	-	-	-	-	-	-	44.57	99	64.77	67.41	15.72

"-" Indicates data not analyzed.

Statistics were calculated using one-half detection limit values.

All data expressed as dry weights.

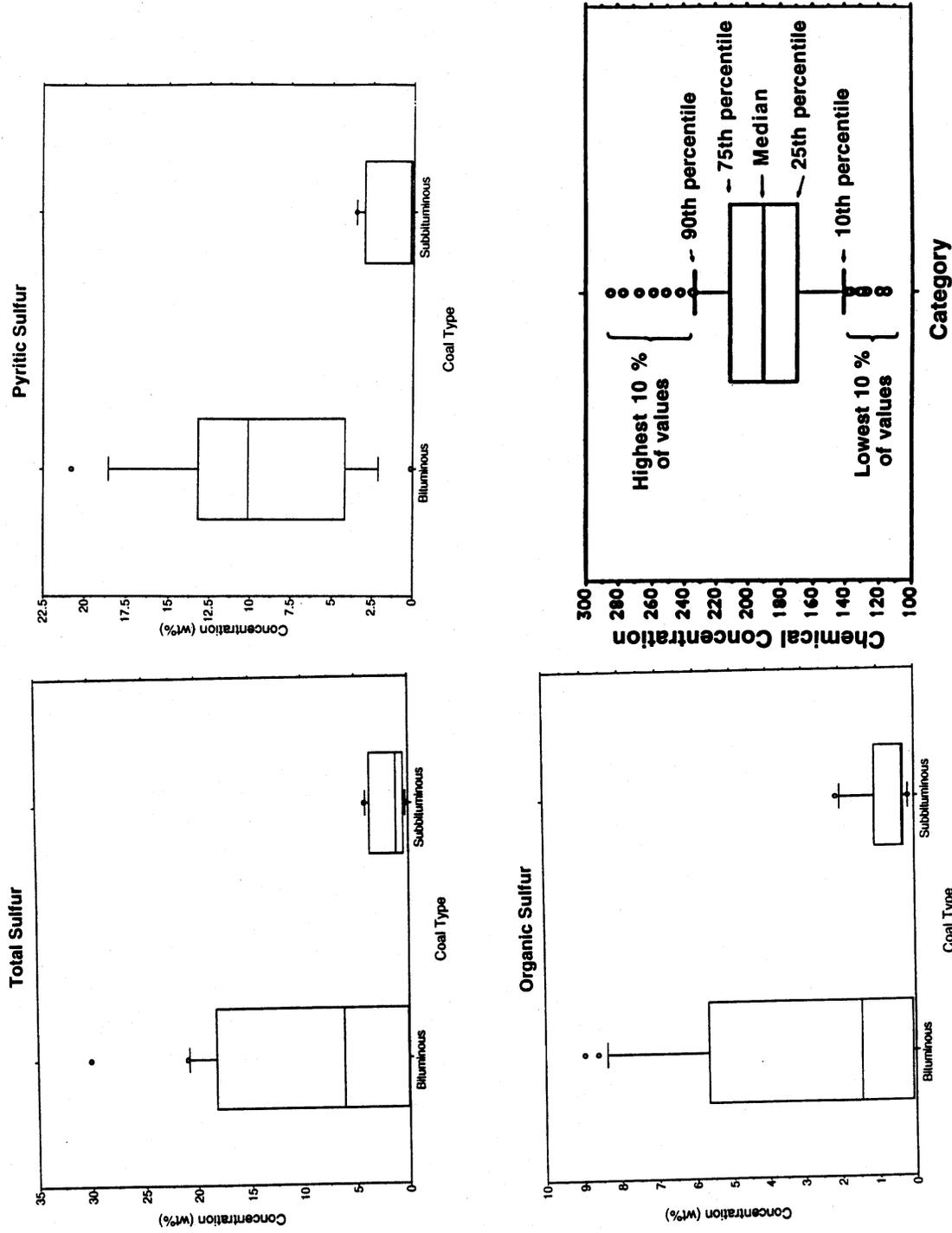


Figure 2-5 Comparison of sulfur forms by coal type in mill rejects collected for this project

**Table 2-9**  
**Analytical Methods Used for Mill Reject Samples from New York Plants**

Analysis	Method	Method Number <sup>a</sup>
<b>Ultimate Analysis</b>	<b>Combustion</b>	<b>ASTM D3176-74</b>
Carbon	Combustion	ASTM D3178-73
Hydrogen	Combustion	ASTM D3178-73
Nitrogen	Acid Digestion	ASTM D3179-73
<b>Ash Content</b>	<b>Combustion</b>	<b>ASTM D3174-82</b>
<b>Moisture Content</b>	<b>Gravimetric</b>	<b>ASTM D3302-83</b>
<b>Hargrove Grindability</b>	<b>Size Fractionation</b>	<b>ASTM D409-71</b>
<b>Forms of Sulfur</b>	<b>Multiple</b>	<b>ASTM D2492-80</b>
Total	Eschka, Gravimetric	ASTM B3177-75
Sulfate	HCl Extraction	ASTM D2492-79
Pyritic	Nitric Acid Extraction	ASTM D2492-79
Organic	By Difference	ASTM D2492-79
<b>Metals</b>		
Aluminum	Furnace AA	202.2 CLP <sup>b</sup>
Arsenic	Furnace AA	206.2 CLP
Barium	Furnace AA	208.2 CLP
Cadmium	Furnace AA	213.2 CLP
Selenium	Furnace AA	270.2 CLP
Silver	Furnace AA	272.2 CLP
Mercury	Manual Cold Vapor Atomic Absorption Technique	245.1 CLP
Iron	Flame AA	236.1 CLP
Lead	Furnace AA	239.2 CLP
Zinc	Flame AA	289.1 CLP
Copper	Furnace AA	202.2 CLP
Magnesium	Furnace AA	202.2 CLP
Chromium	Furnace AA	202.2 CLP
Calcium	Furnace AA	202.2 CLP
Silica	Spectrophotometric	ASTM D2331 <sup>d</sup>
Phenol	Spectrophotometric	420.1 <sup>e</sup>
Carbon Total Organic and Inorganic	Persulfate Digestion I R	7.0 <sup>e</sup>
Base Neutral Series	GC/MS	EPA 625 CLP-M <sup>f</sup>

<sup>a</sup> 1980 Annual Book of ASTM Standards, Part 26 Gaseous Fuels; Coal and Coke; Atmospheric Analysis.

<sup>b</sup> Methods for Chemical Analysis of Water and Wastes (EPA Report No. EPA-600/4-79-020). Modified for the EPA Contract Lab Program. Digestion by EPA/CLP Modification of Method 3050 from Ref. (3).

<sup>c</sup> Test Methods for Evaluating Solid Waste (EPA Report No. SW-846).

<sup>d</sup> 1977 Annual Book of ASTM Standards, Part 31, Water (American Society for Testing and Materials, 1977).

<sup>e</sup> Methods for Chemical Analysis of Water and Wastes (EPA Report No. EPA-600/4-79-020).

<sup>f</sup> Methods for Organic Chemical Analysis Municipal and Industrial Waste Water (EPA-600/4/82-057 July 1982).

Source: Fellman and Horzempa, 1988.

**Table 2-10**  
**Sulfur in Input Coal and Pulverizer Rejects at New York Plants**

Percent in Rejects					
Plant	Total Sulfur	Pyritic-S	Organic-S	Sulfate-S	Ash
A	39.3	29.3	9.8	0.2	62
B	28.7	24.5	4.0	0.15	67.5
D	17.7	11.0	6.2	0.5	36.7
C	30.8	23.8	6.5	0.5	60.5

Percent in Input Coal					
Plant	Total Sulfur	Pyritic-S	Organic-S	Sulfate-S	Ash
A	2.4	1.2	1.2	0.04	10.0
B	2.1	1.2	0.8	0.15	15.9
D	1.5	0.8	0.65	0.06	9.9
C	2.6	1.2	0.85	0.5	9.4

Source: Fellman and Horzempa, 1988.

For the present study, the ash content varied from 44.6 to 99 percent in the sampled mill rejects. The low value occurred in the mill rejects (R-11) from Colorado bituminous coal with low sulfur. The high value occurred in the rejects (R-14) from the Powder River Basin subbituminous coal. This mill reject also had relatively low total sulfur (1.2 percent) with only 0.01 percent as pyritic sulfur (Table 2-8). Western coals generally have high mineral matter. The mean and median ash contents of these mill rejects samples were 44.6 and 67.6 percent, respectively (Table 2-8). The ash content did not correlate well with the sulfur content, probably because sulfur occurs in both mineral and organic fractions.

Major ions and trace elements were also measured in the mill reject samples (Table 2-11). The trace elements that were most often below the detection limit were cadmium, silver, and zinc. Similar chemical data for the New York plants in the Fellman and Horzempa study are shown in Table 2-12. Four additional mill reject samples were analyzed for chemical composition as part of a previous EPRI study (EPRI, 1987). The chemical composition of these samples is shown in Table 2-13. A comparison between the measured concentrations of all the mill reject samples is shown in Table 2-14. The mean concentrations of arsenic, copper, iron, lead and zinc were higher for the bituminous mill rejects from the New York study and for the 1987 rejects than the samples for the present study. These elements are often associated with pyrites. The 1987 mill reject samples had higher concentrations than either of the other two data sets for iron, magnesium, selenium, and zinc, although the ranges were similar.



**Table 2-12**  
**Minor and Trace Elements in Input Coal and Rejects from New York Plants**

<b>Input Coal<sup>a</sup></b>				
	<b>Average Concentration (mg/kg)</b>			
<b>Parameter</b>	<b>Plant A</b>	<b>Plant B</b>	<b>Plant C</b>	<b>Plant D</b>
Aluminum	514.5	732.5	537.5	554.8
Arsenic	12.2	46.5	7.3	35.6
Barium	85.1	194.5	33.4	80.5
Cadmium	0.2	0.2	0.2	0.2
Calcium	4,212.5	389.5	3,062.5	1,292.5
Chromium	7.8	10.0	10.6	10.7
Copper	10.3	26.7	10.5	20.2
Iron	10,775	15,825	10,900	9,750
Lead	5.2	19.0	<0.2	7.3
Magnesium	252.5	160.3	525.0	213.5
Mercury	0.1	0.1	0.04	0.1
Selenium	0.5	2.8	0.4	1.5
Silver	<3	<3	<3	<3
Zinc	38.7	45.8	14.7	33.2

<b>Pulverizer Rejects<sup>a</sup></b>				
	<b>Average Concentration (mg/kg)</b>			
<b>Parameter</b>	<b>Plant A</b>	<b>Plant B</b>	<b>Plant C</b>	<b>Plant D</b>
Aluminum	64.25	1,970.0	1,435.0	2,352.5
Arsenic	314.0	1,447.5	281.8	955.0
Barium	14.4	62.3	52.3	171.8
Cadmium	0.6	2.5	0.5	1.3
Calcium	10,575	473	13,375	4,937.5
Chromium	33.6	17.8	25.1	14.3
Copper	522.5	150.8	217.8	280.3
Iron	323,250	254,000	342,500	113,500
Lead	61.6	137.3	62.6	101.2
Magnesium	945	900	30.1	1,592.5
Mercury	0.3	1.4	3.0	0.2
Selenium	5.1	5.5	1.4	2.8
Silver	<3	<3	7.1	<3
Zinc	49.0	167.3	80.8	225.3

<sup>a</sup> In averaging, values reported as less than the detection limit have been treated as being equal to the detection limit.  
 Source: Fellman and Horzempa, 1988.

**Table 2-13**  
**Chemical Composition of Four Mill Reject Samples (EPRI, 1987)**

Element <sup>a</sup>	Concentration in Different 900-Series Samples (in mg/kg solid except as noted in the Element column)			
	904	909	913	915
Aluminum (%)	2.73 ± 0.33	6.79 ± 0.4	5.48 ± 0.33	2.67 ± 0.2
Aluminum (%)*	1.62 ± 0.08	3.94 ± 0.08	4.39 ± 0.08	2.08 ± 0.08
Antimony	<8.5	<10	<0.9	<7.9
Arsenic	1027 ± 53	1013 ± 51	429 ± 22	99 ± 5.5
Barium	91 ± 10	211 ± 18	164 ± 15	95.1 ± 9.9
Bromine	<8.1	<4.4	17.5 ± 1.7	6.4 ± 0.98
Cadmium	<6.0	<7.3	<6.1	<5.4
Calcium (%)	0.639 ± 0.043	1.175 ± 0.062	0.124 ± 0.01	2.97 ± 0.15
Calcium (%)*	0.35 ± 0.13	0.57 ± 0.13	0.13 ± 0.13	2.3 ± 0.13
Cerium	47 ± 11	77 ± 15	<24	<21
Cesium	<13	23.1 ± 7.4	<12	<11
Chlorine (%)	<0.079	0.051 ± 0.017	0.115 ± 0.012	0.109 ± 0.013
Chromium	2750 ± 160	1019 ± 59	321 ± 23	955 ± 53
Copper	66 ± 12	50.8 ± 5.3	76.6 ± 5	34 ± 3.5
Gallium	<7.2	9.8 ± 1.7	9.9 ± 1.2	4 ± 1
Indium	ND	ND	ND	ND
Iodine	ND	ND	ND	ND
Iron (%)	36.4 ± 1.8	21.5 ± 1.1	11.53 ± 0.58	12.79 ± 0.64
Iron (%)*	34.3 ± 0.18	22.1 ± 0.18	13 ± 16	14.3 ± 0.18
Lanthanum	<19	37 ± 12	30 ± 16	<18
Lead	151 ± 12	72.9 ± 5.3	121.4 ± 6.9	65.4 ± 4.2
Magnesium (%)*	0.258 ± 0.06	0.174 ± 0.06	0.156 ± 0.06	0.756 ± 0.06
Manganese	1232 ± 89	219 ± 27	171 ± 14	167 ± 19
Molybdenum	40.8 ± 3.6	30.4 ± 2.5	15.8 ± 1.5	13.6 ± 1.3
Nickel	712 ± 55	321 ± 24	139 ± 12	249 ± 17
Niobium	<3.4	12 ± 1.3	7.6 ± 0.87	3.83 ± 0.67
Palladium	ND	ND	ND	ND
Phosphorus (%)	1.74 ± 0.16	0.888 ± 0.081	0.417 ± 0.046	0.498 ± 0.053
Potassium (%)	0.273 ± 0.038	1.086 ± 0.061	0.955 ± 0.052	0.429 ± 0.027
Potassium (%)*	0.17 ± 0.17	0.64 ± 0.17	0.72 ± 0.17	0.33 ± 0.17
Rhodium	ND	ND	ND	ND
Rubidium	8.7 ± 1.9	42.6 ± 2.5	40 ± 2.2	17 ± 1.1
Ruthenium	ND	ND	ND	ND
Selenium	57.4 ± 4.4	26.6 ± 1.9	23.9 ± 1.6	11.6 ± 1
Silicon (%)	3.97 ± 0.26	16.62 ± 0.85	10.36 ± 0.53	5.13 ± 0.27
Silicon (%)*	3.03 ± 0.28	11.2 ± 0.28	9.11 ± 0.28	4.86 ± 0.28
Silver	<5.6	<7.0	<6.0	5.5 ± 2.6
Sodium (%)*	0.0518 ± 0.28	0.148 ± 0.02	0.0962 ± 0.02	0.148 ± 0.02
Strontium	<8.6	197 ± 12	61.1 ± 5	136.2 ± 8.1
Sulfur (%)	48.3 ± 5.1	18.87 ± 0.95	9.03 ± 0.46	11.15 ± 0.56
Tellurium	39.6 ± 2	<12	<9.8	<8.6
Tin	48.3 ± 5.1	38.4 ± 5.4	74.9 ± 6.7	139 ± 10
Titanium (%)	0.081 ± 0.013	0.46 ± 0.025	0.299 ± 0.016	0.139 ± 0.008
Uranium	<7.8	<6.1	<5.1	<3.9
Vanadium	<100	<63	<40	<37
Yttrium	6.6 ± 2.2	20.3 ± 1.8	16 ± 1.5	8.38 ± 0.99
Zinc	455 ± 27	88.8 ± 5.8	66.8 ± 4.1	27.3 ± 2.5
Zirconium	21.1 ± 2.5	112.4 ± 8	80.6 ± 5.7	34.6 ± 2.6

<sup>a</sup> Most analyses were performed by x-ray fluorescence under different targets. For information on the target and the detection limits for each element, see EPRI, 1987. An asterisk (\*) designates analyses performed by lithium metaborate dissolution plus atomic absorption spectroscopy.

**Table 2-14  
Comparison of Mill Rejects Composition**

Parameter	Samples from NY Plants <sup>a</sup>		Four 1987 Samples <sup>b</sup>		This Study <sup>c</sup>	
	Mean <sup>d</sup>	Range	Mean	Range	Mean	Range
Arsenic	750	154.5 - 1,535	642	99 - 1,027	104.9	1.5 - 447
Barium	76	2.4 - 269.5	140	91 - 211	370.3	48 - 1,067
Cadmium	1	0.16 - 2.92	6	<5 - <7.3	7.1	<7 - 9
Calcium	7328	455 - 14,300	5590	1240 - 11,760	91,700	6,700 - 267,000
Chromium	22.7	9.2 - 34.2	1261	321 - 2,750	64.8	9 - 3,377
Copper	293	147.5 - 500	56.8	34 - 76.6	23.5	4.5 - 69
Iron	258,313	87,500 - 358,500	205,550	115,300 - 364,000	13,240	9500 - 357,300
Lead	91	<0.2 - 179	102.7	65.4 - 151	21.7	<9 - 121
Magnesium	867	27.2 - 2,230	3,360	1,560 - 7,560	1,420	1,800 - 6,030
Mercury	1.2	0.01 - 5.44	NA	NA <sup>e</sup>	0.35	0.04 - 0.9
Selenium	3.7	1.4 - 6.6	29.9	11.6 - 57.4	11.1	2.5 - 50
Silver	<3	<3 - 12.9	6	5.5 - <7.0	15.1	<9 - 41
Zinc	156	79 - 319	159	27.3 - 455	28.1	<9 - 225

<sup>a</sup> Data are from Fellman and Horzempa, 1988 for four New York Plants (8 samples).

<sup>b</sup> Data are from EPRI, 1987 (4 samples).

<sup>c</sup> Data are from a wider range of coal types and locations (20 samples).

<sup>d</sup> To be comparable, means for all data sets calculated using the detected limit, rather than one-half the value.

<sup>e</sup> Not analyzed.

Units are mg/kg.

Box plots were made showing the distribution of arsenic, iron, and copper, by coal type as shown in Figure 2-6. Arsenic is clearly higher in the bituminous coal rejects, while iron and copper have overlapping ranges. Comparisons between total sulfur and arsenic are shown in Figure 2-7 by coal type. There is a general increase in arsenic concentration with increasing sulfur, but there was considerable scatter in the data for the bituminous coal. Mercury showed positive correlations with both total and pyritic sulfur. The correlation coefficient was 0.44 for total sulfur in bituminous samples and 0.78 in subbituminous samples, while the values were slightly higher for pyritic sulfur, 0.47 for bituminous samples and 0.86 for subbituminous samples. Correlations with organic sulfur were tested for arsenic, mercury, and selenium. The correlation coefficients were all low; selenium had the highest value (0.35).

The mill rejects data from the samples analyzed for this project were combined with data from the two previously mentioned studies (Fellman and Horzempa, 1988 and EPRI, 1987). The combined data set is compared (Table 2-15) to coal fly ash and bottom ash composition from the EPRI (1987) study. This comparison shows that mill rejects had lower maximum concentrations than either fly ash or bottom ash for barium, cadmium, calcium, chromium, copper, lead, potassium, nickel, sodium, and zinc. The elements with maximum concentrations that were higher in mill rejects (iron, sulfur, magnesium, manganese, arsenic, selenium, and silver) than both fly ash and bottom ash were those that are typically associated with pyrites, except for selenium and magnesium.

Figure 2-8 shows that mill rejects had lower median concentrations than coal ash for chromium, copper, lead, nickel, and selenium, and higher concentrations for arsenic. The distributions of the six elements in fly ash, bottom ash, and mill rejects are shown in Figure 2-9. These plots show that mill rejects have a larger percentage of lower concentration samples than fly ash and bottom ash for chromium, copper, and nickel, but a larger percentage of higher concentrations for arsenic and selenium. Plots for iron and sulfur (Figure 2-10) show that mill rejects have a wider range in concentration than either fly ash or bottom ash and a larger percentage of samples with higher concentrations. Similar plots for the remaining elements are included in Appendix B.

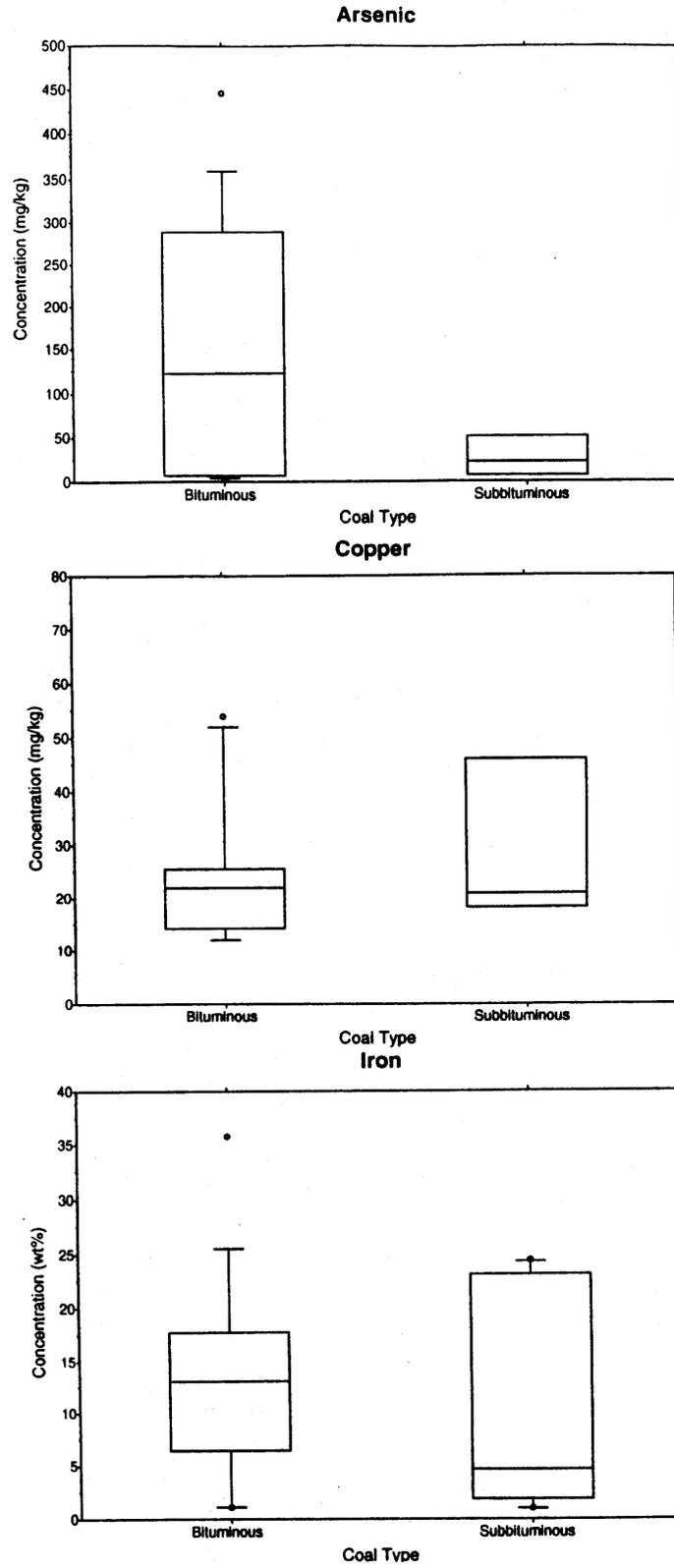
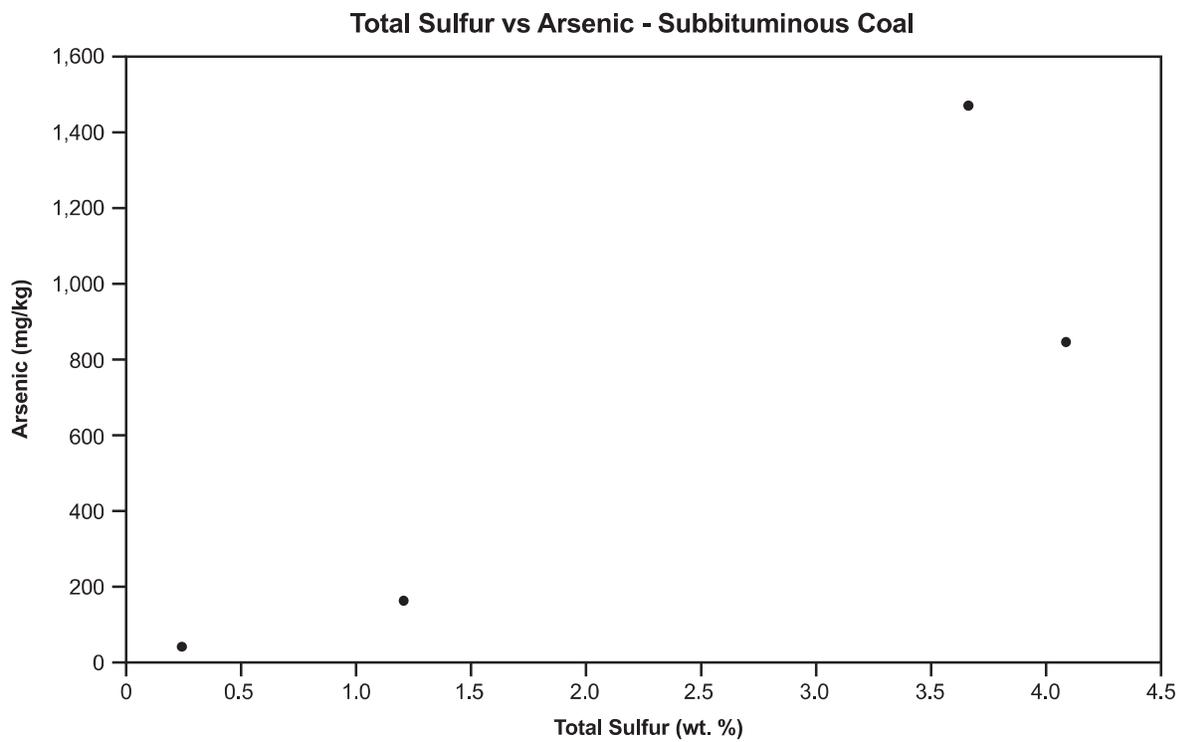
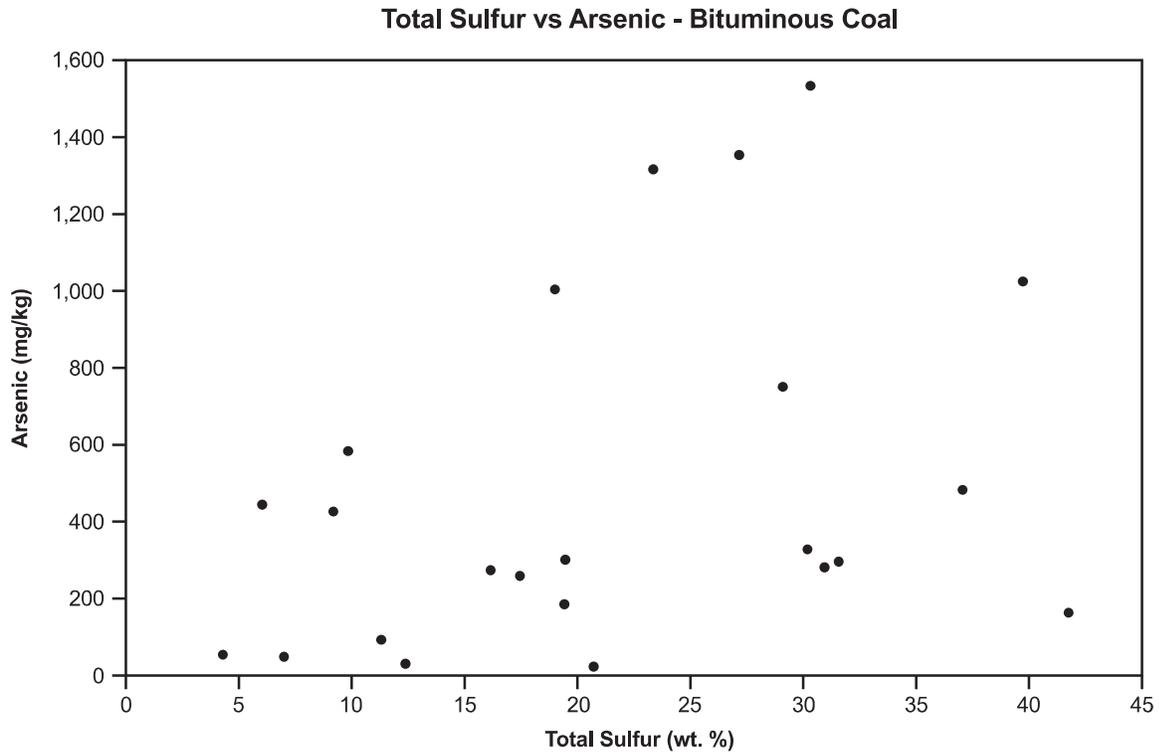


Figure 2-6  
Comparison of arsenic, copper and iron in mill rejects



**Figure 2-7**  
**Comparison of arsenic and sulfur concentrations in mill reject samples**

**Table 2-15**  
**Comparison of Mill Rejects and Coal Ash Chemical Composition**

Element	Typical Coal Ash - EPRI, 1987		Mill Reject Samples
	Fly Ash (39 Samples)	Bottom Ash (40 Samples)	Combined Rejects <sup>a</sup> (32 Samples)
As	7.7 - 1385	ND - 56	ND - 1535
Ba	239 - 10,850	122 - 9360	2.4 - 1067
Cd	ND - 16.9	ND	ND - 9
Ca	7410 - 224,000	2170 - 307,000	455 - 267,000
Cr	ND - 651	ND - 4710	9 - 3377
Cu	44.6 - 1452	20.3 - 146.3	ND - 545
Fe	25,200 - 177,100	19,590 - 201,000	95 - 364,000
Pb	21.1 - 2120	ND - 843	ND - 179
Mg	1560 - 41,800	2520 - 45,500	27.15 - 60,300
Mn	44 - 1332	56 - 1940	71 - 146,100 (24) <sup>b</sup>
Hg	NA	NA	0.01 - 5.44 (24)
K	1800 - 26,600	4360 - 23,900	ND - 19,100 (28)
Ni	22.8 - 353	ND - 1267	9 - 712 (24)
Na	1300 - 62,500	814 - 41,300	ND - 4000 (24)
Se	ND - 46.9	ND - 8.96	ND - 57.4
Ag	ND - 12.9	ND - 7.5	ND - 41
S	1300 - 64,800	ND - 74,000	100 - 417,000
Zn	24.8 - 2880	3.8 - 717	ND - 455

NA = Not analyzed; ND = Not detected.

Units are mg/kg.

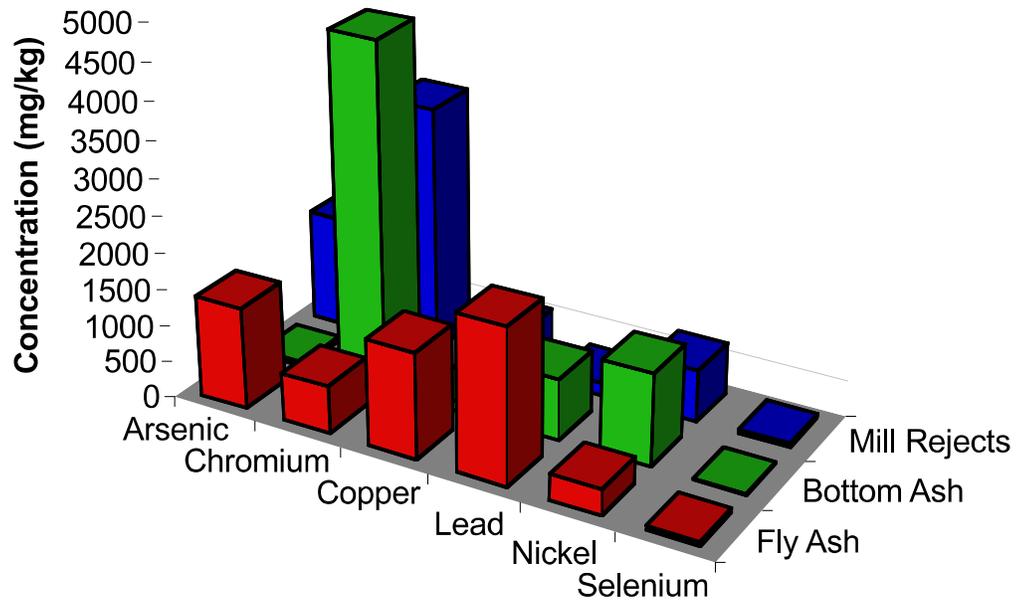
<sup>a</sup> Data are from this project: EPRI, 1987; and Fellman and Horzempa, 1988.

<sup>b</sup> The number in parentheses is the number of samples, if less than 32.

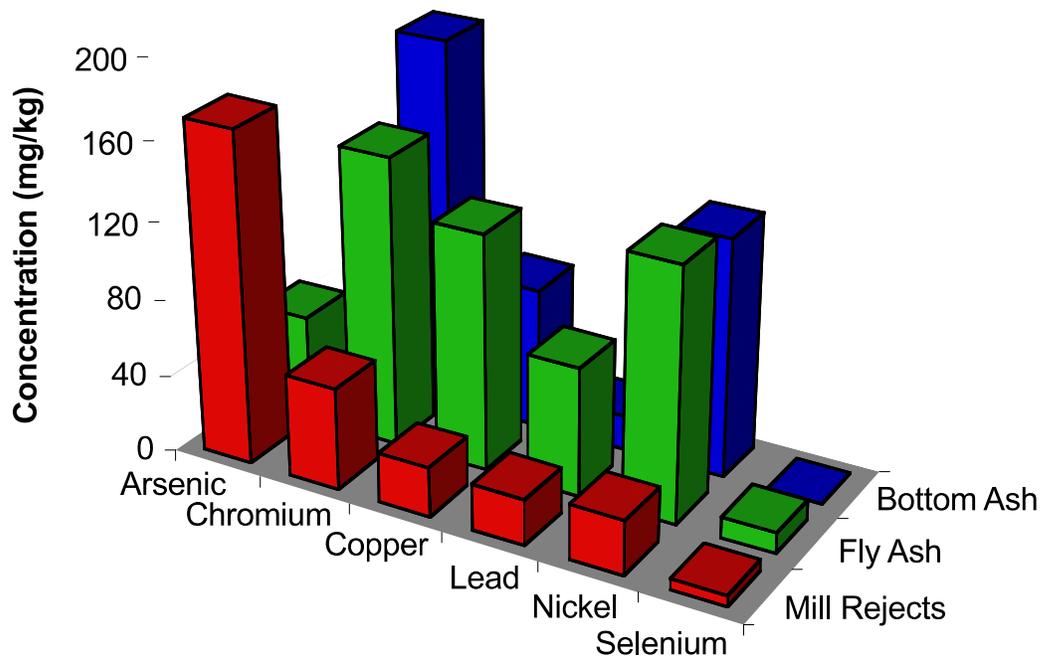
### **Leaching of Mill Rejects**

Leaching of constituents contained in mill rejects varies because acidic leachates produced from pyrites are a result of oxidation and microbial action and not the dissolution and desorption or partitioning reactions commonly applicable to the leaching of other constituents. If pyrites are present and the specific environmental conditions of exposure to oxygen and moisture exist, then oxidation of pyrites can occur. The solution produced as a result of oxidation is acidic, which can increase the solubilities of some metals. This section discusses the major biogeochemical processes involved in oxidation and leaching and the environmental factors that influence these processes. Chemical data from TCLP, EP, and other leaching tests using mill rejects are also discussed.

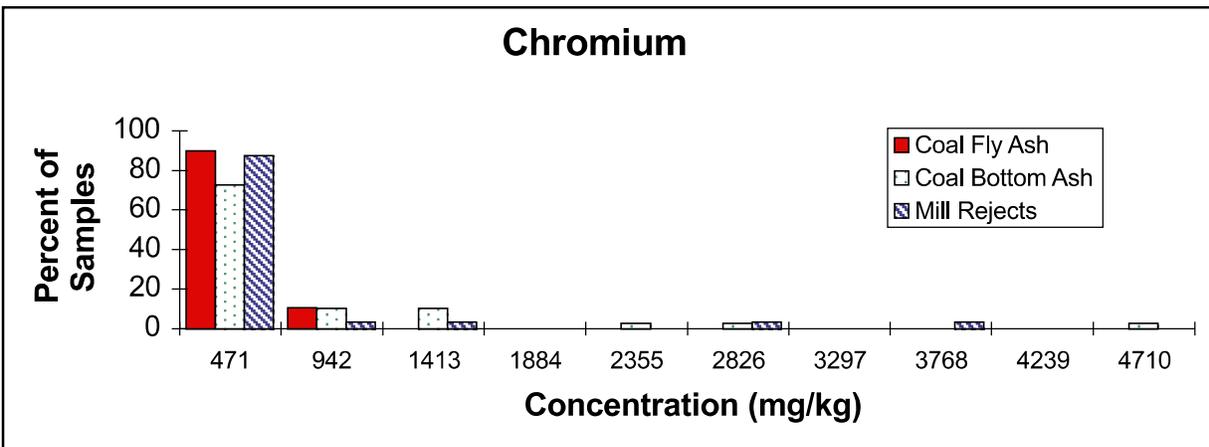
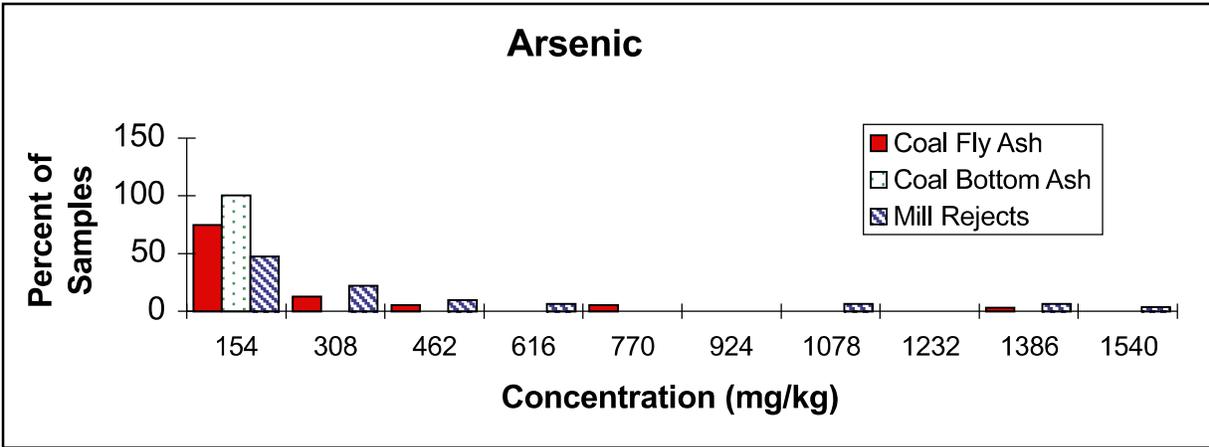
**a) Maximum Values**



**b) Median Values**



**Figure 2-8**  
Maximum and median concentrations of mill rejects and coal ash



**Figure 2-9**  
**Coal ash and mill rejects distributions of selected trace elements for combined data sets**  
 (full-size plots are included in Appendix B.)

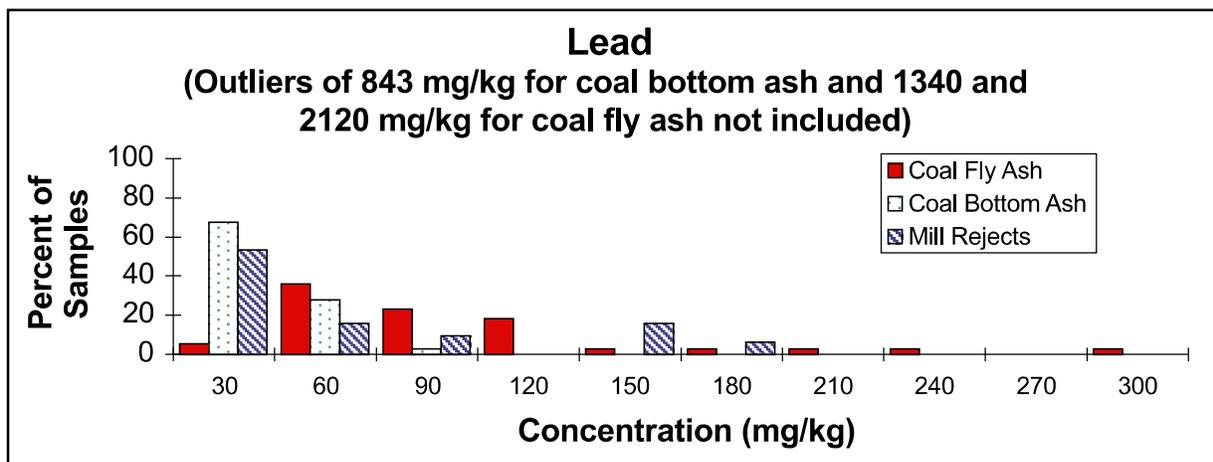
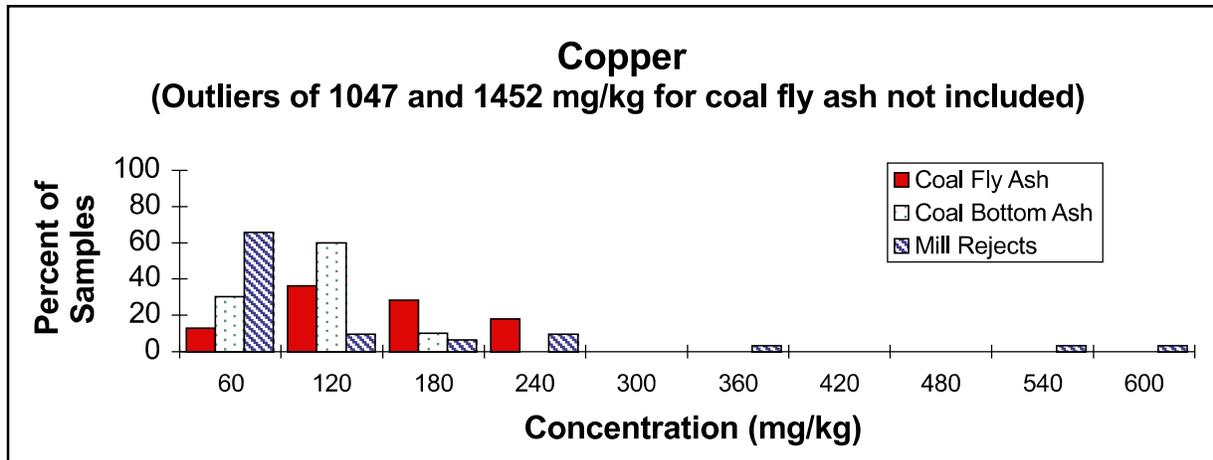


Figure 2-9 (continued)  
 Coal ash and mill rejects distributions of selected trace elements for combined data sets  
 (full-size plots are included in Appendix B.)

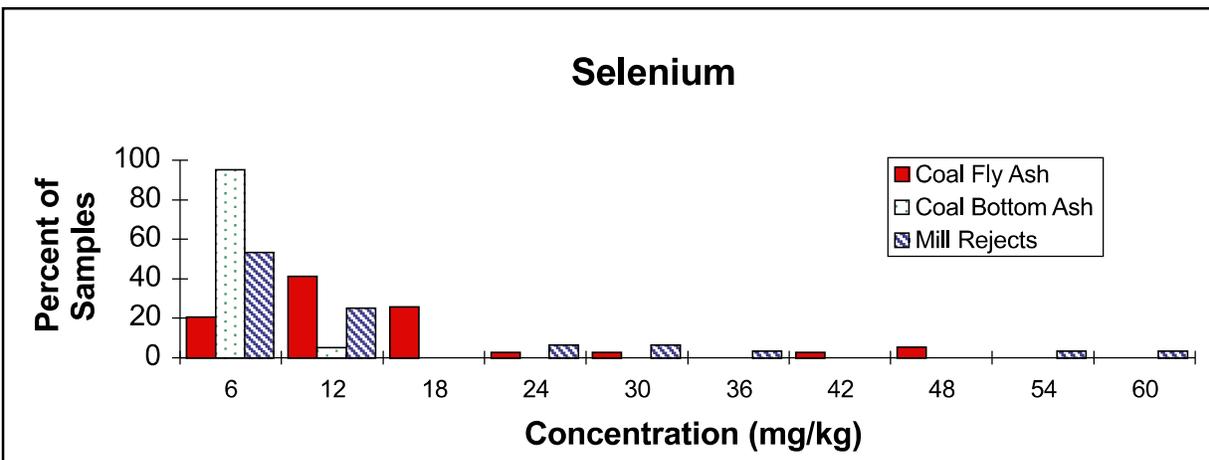
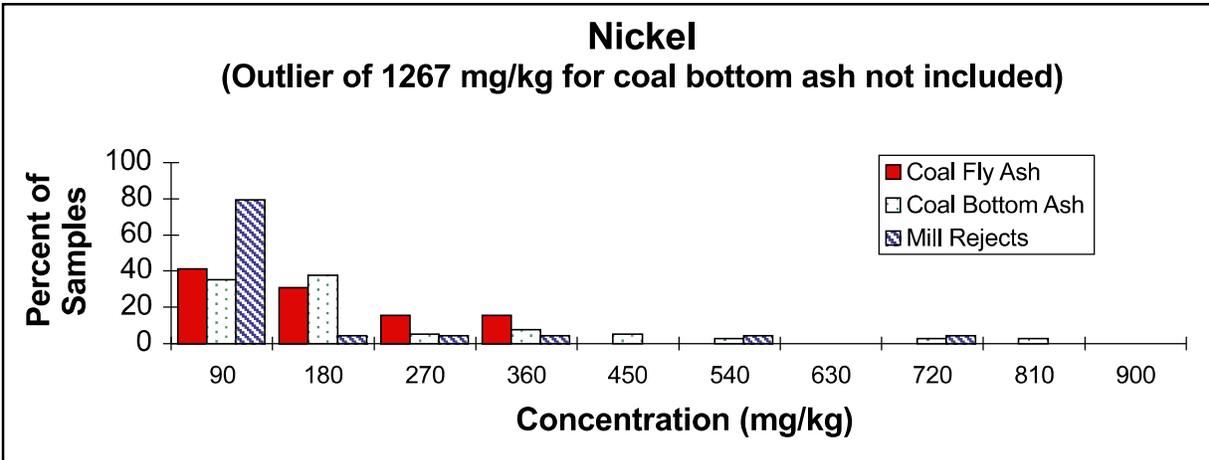
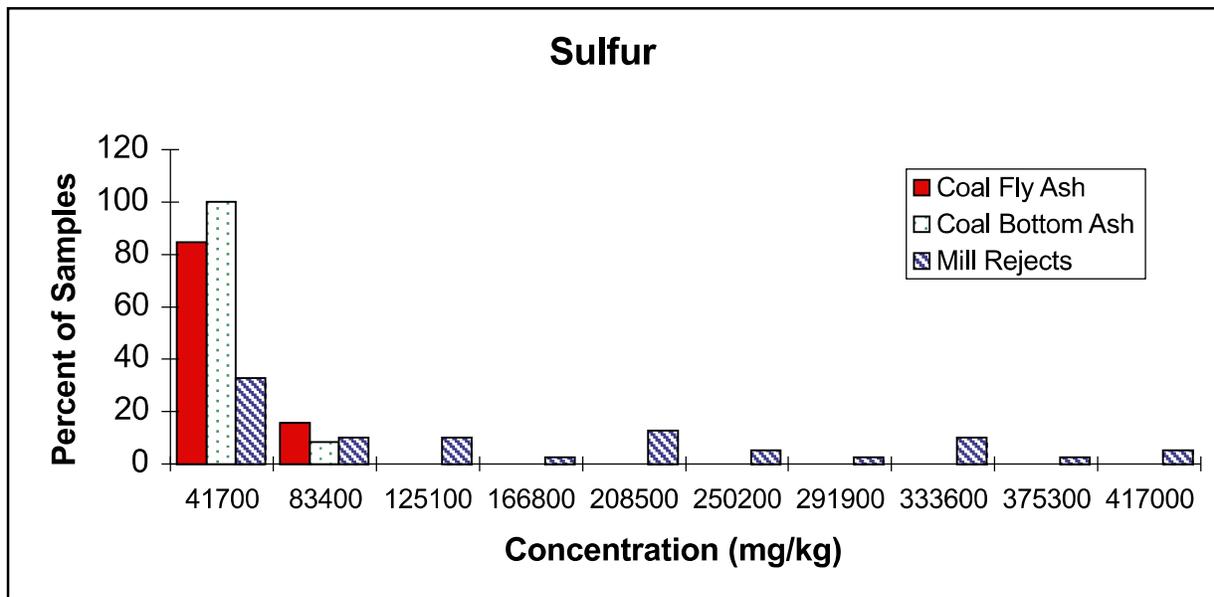
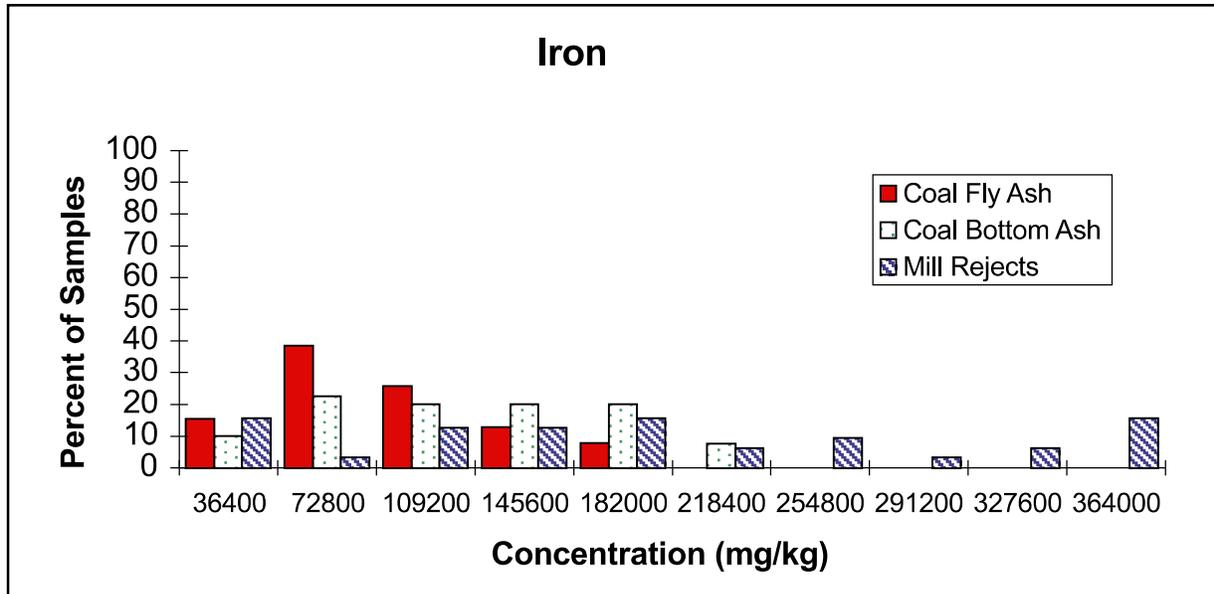


Figure 2-9 (continued)  
Coal ash and mill rejects distributions of selected trace elements for combined data sets  
(full-size plots are included in Appendix B.)



**Figure 2-10**  
Coal ash and mill rejects distributions for iron and sulfur

## Oxidation Processes

Pyrite oxidation is a complex set of processes involving both abiotic geochemical and biotic microbial reactions. Figure 2-11 depicts the stages of pyrite oxidation. The process, shown in this figure, begins when pyrite is exposed to air and water, forming sulfate, and releasing ferrous iron, Fe(II), which is then oxidized to ferric iron, Fe(III), as a result of further reactions with oxygen and water. Both of these reactions release  $H^+$  ion, which is acidic. In Stage 1, the oxidation rate is controlled mostly by abiotic processes. As the reaction proceeds, bacterial oxidation becomes more important (Stage 2). In this stage, some iron can precipitate as iron hydroxide. As oxidation continues, bacterial oxidation becomes the major process and ferric iron also begins to oxidize the pyrite in addition to oxygen (Stage 3). The acidity in this stage further decreases to less than pH 2.5 (Kleinman et al., 1981).

The oxidation of Fe(II) to Fe(III) is greatly enhanced by bacterial action. For example, the presence of sulfur and iron-oxidizing bacteria (e.g., *Thiobacillus ferrooxidans*) can increase the iron oxidation rate by a factor of up to a million (Singer and Stumm, 1970). The Fe(III) ion can then oxidize the pyrite in the same manner as oxygen from air. The relative rates of these reactions from an abiotic viewpoint are shown in Figure 2-12. At low pH (less than 4.5) the rate of oxidation due to Fe(III) is faster than that due to oxygen. The rate-limiting step at low pH was found to be the rate of conversion of Fe(II) to Fe(III) (Singer and Stumm, 1970). Part of the Fe(III) can combine with hydroxide ion to form  $Fe(OH)_3$  precipitate, particularly at alkaline pH. In the past, oxygen was thought to be the major abiotic oxidant in neutral to alkaline conditions, as shown by Reaction II in Figure 2-12. However, recent experiments suggest that Fe(III) is still the preferred oxidant, even at higher pH values (Moses et al., 1987; Moses and Herman, 1991; and Brown and Jurinak, 1989). Luther (1987) showed that Fe(III) can bind to the pyrite surface more effectively than oxygen. Oxygen is still important in this process, because it can oxidize the Fe(II) to Fe(III) (Luther, 1990 and 1987, and Moses and Herman, 1991). The latter reference refers to this concept as the extended Singer-Stumm model. Oxidation of pyrites by oxygen is less under saturated or submerged conditions, because the diffusion rate of oxygen through water is less than through air. Flooding pyrite-containing material can reduce the rate of oxygen diffusion into the material to a rate less than 1/10,000th that in air and slows the bacterial oxidation (Kleinman and Crerar, 1979). Even after dewatering, oxygen diffusion through thick deposits of fine-grained material (e.g., 20 to 50 ft.) is slow. Other factors influencing the abiotic reaction rate are the concentrations of hydroxyl ions present, the particular subspecies of ferric iron present, and the concentrations of carbon dioxide, bicarbonate, and other anions in solution. Crystalline pyrite, found in some types of coal, is less reactive than other types of pyrite such as framboidal pyrite, regardless of particle size or surface area.

The rate of pyrite oxidation due to abiotic reactions is slower than when specific bacteria are present, unless the pH is below about 2.2 (Evangelou and Zhang, 1995). Bacteria such as *Thiobacillus ferrooxidans* can oxidize Fe(II) at a much faster rate than oxygen alone. For example, the oxidation reaction rate with 1.5 mg bacteria present was 132 times faster at pH 5.5

<b>Pyrite Oxidation Reactions</b>		
1.		$\text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$
2.		$\text{Fe}^{2+} + \frac{5}{2} \text{H}_2\text{O} + \frac{1}{4} \text{O}_2 \rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 2\text{H}^+$
3.		$\text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O}$
4.		$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$
<b>Stage 1</b>		
<b>Mechanism</b>	Reaction 1:	Proceeds mostly abiotically with some direct bacterial oxidation
	Reaction 2:	Proceeds abiotically, slows down as pH falls
<b>Chemistry</b>	pH approximately 4.5; high sulfate; low iron; little acidity	
<b>Stage 2</b>		
<b>Mechanism</b>	Reaction 1:	Proceeds abiotically and by direct bacterial oxidation
	Reaction 2:	Proceeds at rate determined primarily by activity of <i>T. ferrooxidans</i>
<b>Chemistry</b>	Approximate pH range of 2.5 - 4.5; high sulfate, acidity, and total iron, increasing low $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio	
<b>Stage 3</b>		
<b>Mechanism</b>	Reaction 3:	Proceeds at a rate totally determined by activity of <i>T. ferrooxidans</i>
	Reaction 4:	Proceeds at rate primarily determined by rate of Reaction 3
<b>Chemistry</b>	pH below approximately 2.5; high sulfate, acidity, total iron, and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio	

**Figure 2-11**  
**Stages of pyrite oxidation (after Kleinman et al., 1981).**

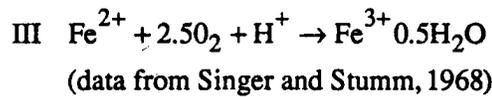
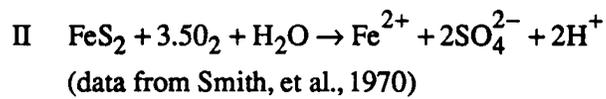
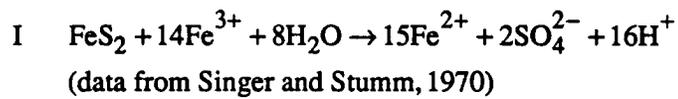
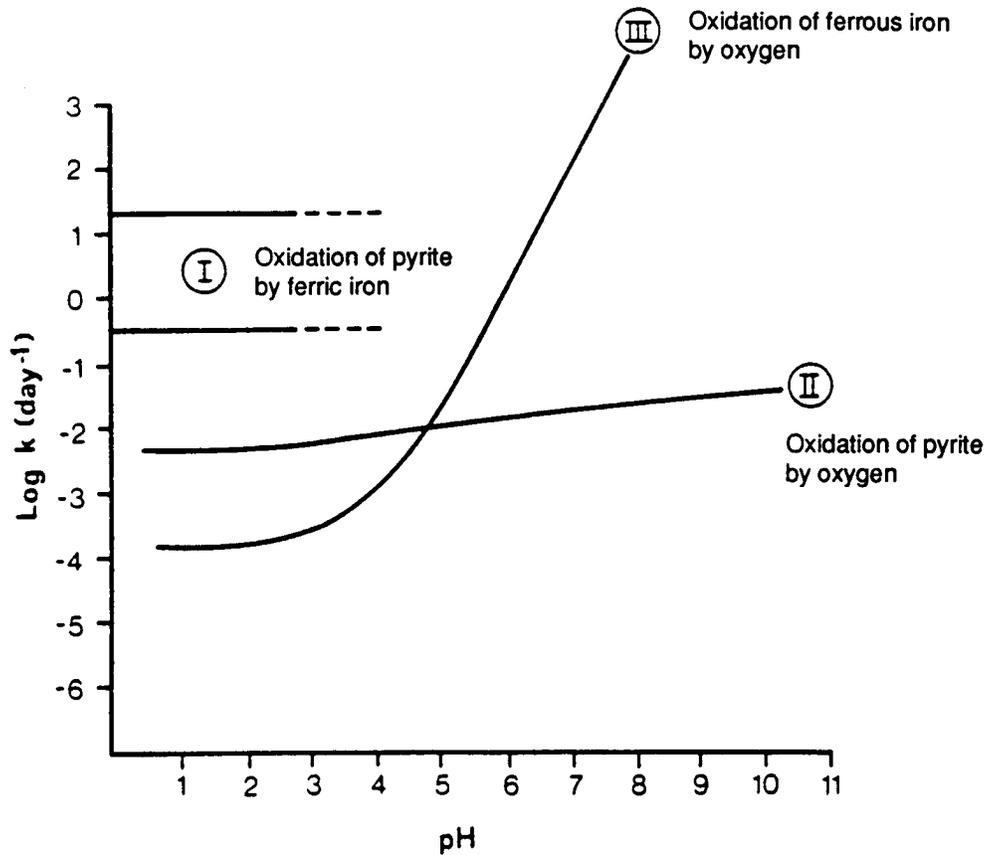


Figure 2-12  
 Comparison of rate constants for pyrite oxidation as a function of pH (Nordstrom, 1982).

and 13,200 times faster at pH 4.5 than when only oxygen was present (Pesic et al., 1989). The oxidation reaction rate is also influenced by pH, temperature, and oxygen concentration as illustrated in Figure 2-13. Optimum conditions for *Thiobacillus ferrooxidans* bacteria are about 30°C, pH 3.2, and an oxygen content of 1 percent or greater. The products of this type of bacterial oxidation of pyrites are ferric and ferrous sulfate. Other bacteria (e.g., *Thiobacillus thiooxidans*) can also microbially mediate oxidation reactions of pyrites by reducing sulfides to sulfate, thiosulfates, and in some cases elemental sulfur (Schippers et al., 1996).

Nicholson et al. (1988 and 1990) investigated pyrite oxidation in neutral to alkaline conditions. They suggested that in these environments the pyrite surface could be coated with iron-oxides, thus reducing the oxidation rate. They used X-ray photoelectron spectroscopy and auger electron spectroscopy to identify iron oxide coatings of about 0.6 µm in thickness. Iron coatings decrease the oxidation rate after their thickness has built up to a threshold. For example, the oxidation rate at pH 7.5 to 8.5 first increased, then decreased, as shown in Figure 2-14. Column leaching experiments have also shown a slowdown in leaching rate due to the build-up of reaction products such as iron oxides on pyrite surfaces (Nicholson et al., 1990).

Another influence on pyrite oxidation is manganese oxide, which can be present in mill rejects, coal ash, or soils. Asghar and Kaehiron (1981) showed that MnO<sub>2</sub> could oxidize Fe(II) to Fe(III) at pH values less than or equal to 5.5. The Fe(III) can then oxidize the pyrite.

### **Chemical Composition of Laboratory-Derived Leachates**

Some leaching tests have been conducted with mill rejects using the standard tests of the U.S. Environmental Protection Agency (e.g., EP or TCLP). TCLP and EP tests were conducted on eight mill reject samples from eastern bituminous coals (Fellman and Horzempa, 1988) and on four other mill reject samples (EPRI, 1987). The leachate concentrations and summary statistics are shown in Tables 2-16 and 2-17 for the TCLP and EP tests, respectively. All concentrations for both tests were less than the RCRA regulatory criteria. In most cases, the TCLP leachate concentrations in the mill reject samples were less than one-tenth of the criteria, except for selenium. The highest concentrations in the mill reject TCLP samples were found for nickel and manganese. The TCLP concentrations for a given parameter were either similar to or higher than the same parameter from the EP tests except for one sample for nickel (sample C-day 1). The other mill reject samples from this plant had lower nickel concentrations by a factor of 16. All the other samples contained higher nickel concentrations in the TCLP leachate than the EP leachate. Thus, this is considered to be an unusual case and not typical.

Mill reject leachates were compared to leachates from fly ash and bottom ash using the TCLP data for fly ash and bottom ash samples from the EPRI (1987) study (Table 2-18). Maximum and median mill reject and coal ash concentrations are shown in Figure 2-15 for arsenic, barium, cadmium, chromium, lead, and selenium. These plots show that mill rejects have lower trace metal concentrations in leachates than either fly ash or bottom ash for all these elements, except for selenium. As shown more clearly in Figure 2-16, selenium was low in all the leachates, but mill rejects had higher maximum and median concentrations. The other metals shown had

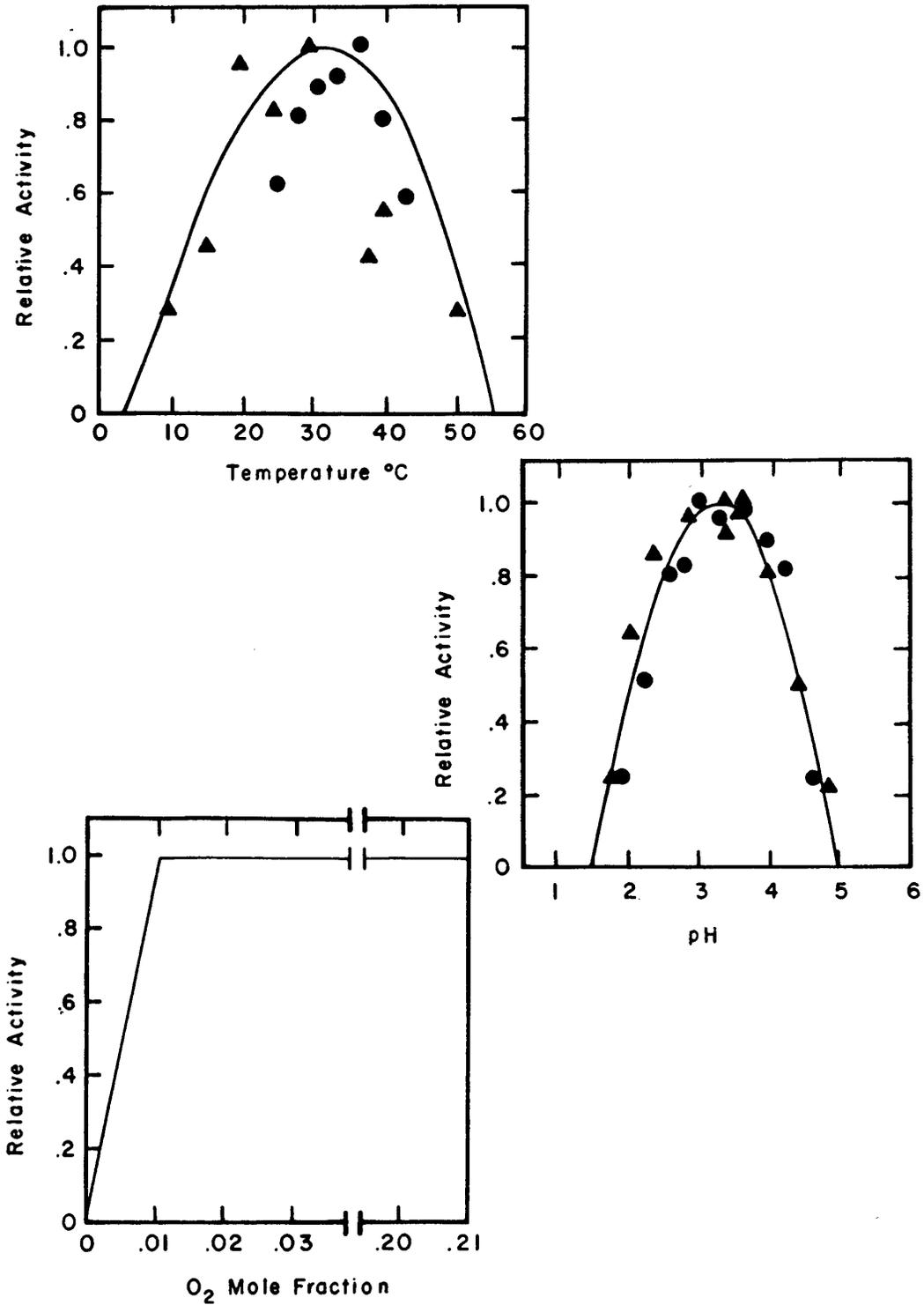


Figure 2-13  
Effect of key parameters on activity of *T. ferrooxidans*  
(Evangelou and Zhang, 1995).

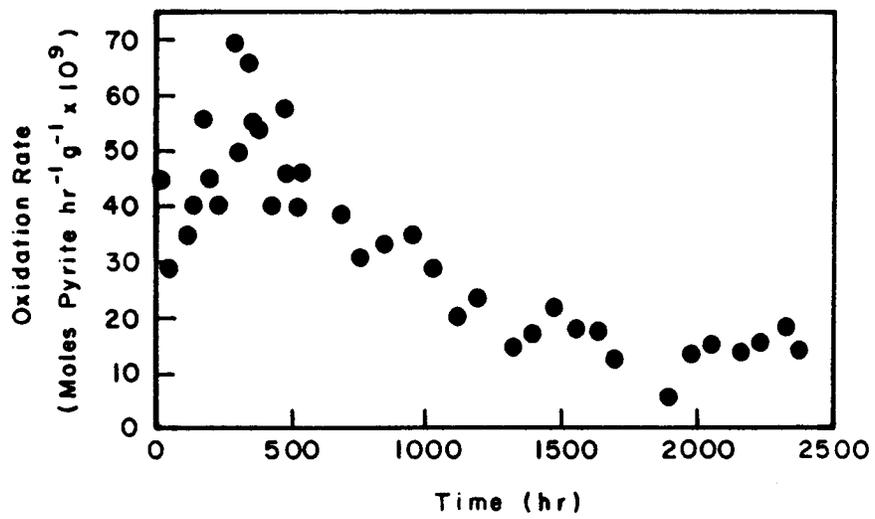


Figure 2-14  
Example of pyrite oxidation rate in pH range of 7.5 to 8.6  
(Nicholson et al., 1988)

**Table 2-16  
Summary of TCLP Results for Mill Rejects**

Sample ID	As	Ba	B	Cd	Cr	F	Pb	Mn	Hg	Ni	Se	Ag	Tl	V	Zn
A-Day 1	<0.06	0.30	NA	0.010	<0.01	NA	<0.08	NA	0.0003	1.90	0.20	<0.02	<0.0005	NA	NA
A-Day 2	<0.06	0.28	NA	0.010	<0.01	NA	<0.08	NA	<0.0002	1.90	0.27	<0.02	<0.0005	NA	NA
B-Day 1	0.09	0.10	NA	0.010	0.030	NA	0.130	NA	0.0002	3.10	<0.27	<0.04	<0.0005	NA	NA
B-Day 2	0.07	0.07	NA	0.010	0.030	NA	0.240	NA	0.0003	3.10	<0.27	<0.04	0.020	NA	NA
C-Day 1	<0.06	0.39	NA	0.020	0.03	NA	0.140	NA	<0.0002	2.54	0.15	<0.01	<0.03	NA	NA
C-Day 2	<0.06	0.56	NA	0.020	0.02	NA	0.09	NA	0.0002	1.30	0.14	<0.01	<0.03	NA	NA
D-Day 1	<0.06	0.34	NA	0.020	0.09	NA	0.36	NA	<0.0002	2.90	0.26	<0.01	<0.03	NA	NA
D-Day 2	<0.06	0.30	NA	0.010	0.06	NA	<0.08	NA	<0.0002	3.00	0.12	<0.01	0.03	NA	NA
904	0.0074	0.223	0.131	<0.01	0.045	0.08	0.11	0.703	<0.0001	NA	0.006	<0.01	NA	<0.01	0.064
909	0.0580	0.363	0.071	<0.01	<0.02	0.22	<0.01	5.130	<0.0001	NA	0.001	<0.01	NA	<0.01	0.099
913	0.0028	0.194	<0.02	<0.01	<0.02	<0.05	0.014	0.398	<0.0001	NA	0.005	<0.01	NA	<0.01	0.090
915	0.0040	0.196	0.037	<0.01	<0.02	0.29	<0.01	0.961	<0.0001	NA	<0.001	<0.01	NA	<0.01	0.024
Minimum	0.0028	0.07	0.010	0.005	0.005	0.025	0.005	0.398	0.0001	1.30	0.0005	ND	0.0025	ND	0.024
Maximum	0.0900	0.56	0.131	0.20	0.09	0.29	0.36	5.130	0.0003	3.10	0.27	ND	0.030	ND	0.099
Mean	0.0344	0.2763	0.0623	0.0108	0.0288	0.1538	0.1012	1.798	0.0001	2.4675	0.1185	ND	0.0128	ND	0.0768
Median	0.0300	0.2900	0.0540	0.010	0.0250	0.1500	0.065	0.8320	0.0001	2.720	0.1350	ND	0.0150	ND	0.0920
Count	12	12	4	12	12	4	12	4	12	8	12	12	8	4	4
# of Detected Samples	6	12	3	8	7	3	7	4	4	8	9	0	2	0	4

Statistics were calculated using 1/2 detection limit values.

ND = Indicates that all values were below the detection limit.

NA = Indicates data not analyzed.

Units are in mg/L.

Data are from Fellman and Horzempa, 1988 and EPRI, 1987.

**Table 2-17  
Summary of EP Toxicity Results for Mill Rejects**

Sample ID	As	Ba	B	Cd	Cr	F	Pb	Mn	Hg	Ni	Se	Ag	Tl	V	Zn
A-Day 1	<0.06	<0.42	NA	<0.03	<0.01	NA	<0.1	NA	<0.0002	0.30	0.70	0.03	<0.0005	NA	NA
A-Day 2	<0.06	0.42	NA	<0.03	<0.01	NA	<0.1	NA	<0.0002	0.26	0.14	<0.03	<0.0005	NA	NA
B-Day 1	0.13	0.040	NA	0.020	<0.01	NA	<0.08	NA	<0.0002	2.33	<0.1	0.02	<0.0005	NA	NA
B-Day 2	<0.06	0.040	NA	0.007	<0.01	NA	<0.08	NA	<0.0002	2.32	0.10	<0.01	<0.0005	NA	NA
C-Day 1	<0.06	0.32	NA	<0.007	0.02	NA	0.10	NA	<0.0002	1.4	0.20	<0.01	<0.0005	NA	NA
C-Day 2	<0.06	0.32	NA	0.010	0.01	NA	<0.08	NA	<0.0002	0.85	0.19	<0.01	<0.0005	NA	NA
D-Day 1	<0.06	0.14	NA	0.020	0.01	NA	<0.08	NA	<0.0002	0.77	<0.7	0.01	0.05	NA	NA
D-Day 2	<0.06	0.09	NA	0.010	0.01	NA	0.12	NA	<0.0002	12.4	<0.6	0.01	0.08	NA	NA
904	0.0246	0.05	0.1730	<0.01	<0.02	0.11	0.024	0.857	<0.0001	NA	0.0048	<0.01	NA	<0.01	0.092
909	0.0085	0.084	<0.02	<0.01	<0.02	<0.05	<0.01	1.36	<0.0001	NA	0.0054	<0.01	NA	<0.01	<0.02
913	<0.0006	0.076	0.027	<0.01	<0.02	0.07	<0.01	0.373	<0.0001	NA	0.043	<0.01	NA	<0.01	0.10
915	0.0012	0.041	0.051	<0.01	<0.02	0.60	<0.01	0.119	<0.0001	NA	0.003	<0.01	NA	<0.01	<0.02
Minimum	0.0003	0.04	0.010	0.0035	0.005	0.025	0.005	0.119	ND	0.26	0.003	0.005	0.0025	ND	0.01
Maximum	0.13	0.42	0.173	0.020	0.020	0.60	0.12	1.36	ND	12.4	0.20	0.03	0.080	ND	0.10
Mean	0.0312	0.1526	0.0653	0.010	0.0092	0.2013	0.0433	0.6773	ND	2.5788	0.0726	0.01	0.0181	ND	0.053
Median	0.0300	0.087	0.039	0.0085	0.010	0.09	0.04	0.6150	ND	1.125	0.0465	0.005	0.0025	ND	0.051
Count	12	12	4	12	12	4	12	4	12	8	12	12	8	4	4
# of Detected Samples	4	11	3	5	4	3	3	4	0	8	9	4	2	0	2

Statistics were calculated using 1/2 detection limit values.

ND = Indicates that all values were below the detection limit.

NA = Indicates data not analyzed.

Units are in mg/L.

Data are from Fellman and Horzempa, 1988 and EPRI, 1987.

**Table 2-18  
TCLP Leachate Data for Fly Ash and Bottom Ash**

Sample No.	Type	As <sup>b</sup>	B <sup>a</sup>	Ba <sup>a</sup>	Cd <sup>a</sup>	Cr <sup>a</sup>	F <sup>c</sup>	Pb <sup>e</sup>	Mn <sup>a</sup>	Hg <sup>d</sup>	Se <sup>b</sup>	Ag <sup>a</sup>	V <sup>a</sup>	Zn
137	FA	0.0039	0.12	0.362	<0.01	<0.02	2.31	<0.01	<0.002	<0.0001	0.013	<0.01	<0.05	0.02
138	BA	0.032	10.8	0.71	0.011	0.28	4.73	<0.01	0.289	<0.0001	0.15	<0.01	0.152	0.18
237	BA	<0.0006	0.26	0.254	<0.01	<0.02	0.93	<0.01	<0.002	<0.0001	0.0038	<0.01	<0.05	<0.02
238	BA	<0.0006	0.17	0.86	<0.006	<0.02	0.21	<0.01	0.052	<0.0001	0.0014	<0.01	<0.01	<0.02
337	BA	0.0013	0.319	0.305	<0.01	<0.02	0.52	<0.01	<0.002	<0.0001	0.0013	<0.01	<0.05	<0.02
900	F	1.22	0.554	0.214	0.254	0.188	0.47	1.42	0.436	<0.0001	<0.003	<0.01	0.499	55.2
901	B	0.0008	0.047	0.130	<0.01	0.025	0.5	0.047	0.049	<0.0001	<0.001	<0.01	<0.01	0.176
902	F	0.134	0.334	0.279	0.013	<0.02	1.28	<0.01	0.271	<0.0001	0.041	<0.01	0.044	0.331
903	B	0.0328	0.156	1.61	<0.01	<0.02	<0.05	<0.01	0.076	<0.0001	<0.001	<0.01	<0.01	0.165
905	FA	2.26	1.09	0.113	0.564	4.64	0.550	2.94	1.38	<0.0001	<0.001	<0.01	0.334	103.0
906	BA	0.0006	0.059	0.134	<0.01	<0.02	<0.05	<0.01	0.033	<0.0001	<0.001	<0.01	<0.01	0.078
907	F	0.294	0.826	0.273	<0.01	<0.02	0.98	<0.01	0.104	<0.0001	0.026	<0.01	0.038	0.117
908	B	0.0120	0.033	1.10	<0.01	<0.02	<0.05	0.02	0.021	<0.0002	<0.001	<0.01	<0.01	0.021
911	F	2.68	1.04	0.181	0.037	0.218	6.05	0.029	0.690	<0.0001	0.004	<0.01	0.284	1.15
912	B	<0.0006	0.044	0.154	<0.01	<0.02	<0.05	<0.01	0.231	<0.0001	<0.001	<0.01	<0.01	<0.02
916	B	0.0148	0.405	0.210	<0.01	<0.02	<0.05	<0.01	0.111	<0.0003	<0.001	<0.01	<0.01	<0.02

<sup>a</sup> Determined by inductively coupled argon plasma emission spectrometry (ICP).

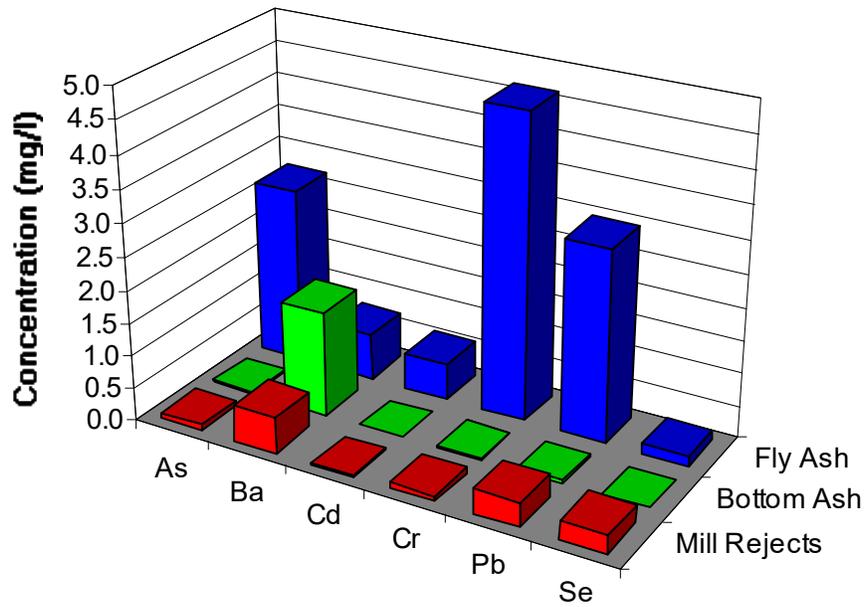
<sup>b</sup> Determined by hydride generation atomic absorption spectrometry (HGAA).

<sup>c</sup> Determined by ion selective electrode (ISE).

<sup>d</sup> Determined by cold vapor atomic absorption (CVAA).

<sup>e</sup> Determined by graphite furnace atomic absorption (GFAA).  
Data are from EPRI, 1987.

a) Maximum Values



b) Median Values

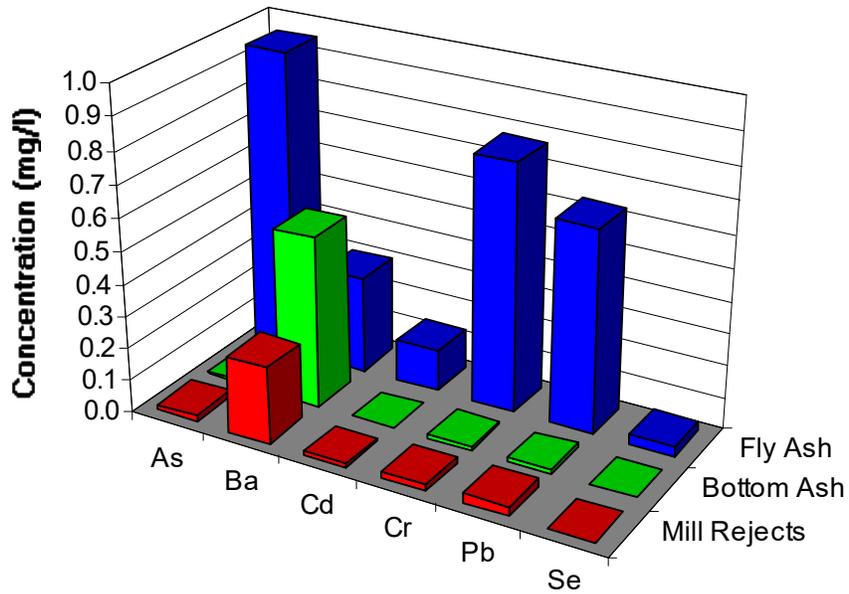
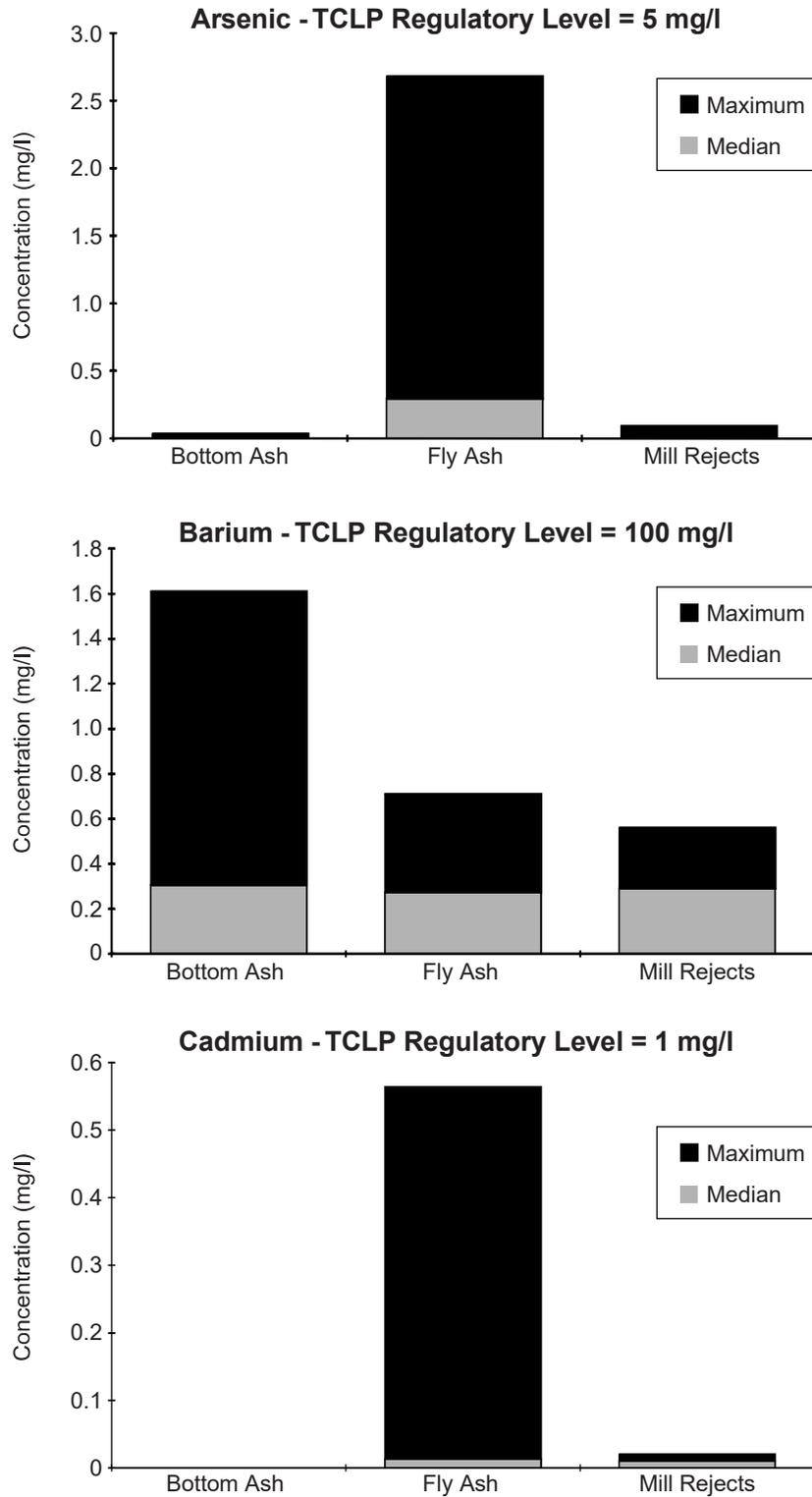


Figure 2-15  
Comparison to TCLP leachates from mill rejects and coal ash



**Figure 2-16**  
Detailed comparison of TCLP leachate data

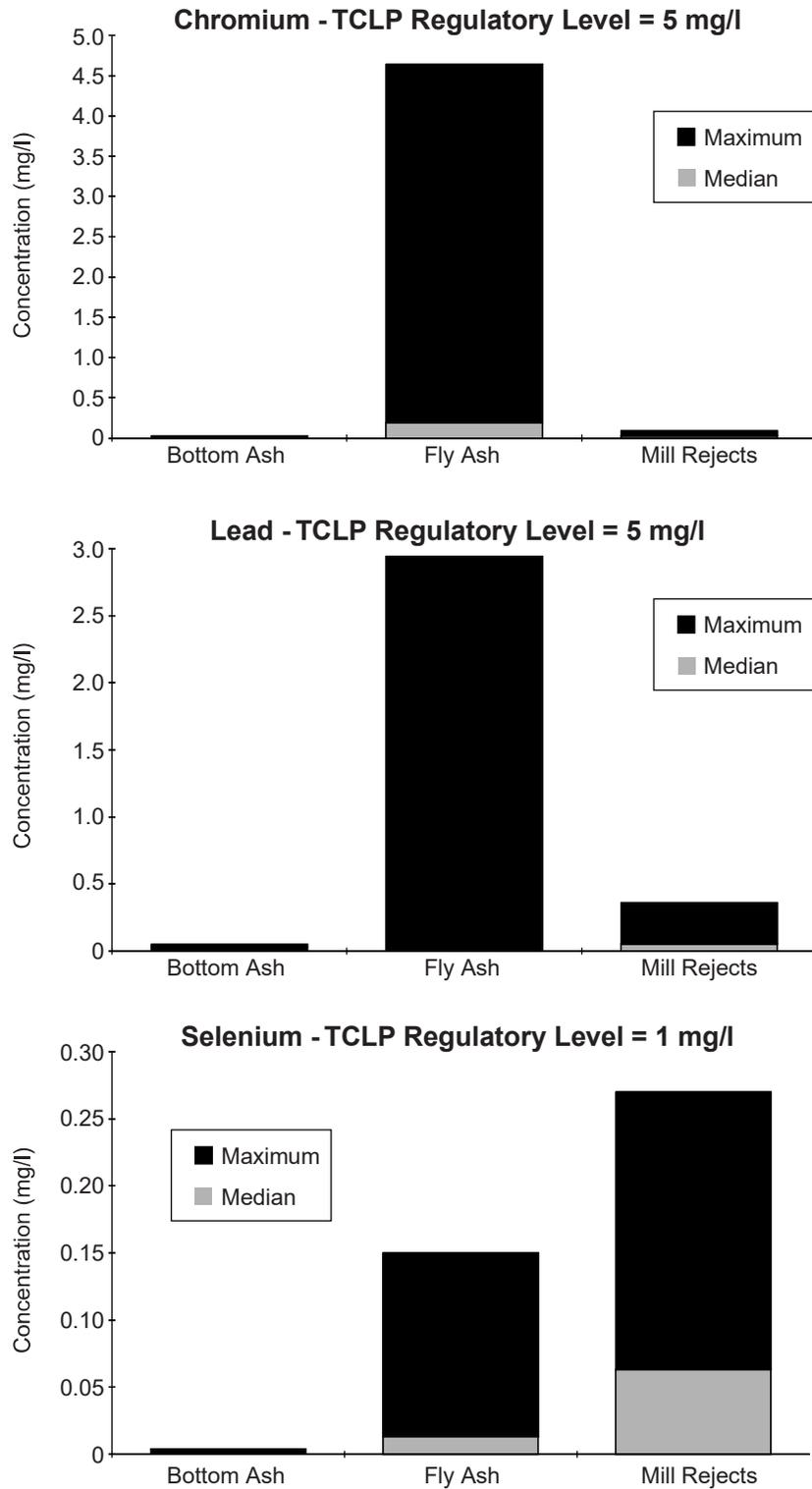


Figure 2-16 (continued)  
Detailed comparison of TCLP leachate data

higher maximum concentrations in fly ash, except for barium, which was higher in bottom ash. In addition to the elements with RCRA criteria, other elements were measured in the leachate in at least one of the studies, including boron, fluoride, manganese, nickel, thallium, vanadium, and zinc. Silver, vanadium, and most of the thallium concentrations were not detected in any of the mill reject samples. With the exception of manganese and nickel, TCLP leachate concentrations in the mill rejects were low (less than 0.3 mg/l). The EP tests also showed low concentrations in leachates from mill rejects for all elements tested, except manganese and nickel.

The intent of the TCLP and EP tests is to estimate leachate quality if the materials tested are comanaged with municipal wastes, for regulatory purposes. Thus, a weak organic acid solution at a pH of about 5 is used as the leaching medium. Because most coal ash and mill rejects are not comanaged with municipal wastes, these leaching tests do not provide an accurate estimate of field leachates at ash/mill reject sites. The TCLP and EP tests represent leaching of the material as it exists at the time of the test, and thus do not provide an estimate of future leachate quality if any pyrites present in the material later oxidize.

### ***Chemical Composition of Field-Scale Leachates***

Field leachates collected from wells screened in pyritic mill rejects that have been oxidized show high acidity and high concentrations of sulfate, iron, and manganese. Some trace metals such as arsenic, copper, nickel, and zinc are also above typical detection limits. Examples of sites where field data from borings with oxidized mill rejects were available include the BR and MO sites discussed in Section 3 containing case studies. Table 2-19 shows porewater composition data from some of the samples where pyrite oxidation has occurred. Sulfate and iron concentrations were the highest at the MO site. Sulfate varied from 4,047 to 70,748 mg/l; iron ranged from 655 to 25,400 mg/l. Arsenic and zinc were also elevated in these samples (>1 mg/l), due to the acidic pH of the porewater (1.1 to 3.79). At the BR site, the upper part of the landfill where pyrite oxidation occurred was unsaturated. The sulfate and iron were considerably less than at the MO site. Sulfate ranged from 189 to 5,634 mg/l while iron ranged from 0.5 to 73.6 mg/l. The pH of these samples varied from 2.8 to 4.06. Arsenic and zinc concentrations were lower (less than 0.05 and 0.08 mg/l respectively) than the MO site. Trace element content is highly dependent on coal composition, which varies considerably between sites, and on the geochemical conditions at a given location.

In coal mining, pyrites are also exposed to water and oxygen resulting in their oxidation. The resulting leachate is recognized as acid mine drainage and can be viewed as a field-scale leachate from pyrites. In a recent paper, Hyman and Watzlaf (1997) reported a summary of water quality data based on 128 different water samples from untreated coal mine drainage from active, reclaimed, and abandoned surface and underground mines, as well as coal waste materials. Approximately 75% of the water samples had pH values of less than 4.5 and the pH for the remaining 25% of the samples ranged between 4.5 and 6.9. Sulfate concentrations varied between 71 mg/l to 52,700 mg/l with a mean value of 2,360 mg/l. Arsenic concentrations ranged from non-detect to 16.1 mg/l with a mean of 0.19 mg/l. Iron concentrations were found to be

**Table 2-19  
Porewater Composition from Oxidized Mill Reject/Ash Samples**

Element	Conc.	BR-C2	BR-C2	BR-C2	BR-C4	BR-C4	BR-C4	BR-C4	MO-B	MO-C	MO-C	MO-C	MO-C	MO-1	MO-4	MO-5	MO-6	MO-7
		0.5 ft.	1.75 ft.	3.0 ft.	4.5 ft.	1.25 ft.	3.0 ft.	4.5 ft.	9.6-12.1 ft.	4-6 ft.	2-3.5 ft.	6-8.2 ft.	8-10 ft.	12-14 ft.	Pit	Pit	Pit	Pit
Al	mg/L	53.7	6.6	13.1	46.8	58.7	511.0	763.0	1339	NA	NA	NA	NA	34.9	205	114	658	500
As	mg/L	<0.0005	0.043	0.004	<0.0005	<0.0005	0.004	0.008	NA	14.4	11.4	3.1	6.6	0.1	19.5	6.4	86.0	11.9
B	mg/L	0.80	<0.237	0.40	0.60	<0.24	0.50	2.20	NA	16.1	10.9	33	35.3	0.95	1.17	1.54	4.23	1.13
Ba	mg/L	0.68	0.73	0.73	0.70	<0.03	<0.03	<0.03	NA	0.030	0.021	0.015	0.014	0.036	0.013	0.012	0.022	0.016
Ca	mg/L	12.3	2.8	34.2	537	567	504	482	452	492	496	535	562	610	479	489	557	444.3
Cd	mg/L	0.075	0.075	0.075	0.075	<0.1	<0.1	<0.1	1.3	0.20	0.09	0.13	0.26	0.05	0.02	0.06	0.09	0.02
Cl	mg/L	1.7	0.5	0.3	10.5	5.0	3.4	2.7	40.5	2.7	6.7	8.3	3.9	<2.2	7.58	6.44	<55	10.15
Co	mg/L	0.230	0.230	1.150	0.230	<0.09	0.100	0.200	12	NA	NA	NA	NA	4.46	0.83	1.37	5.99	NA
Cr	mg/L	NA	NA	NA	NA	NA	NA	NA	NA	0.10	0.26	0.44	0.59	0.01	0.19	0.68	0.72	0.82
Cu	mg/L	0.10	0.10	5.78	0.65	<0.02	0.98	2.42	NA	0.07	0.06	0.13	0.16	0.07	0.06	0.13	0.16	0.25
Fe*	mg/L	0.15	43.74	17.34	39.38	3.30	2.00	64.30	19559	NA	NA	NA	NA	522	3788	5162	11470	3806
Fe <sup>3+</sup>	mg/L	0.17	1.73	1.02	2.38	0.57	23.47	7.08	4264	NA	NA	NA	NA	133	1044	1029	7953	824
Fe, total	mg/L	0.525	53.30	21.80	49.30	3.70	25.60	73.60	23352	6130	6520	21940	18340	655	4832	6191	19424	4630
K	mg/L	4.20	15.90	1.80	10.00	8.60	<1.2	1.20	<8.09	26	36.8	23.3	39.9	23.5	58.8	4.29	73.9	40.1
Mg	mg/L	7.00	3.10	1.70	4.90	9.97	44.70	47.30	946.2	156	178	481	524	213	53.9	358	174	75.4
Mn	mg/L	0.90	0.50	0.30	0.40	0.83	4.00	4.47	448	58.5	48.5	131	132	21.5	11.1	46.6	48	11.5
Mo	mg/L	<1	<1	<1	<1	<1	<1	<1	NA	<1	<1	<1	<1	<0.5	0.35	<0.5	1.82	0.37
Na	mg/L	3.10	2.60	3.70	3.60	6.90	4.70	9.90	NA	12.5	12.8	19.2	20.7	32.5	15.2	24.1	12.2	12.4
Ni	mg/L	1.10	1.00	1.10	0.60	0.25	1.30	1.50	NA	7.031	5.671	16.049	23.1	5.85	1.89	2.87	11.2	1.97
SO3	mg/L	<0.72	<0.72	<0.72	<0.72	<1	<1	<1	NA	<20	<10	<10	<10	<5	<10	<10	<100	<2.5
SO4	mg/L	387	189	237	1799	1575	4569	5634	70748	14800	15520	42010	64478	4047	15887	15332	58672	17683
Zn	mg/L	<0.02	<0.02	0.08	0.08	<0.02	1.40	1.80	85.7	15.9	13	43.5	38.7	8.98	2.05	10.7	17	2.2

**Other Chemical Parameters**

pH	S.U.	3.50	3.94	4.05	4.06	3.55	2.80	3.63	4.28	3.72	3.59	3.79	3.64	3.01	1.51	2.09	1.1	1.92
EC	(umhos/cm)	1207	1422	1126	2764	3009	5078	5313	NA	10800	10800	19900	19900	NA	27600	15450	14200	30500

NA - Not Analyzed

from non-detect to 930 mg/l and showed a rapid drop-off between pH 3 and 4.5. Total iron ranged in concentrations from non-detect to 19,800 mg/l with the ferrous-iron ranging from non-detect to 15,700 mg/l, thereby accounting for most of the iron in solution. Manganese concentrations ranged from non-detect to 164 mg/l and zinc showed a concentration range of 0.01 mg/l to 146 mg/l.



# 3

## CASE STUDIES RELATED TO MILL REJECTS

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### Current Disposal Practices for Mill Rejects

A survey of utility waste management practices at 264 coal-fired power plant facilities, representing 88 utilities, was completed in 1995 (EPRI, 1997). This survey indicated that 55 percent of the utilities comanage mill rejects with high-volume by-products. In fact, coal mill rejects constitute the most commonly comanaged low-volume waste. Mill rejects are comanaged in 55 percent of the ash impoundments, and at 45 percent of the landfills surveyed. Coal ash is used as fill material in minefills at about 3 percent of the sites; some of these sites may have also included mill rejects with the coal ash.

The 1996 survey for the present project (Table 3-1) confirmed that most plants comanage mill rejects with coal ash in impoundments or landfills. Mixing of mill rejects with ash is a common practice. The limited amount of data from the mill rejects comanagement sites contained in this report show that when pyrite oxidation occurs, acidic leachates are generated, but when the pyrites are kept submerged in ash impoundments, oxidation of the pyrites does not occur, therefore no acidic leachates are generated. There are two mill rejects comanagement sites where pyrites were oxidized, resulting in acidic leachates with elevated amounts of sulfate and iron, along with elevated concentrations of some trace metals, such as arsenic, copper, nickel, and zinc. Observations at the MO site indicate that pyrite oxidation occurred because the mill rejects were concentrated in one area, were allowed to be partially exposed to the air, and a sufficient amount of water was present. Observations at the BR site indicate the presence of oxidized pyrite in the shallow depths of the landfill where partially saturated conditions existed with free diffusion of oxygen.

Mill rejects at some power plants have been placed in separate landfills or ponds. This practice occurs where coal ash is generally not disposed of at the power plant site.

### Overview of Case Studies

EPRI and individual utilities sponsored investigations at six sites where mill rejects containing pyrites have been disposed of with coal combustion by-products. These investigations showed that if the mill rejects contain a significant amount of pyrites and if pyrite oxidation occurs, then iron, sulfate, manganese, aluminum, acidity, and some trace metals (i.e., arsenic, copper, nickel, and zinc) can be leached. The case studies presented here summarize the handling and disposal methods for mill rejects used at these sites, the groundwater flow regime, and the observed groundwater quality and to some extent surface water quality effects, if any. Detailed information on these sites is available in separate reports.

**Table 3-1  
Mill Rejects Handling and Disposal Methods for the Power Plants Surveyed**

Sample Number	Utility	Plant Name	State	Quantity of Rejects Generated	Mill Rejects Handling Procedure	Disposal Method for Mill Rejects	Rejects and Ash Comanaged
NA	1	AA	AZ	NA	Separated at the mill	Mixed with ash (used for roadwork or disposed of in lined ash pond)	Yes*
NA	1	BB	AZ	NA	Separated at the mill	Disposed of in an unlined construction debris landfill (on-site)	Yes
R-1	2	CC	CO	NA	Separated at the mill	Mixed with ash and disposed of in an unlined landfill on mine property	Yes
NA	2	DD	CO	None generated	Burned with coal	Not needed	None*
R-4	3	EE-Unit #1	FL	70-100 lbs/day	Vacuumed (mixed with water)	Mixed with ash and disposed of in ash pond	Yes*
R-15	4	F	GA	NA	Manually removed (mixed with water)	Wet sluiced to ash pond	Yes
R-17	4	G - Units #1&2	GA	NA	Collected in holding hopper (mixed with water)	Wet sluiced to ash pond	Yes
R-16	4	G - Units #3&4	GA	NA	Collected in holding hopper (mixed with water)	Wet sluiced to ash pond	Yes
NA	5	H - Unit #3	IL	NA	Separated at the mill	Mixed with water and bottom ash and disposed of in ash landfill	Yes*
NA	5	H - Units #1 and 2	IL	NA	Collected at the mill	Mixed with bottom ash and wet sluiced to ash pond	Yes*
NA	5	HA	IL	NA	Collected at the hopper (mixed with water)	Mixed with bottom ash and wet sluiced to ash pond (comanaged with fly ash)	Yes*
NA	6	HN - Units #1 & 2	IL	0.8 tons/day	Separated at the mill	Dewatered rejects stockpiled at station	No*
NA	6	J - Unit #3	MD	100 tons/yr	Separated at the mill (sluiced to hydrobin)	Dewatered rejects stockpiled at station	No*
NA	6	J - Unit #4	MD	200 tons/yr	Separated at the mill (sluiced to hydrobin)	Dewatered rejects stockpiled at station	No*
R-12	7	K	MO	3 to 6 tons/day/plant	Collected at the hopper (mixed with water)	Pumped into bottom ash pond	Yes*
R-19	7	M	MO	NA	Collected at the hopper (mixed with water)	Pumped into on-site ash pond (both bottom and fly ash in pond)	Yes
R-18	7	N	MO	NA	Collected at the hopper (mixed with water)	Pumped into on-site ash pond (both bottom and fly ash in pond)	Yes
NA	8	P	NC	NA			Yes
NA	9	G - Units #1&2	NM	NA	Conveyed to bottom ash hopper	Mixed with ash and disposed of in unlined landfills	Yes
NA	9	G - Units #3&4	NM	NA	Conveyed to bottom ash hopper	Mixed with ash and disposed of in unlined landfills	Yes
NA	19	KK	NV	NA	Not separated (mixed with ash)	Mixed with the ash and disposed of in unlined landfills (on-site)	Yes
NA	10	B	NY	NA	Separated at the mill	Mixed with fly ash and used for strip mine reclamation (some is landfilled)	Yes
NA	10	NN	NY	NA	Separated at the mill	Mixed with bottom ash and disposed of in on-site ash pond	Yes
NA	10	C - Unit #1	NY	NA	Separated at the mill (mixed with water)	Wet sluiced to a dewatering bin then disposed in landfill	No*
NA	11	D	NY	NA	Separated at the mill	Disposed of in ash landfill with layers of fly ash and pyrites/bottom ash	Yes*
R-8, R-9, R-10	12	R - Unit #12	NY	NA	Separated at the mill (mixed with bottom ash)	Processed by a contractor for use as a traction agent at local roadway	Yes
NA	12	A - Units #1,2,3,&4	NY	NA	Separated at the mill	Mixed with bottom ash and disposed of in a landfill (separate from fly ash)	Yes*
NA	13	S - Unit #2	OH	NA	Collected in rejects bin	Disposed of at municipal landfill	No
R-2	14	T - Unit #1	OH	NA	Collected in rejects bin	Disposed of at municipal landfill	No
NA	15	U	OK	25 lbs/wk	Separated in a mill reject hopper	Mixed with bottom ash and sold	Yes
NA	6	V - Units #1&2	PA	None generated	NA	NA	NA
NA	6	W - Units #1,2,&3	PA	2400-3600 tons/yr/plant	Separated at the mill (sluiced to bottom ash hydrobin)	Mixed with bottom ash and used as construction aggregate for the landfill	Yes*
NA	6	I - Unit #33	PA	1000 tons/month	Separated at the mill (sluiced to bottom ash hydrobin)	Stockpiled at FGD disposal site (bottom ash used for landfill construction)	Yes*
R-5	16	BR - Unit #1 & 2	PA	NA	Separated at the mill	Wet sluiced with bottom ash to settling basin	Yes
R-11	17	X	TX	400 lbs/day (20 lbs/mill)	Separated at the mill (mixed with water)	Mixed with fly and bottom ash and wet sluiced into ash pond (clay lined)	Yes*
NA	18	MM	TX	NA	Separated at the mill	Disposed of in a lined landfill (off-site)	No
R-13	18	Y	TX	NA	Separated at the mill	Disposed of in a lined ash pond (on-site)	Yes
R-14	18	Z	TX	NA	Separated at the mill	Disposed of in a lined ash landfill (off-site)	No
NA	20	LL	TX	NA	Separated at the mill	Mixed with the bottom ash and disposed of in a clay lined ash pond	Yes
NA	6	EE - Unit #3	WV	250 tons/month	Conveyed to storage bin, trucked to ash site	Mixed with bottom ash and fly ash and disposed of in ash landfill	Yes*
NA	6	EE - Units #1 & 2	WV	None generated	none	NA	NA
NA	6	FF - Units #1&2	WV	50 tons/month/unit	Separated at the mill (sluiced to hydrobin)	Mixed with bottom ash and fly ash and disposed of in a landfill	Yes*
NA	6	GG - Units #1,2,&3	WV	None generated	none	not needed	NA
NA	6	HH - Units #1&2	WV	None generated	none	not needed	NA
NA	6	II - Unit #5	WV	None generated	none	not needed	NA
NA	6	JJ - Unit #6	WV	100 tons/yr	Separated at the mill (sluiced to ash bin)	Mixed with fly ash and bottom ash and disposed of in a landfill	Yes*
NA	6	JJ - Unit #1	WV	1000 tons/yr	Separated at the mill (transferred to hopper)	Mixed with fly ash in the landfill	Yes*
NA	6	JJ - Unit #2	WV	None generated	none	not needed	NA
NA	16	MO	PA	10,000-20,000 tons/yr	Separated at mill (sluiced to ash pond)	Disposed in part of ash pond	Yes*
NA	21	AP	AZ	Not usually generated	Any mixed with bottom ash & sluiced	If needed- to ash pond	Yes*
NA	22	OO	MD	NA	Separated at mill	Disposed in separate on-site lined landfills	No*
NA	23	L	SC	NA	Separated at mill (sluiced to ash pond)	Disposed of in ash pond	Yes*
NA	24	PP	MN	NA	Separated at mill	Disposed in lined ash landfill	Yes*

NA - Not available or applicable  
\*Monitoring data is collected at these locations.

## **Case Study HA**

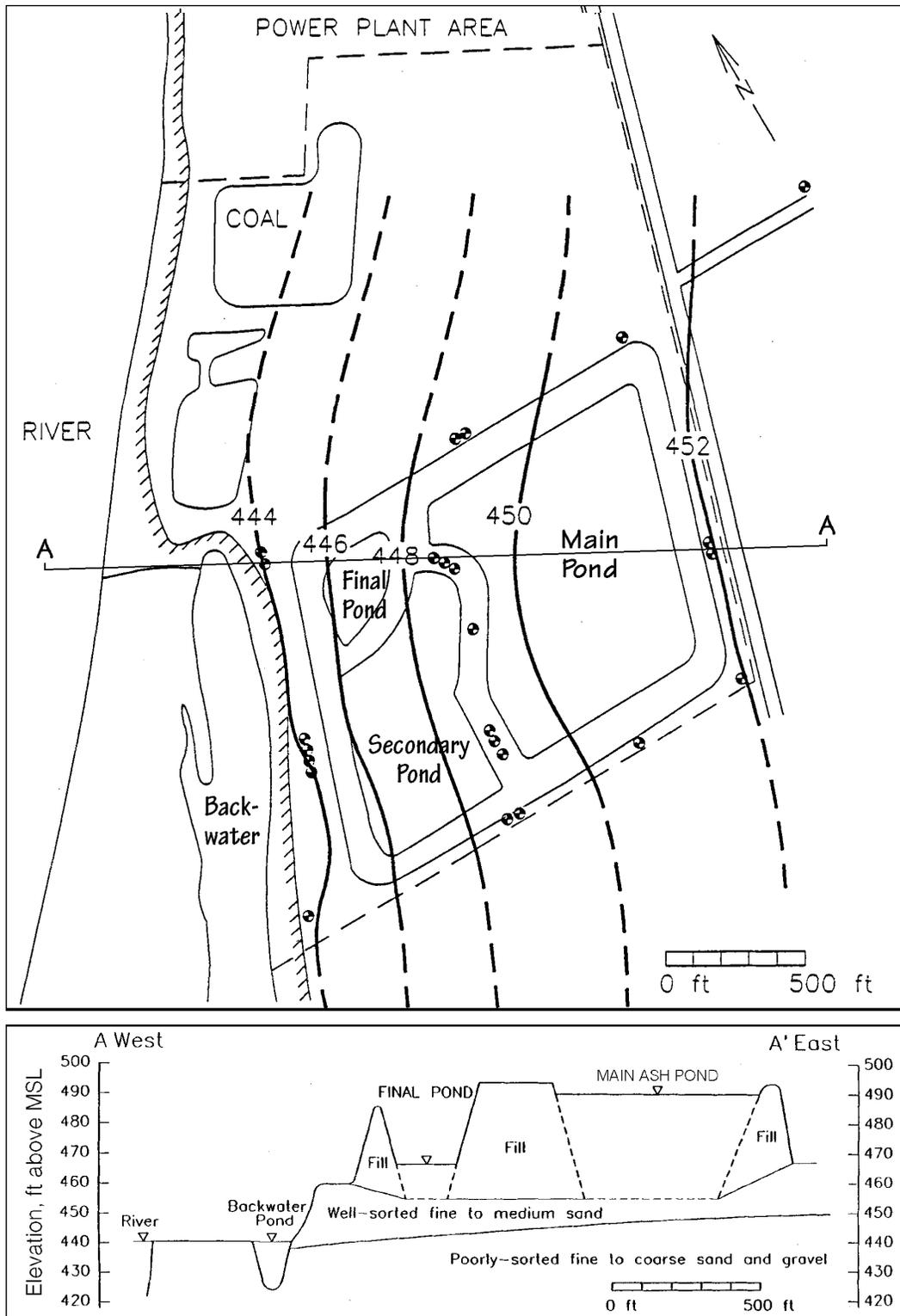
This case study provides an example of comanagement of mill rejects in an alkaline fly ash impoundment that was unlined and is underlain by highly permeable aquifer material. Either no oxidation of pyrites occurred during the operating and postoperating period of 5 years, (groundwater quality has not been impacted by the acidity, iron, sulfate, or other metals characteristic of typical leachates from oxidized pyrites), or the comanaged mill rejects did not contain much pyritic material.

This power plant has one 410-MW coal-fired unit with a Babcock and Wilcox drum type dry bottom boiler. There are also five oil-fired units at the power plant, which are not discussed in this report. HA plant burns low-sulfur bituminous coal from Kentucky and western states. The coal feed rate is about 200 tons/hr. The typical average sulfur content of the coal is 0.7 percent with an average ash content of 8 to 10 percent. The coal is ground using a Combustion Engineering Raymond bowl mill. The mill reject generation rate is not available. The rejects are collected from the hopper with water and then mixed with bottom ash, prior to sluicing. Between 1978 and November 1993, cooling tower blowdown water was used to sluice fly ash and bottom ash combined with mill rejects to the south unlined ash impoundment, located about 1,000 ft east of the nearby river. Additional low-volume wastes and coal pile runoff were also placed in the same pond. After November 1993, ash was sluiced to a new lined pond located east of the power plant.

Originally, a series of three ponds were constructed in 1977 on the river terrace by forming berms of local sandy material to a height of 20 ft; later an additional 10 ft was added to the height of the berms. The river floodplain is about 20 ft below the river terrace. Until November 1993, the ash was sluiced first to the main pond with a surface area of 17.8 acres. Supernatant from this pond was then routed to a secondary pond with a surface area of 8.4 acres, and finally to a polishing pond with a surface area of 2.4 acres. The supernatant from the polishing pond was discharged to the nearby river. The utility closed the south impoundment in November 1993, and dewatered the ponds under natural gradient (i.e., no pumping of pond water), and finally capped the impoundment with local soils in 1994.

The ponds are situated on highly permeable sand and gravel deposits underlain by relatively impermeable limestone and shale bedrock, at a depth of about 64 ft. The general groundwater flow direction is to the west toward the river (Figure 3-1). The estimated seepage velocity of the sand and gravel formation is about 440 ft/yr. in the upper portion of the formation and about 2,000 ft/yr. in the deeper portion of the formation. Average long-term precipitation in the area is about 34.9 in/yr. Recharge to the sand and gravel deposits is estimated to be about 10.3 in/yr.

The ash composition data (Table 3-2) showed that the ash is dominated by the fly ash, as evidenced by its high pH and calcium content. Comparison of the core solid-phase composition with typical ash and mill reject composition (See Table 2-12) showed that the sulfate and iron concentrations in ash samples from the HA site were more representative of coal ash. Trace metal concentrations for arsenic, copper, nickel, and zinc were detected, but were not elevated



**Figure 3-1**  
**Map showing HA ash ponds and groundwater flow direction**  
**(after STMI, 1994)**

**Table 3-2**  
**Bulk Composition of Ash Samples from HA Ash Impoundment**

<b>Sample #</b>		<b>HA-1</b>	<b>HA-10</b>	<b>HA-23</b>	<b>Average</b>
<b>Depth (ft)</b>		<b>7</b>	<b>13</b>	<b>18</b>	
Solids	percent	73	68	54	65
Alkalinity	mg/kg	<100	<100	<100	<100
Aluminum	mg/kg	5300	3700	8000	5700
Arsenic	mg/kg	15	8	6	9.7
Barium	mg/kg	210	140	210	190
Boron	mg/kg	18	12	12	14
Cadmium	mg/kg	<0.50	<0.50	<0.50	<0.50
Calcium	mg/kg	3600	2400	5500	3800
Chromium	mg/kg	12	11	16	13
Copper	mg/kg	40	29	38	36
Iron	mg/kg	2900	4700	4000	3900
Lead	mg/kg	9.6	6.5	10	8.7
Lithium	mg/kg	6.1	4.1	6.8	5.7
Manganese	mg/kg	36	39	170	82
Mercury	mg/kg	<0.13	<0.13	<0.13	<0.13
Molybdenum	mg/kg	<1.0	<1.0	<1.0	<1.0
Nickel	mg/kg	11	10	14	12
Selenium	mg/kg	1.1	<1.0	<0.005	<1.0
Silver	mg/kg	<1.0	<1.0	<1.0	<1.0
Strontium	mg/kg	220	86	96	130
Sulfur	percent	<0.02	<0.02	<0.02	<0.02
Zinc	mg/kg	22	14	21	19
pH (porewater)	Std. Units	9.1	9.1	8	8.7

Data are from STMI, 1994.

above typical coal ash levels. Cadmium, mercury, molybdenum, and silver were below the detection limit in the cores from the impoundment. Four ash cores, one of which contained mill rejects, were collected from the main pond after it was dewatered. The porewater chemical analyses for the sample with mill rejects showed that most of the chemicals, including sulfate, arsenic, copper, nickel, and zinc, were similar to the observed range for the ash leachates. No evidence of pyrite oxidation was observed in the core with mill rejects.

The porewater and pondwater composition data (Table 3-3) showed relatively low sulfate concentrations in the porewater and pondwater (200 mg/l and 195 mg/l, respectively) and moderate calcium concentrations (99 mg/l and 80 mg/l, respectively). The sulfate and calcium concentrations in the porewater and pondwater are due to the rapid dissolution during sluicing of the more soluble components of the ash (EPRI, 1994). Low sulfate and low iron concentrations such as occur at this site indicate that any pyrites present in the mill rejects have not been oxidized. Manganese was also low (<0.1 mg/l). Trace metals were low in the porewater. For example cadmium, chromium, copper, lead, mercury, selenium, and silver were all below the detection limit.

Groundwater monitoring was performed by the utility using a network of 14 wells. Both preclosure and postclosure data are available through 1998. The groundwater around the main ash impoundment prior to closure in 1993 had elevated sulfate and boron concentrations relative to those in upgradient wells (Figure 3-2). Groundwater quality monitoring results for boron, pH, and sulfate from a selected number of monitoring wells for 1993 to 1998 are summarized in Table 3-4. Following the dewatering of the basin, the sulfate and boron concentrations in the downgradient wells decreased. Boron and sulfate concentrations are now similar to background concentrations (see Table 3-4).

These groundwater monitoring data indicate that either pyrites have not oxidized or the comanaged mill rejects did not contain much pyritic material. During the period of the pond operation, the mill rejects were mixed with bottom ash prior to sluicing and were kept submerged under water, minimizing the potential for oxidation of the pyrite.

## **Case Study HN**

This case study provides another example of comanagement of mill rejects in a neutral to alkaline fly ash pond, which was unlined and is situated on top of a highly permeable aquifer material. Either oxidation of pyrites has not occurred at this site during the operating years and post-operating period of 2 years, or the comanaged mill rejects did not contain much pyritic material.

This power plant has two coal-fired units with tangential-fired Combustion Engineering boilers. Unit 1 (70 MW) was constructed in 1953, and Unit 2 (210 MW) was constructed in 1959. The coal burned is high-sulfur coal from Illinois. The coal feed rate is about 420 tons/hr. The average sulfur content is 2.9 percent. The coal source has changed several times, most recently in 1985. The coal is ground using a Combustion Engineering Raymond bowl mill. Mill rejects are generated at a rate of about 1,600 lbs/day. Mill rejects are collected and then mixed with

**Table 3-3**  
**Pond Water and Ash Porewater Composition at the HA Site Ash Impoundment**

Parameter	Pond Water Concentration <sup>1</sup> mg/l	Porewater Concentration <sup>2</sup> mg/l
Alkalinity (total as CaCO <sub>3</sub> )	230	62
Aluminum	NA	0.65
Arsenic	NA	0.18
Barium	NA	0.11
Boron	1.5	1.7
Cadmium	NA	<0.005
Calcium	99	80
Chloride	41	58
Chromium	NA	<0.01
Copper	NA	<0.05
Hardness (total as CaCO <sub>3</sub> )	420	220
Iron	<0.05	<0.05
Lead	NA	<0.05
Lithium	NA	0.12
Magnesium	35	<10
Manganese	<0.1	<0.1
Mercury	NA	<0.0005
Molybdenum	NA	0.075
Potassium	10	11
Selenium	NA	<0.005
Silver	NA	<0.01
Sodium	30	53
Strontium	NA	2.1
Sulfate	195	200
Total Dissolved Solids	573	460

<sup>1</sup> Average of four samples from STMI, 1994.

<sup>2</sup> From sample collected in drive point piezometer.

NA = Not Analyzed.

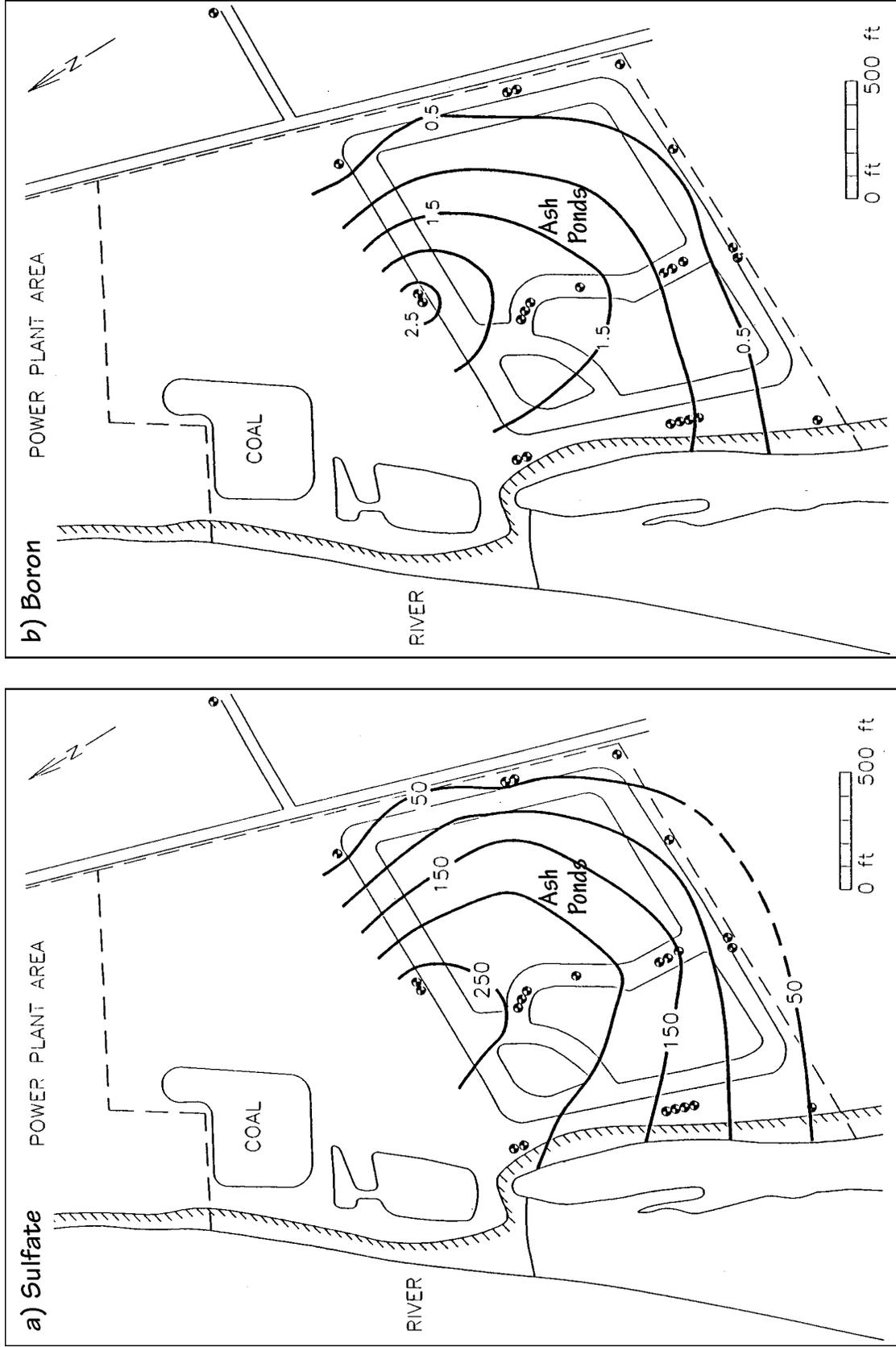


Figure 3-2  
Groundwater concentrations in June 1993 at HA site for a) sulfate and b) boron

**Table 3-4**  
**Median Annual Concentrations at HA South Ash Impoundment**

Well	Position	Description	Depth (ft)	Analyte	Median Concentrations					
					1993	1994	1995	1996	1997	1998
01	Upgradient	East end of impoundment	24	Boron	<0.2	<0.2	0.16	0.12	0.06	0.07
04	Downgradient	West end	27.7	Boron	0.84	0.21	0.17	0.11	<0.05	0.067
05	Downgradient	West end	37.3	Boron	0.85	0.24	0.135	0.01	<0.05	0.05
10	Upgradient	East end of impoundment	33.7	Boron	<0.2	<0.02	na	na	0.06	na
14	Downgradient	West end	22.5	Boron	1.1	1.3	0.645	0.30	0.12	0.13
15	Downgradient	West end	64	Boron	0.21	<0.2	0.11	0.21	0.015	<0.05
17	Downgradient	Northwest corner	22.5	Boron	1.1	1.35	1.5	1.20	1.1	0.8
18	Downgradient	Northwest corner	37	Boron	1.3	0.94	0.57	0.28	0.115	0.075
21	Intermediate	On berm, south	53.2	Boron	1.1	1.4	na	na	na	na
22	Intermediate	On berm, south	74	Boron	0.3	<0.2	na	na	<0.05	na
24	Intermediate	On berm, north	54	Boron	1.6	3.15	1.9	0.99	na	0.365
25	Intermediate	On berm, north	75	Boron	0.64	0.245	0.155	0.12	0.06	<0.05
01	Upgradient	East end of impoundment	24	pH, field	7.30	7.52	7.59	7.22	7.49	7.39
04	Downgradient	West end	27.7	pH, field	7.11	7.32	7.65	7.22	7.43	7.48
05	Downgradient	West end	37.3	pH, field	7.12	7.35	7.71	7.33	7.37	7.21
10	Upgradient	East end of impoundment	33.7	pH, field	7.52	7.55	na	na	7.58	na
14	Downgradient	West end	22.5	pH, field	7.35	7.39	7.57	7.17	7.28	7.22
15	Downgradient	West end	84	pH, field	7.25	7.35	7.61	7.38	7.46	7.20
17	Downgradient	Northwest Corner	22.6	pH, field	7.31	7.30	7.78	6.94	7.26	7.43
18	Downgradient	Northwest corner	37	pH, field	7.47	7.48	7.83	7.42	7.59	7.45
21	Intermediate	On berm, south	53.2	pH, field	7.14	7.18	na	na	na	na
22	Intermediate	On berm, south	74	pH, field	7.33	7.52	na	na	na	na
24	Intermediate	On berm, north	54	pH, field	7.79	7.54	7.86	7.08	na	7.29
25	Intermediate	On berm, north	75	pH, field	7.5	7.51	7.77	7.24	7.03	7.46
01	Upgradient	East end of impoundment	24	Sulfate	20	18	19.5	16	14	16
04	Downgradient	West end	27.7	Sulfate	78	63	53.5	58.5	55	54
05	Downgradient	West end	37.3	Sulfate	89	66	50	65	56.5	61
10	Upgradient	East end of impoundment	33.7	Sulfate	23	22	na	na	25	na
14	Downgradient	West end	22.5	Sulfate	170	130	53	26	36	62
15	Downgradient	West end	64	Sulfate	82	58	53.5	53	68.5	36
17	Downgradient	Northwest corner	22.5	Sulfate	150	165	215	77	54	67
18	Downgradient	Northwest corner	37	Sulfate	190	69	91.5	69.50	57.5	62
21	Intermediate	On berm, south	53.2	Sulfate	150	110	na	na	na	na
22	Intermediate	On berm, south	74	Sulfate	74	53	na	na	na	na
24	Intermediate	On berm, north	54	Sulfate	210	130	43	44	na	25.5
25	Intermediate	On berm, north	75	Sulfate	57	63	53.5	54.5	57	55

Units are mg/l except pH.

na indicates not analyzed

Impoundment removed from service in November 1993.

bottom ash prior to sluicing to an ash impoundment, along with fly ash. The ponds are located close to the nearby river. Other low-volume wastes were also comanaged in these ponds, including plant floor drains, sump discharges, and cleaning/treatment wastes from the plant. The low-volume discharges comprised less than 10 percent of the total discharge to the impoundments.

The east impoundment (Pond 2) was built in 1958 by constructing elevated berms of local sandy soils. This unlined impoundment (Figure 3-3) was used for ash from Unit 2 until January 1997 when a new lined pond south of Pond 2 went into operation. During operation, the sluiced volume was 2 million gal/day. There was no overflow discharge from the pond to the river. Pond 4 was a former gravel quarry excavated in the early 1980s. This pond was used for ash disposal in the mid-1980s.

The ponds are located on a sand and gravel terrace above the river. Near the river, alluvial formations occur consisting of silts and clays. These deposits are up to 130 ft thick on the upper terrace. The formation is highly permeable, with a hydraulic conductivity of about 0.01 cm/s to 0.1 cm/s. Because of the steep gradient from the pond, the groundwater seepage velocities are high, between 100 and 1,000 ft/yr. The flow direction at the time of the 1993 monitoring was toward the river, except that a mounded flow system existed beneath the pond (Figure 3-3). The pond dewatering under natural gradient (no pumping) began in December 1996, and dewatering was completed within six months. There is no cap placed on the ash because the ash is now being mined.

Groundwater monitoring was carried out by the utility both before closure in 1996 and subsequent to the closure in 1997 and 1998. Groundwater samples from sixteen wells were analyzed for alkalinity, total dissolved solids, boron, calcium, chloride, iron, magnesium, manganese, potassium, sodium, and sulfate beginning in November 1994. A comparison of up-gradient and downgradient concentrations showed that boron, chloride, sodium, sulfate, and total dissolved solids levels were elevated in the downgradient wells (Table 3-5) before the closure of the pond. Additional monitoring data for 1997 and 1998 are also summarized in this table. Only boron and sulfate in some wells exceeded the state standards of 2 mg/l and 400 mg/l, respectively (Figure 3-4). Both iron and sulfate concentrations are low, indicating that leaching is dominated by dissolution of ash and that pyrite oxidation is not occurring. No effects from the disposal of mill rejects were identified. At this site, the mill rejects were sluiced and submerged until closure, which minimized the potential for oxidation.

## **Case Study L**

This case study provides an example of comanagement where pyrites in the ash pond have undergone some oxidation resulting in the generation of acid leachates with elevated levels of iron, sulfate, manganese, and nickel. The downgradient groundwater had higher sulfate than the upgradient wells, although less than 250 mg/l. However, iron and manganese, concentrations were elevated to a lesser extent with nickel showing no increase in downgradient groundwater (Table 3-6).

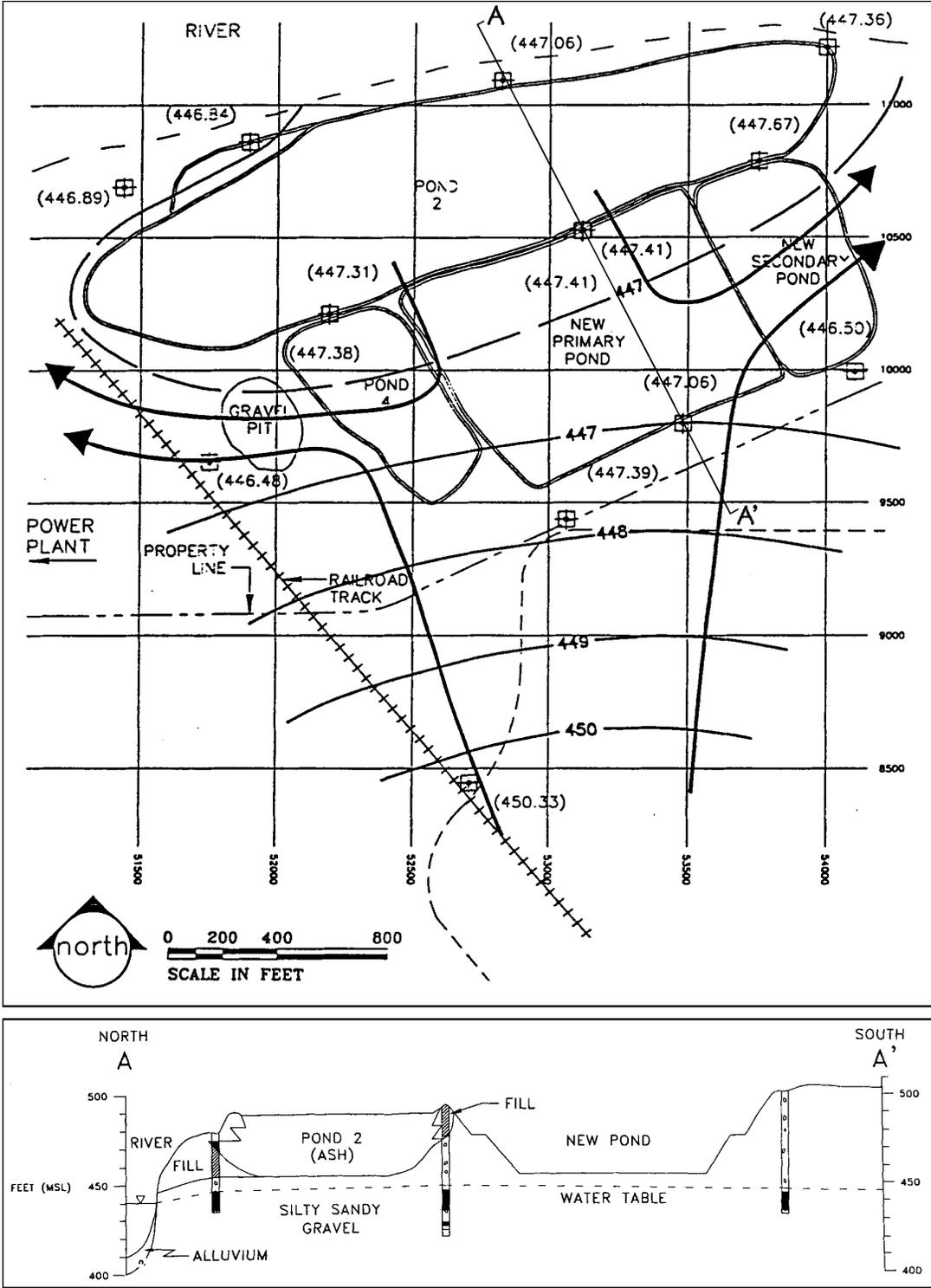


Figure 3-3  
Map showing HN ash ponds and groundwater (after STMI, 1996)

**Table 3-5**  
**Median Annual Concentrations at HN East Ash Impoundment**

Well	Position	Description	Depth (ft)	Analyte	Median Concentration				
					1994	1995	1996	1997	1998
3	downgradient	west-center	53.2	Boron	11	11	13	12	9
4	downgradient	east	45.8	Boron	12	14	16	13	11.5
5	downgradient	east-center	48.9	Boron	10	11	12	11.5	12
6	downgradient	west	38.7	Boron	5.6	7.85	8.4	4.85	1.5
7	upgradient	south	77.5	Boron	0.22	0.175	0.14	0.05	0.06
10	intermediate	west	58.8	Boron	ns	5.7	13	4.75	0.735
11	intermediate	west	68.2	Boron	ns	11	13.5	1.1	1.225
12	intermediate	center	59.5	Boron	ns	17.5	15	5.25	4.85
13	intermediate	center	69.0	Boron	ns	12.5	15	7.7	6.35
15	intermediate	east	60.7	Boron	ns	17	13	1.8	1.555
3	downgradient	west-center	53.2	Iron	ns	<0.05	<0.05	<0.025	<0.025
4	downgradient	east	45.8	Iron	ns	<0.05	<0.05	<0.025	<0.025
5	downgradient	east-center	48.9	Iron	ns	<0.05	<0.0375	<0.025	<0.025
6	downgradient	west	38.7	Iron	ns	<0.05	<0.05	<0.025	<0.025
7	upgradient	south	77.5	Iron	ns	<0.05	<0.05	<0.025	<0.025
10	intermediate	west	58.8	Iron	ns	<0.05	<0.05	<0.025	<0.025
11	intermediate	west	68.22	Iron	ns	<0.05	<0.05	0.0245	<0.025
12	intermediate	center	59.45	Iron	ns	<0.05	<0.05	<0.025	<0.025
13	intermediate	center	69	Iron	ns	<0.05	<0.05	<0.025	<0.025
15	intermediate	east	60.65	Iron	ns	<0.05	<0.05	<0.025	<0.025
3	downgradient	west-center	53.2	pH	7.99	8.52	9.01	9.2	8.52
4	downgradient	east	45.8	pH	7.36	8.94	9.3	9.38	9.405
5	downgradient	east-center	48.9	pH	8.57	8.815	8.8	8.78	8.765
6	downgradient	west	38.7	pH	7.93	8.045	7.56	7.41	7.105
7	upgradient	south	77.5	pH	7.7	7.95	7.4	7.33	7.265
10	intermediate	west	58.8	pH	ns	8.36	8.09	7.1	6.975
11	intermediate	west	68.22	pH	ns	8.56	8.4	6.73	7.12
12	intermediate	center	59.45	pH	ns	9.6	9.2	8.36	7.685
13	intermediate	center	69	pH	ns	9.68	9.61	9.34	8.06
15	intermediate	east	60.65	pH	ns	9.61	9.22	7.86	7.8
3	downgradient	west-center	53.2	Sulfate	300	370	380	200	170
4	downgradient	east	45.8	Sulfate	360	350	440	315	150
5	downgradient	east-center	48.9	Sulfate	370	355	360	400	335
6	downgradient	west	38.7	Sulfate	220	315	340	200	145
7	upgradient	south	77.5	Sulfate	64	68	67	79	81.5
10	intermediate	west	58.8	Sulfate	ns	230	310	205	145
11	intermediate	west	68.22	Sulfate	ns	320	360	155	115
12	intermediate	center	59.45	Sulfate	ns	360	340	130	155
13	intermediate	center	69	Sulfate	ns	345	340	175	170
15	intermediate	east	60.65	Sulfate	ns	350	330	90	103

ns indicates no sample  
units are mg/l except pH

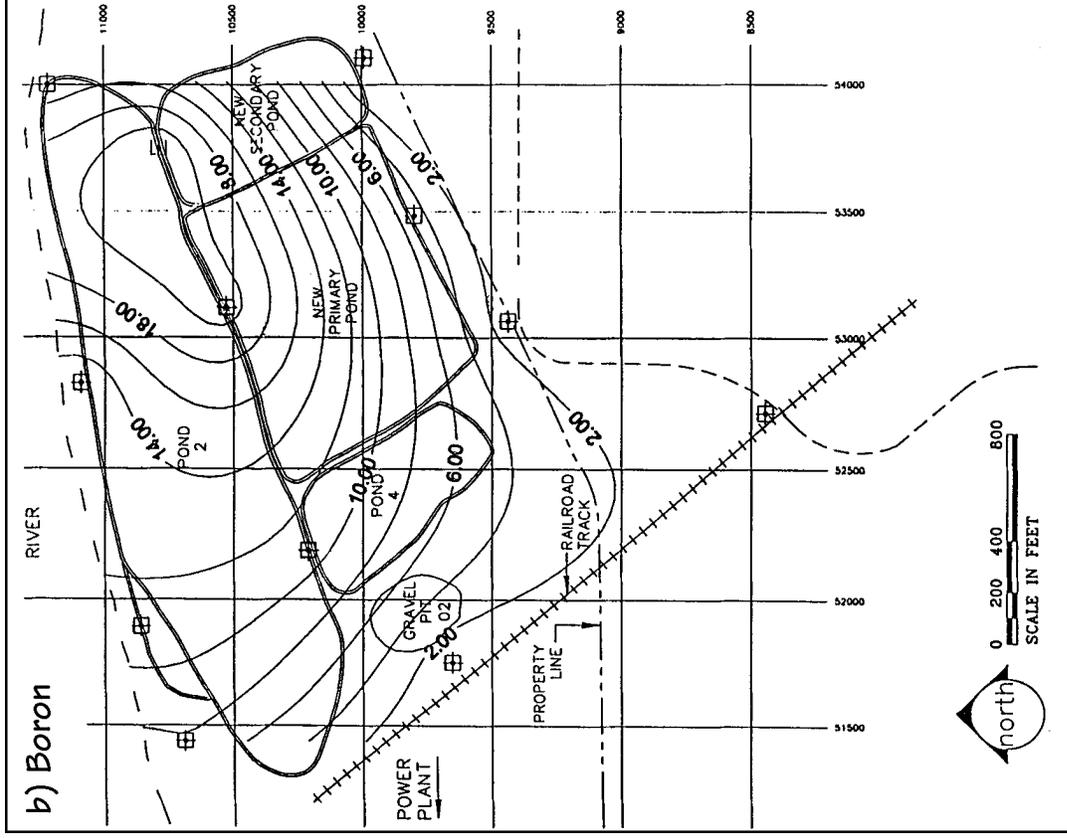
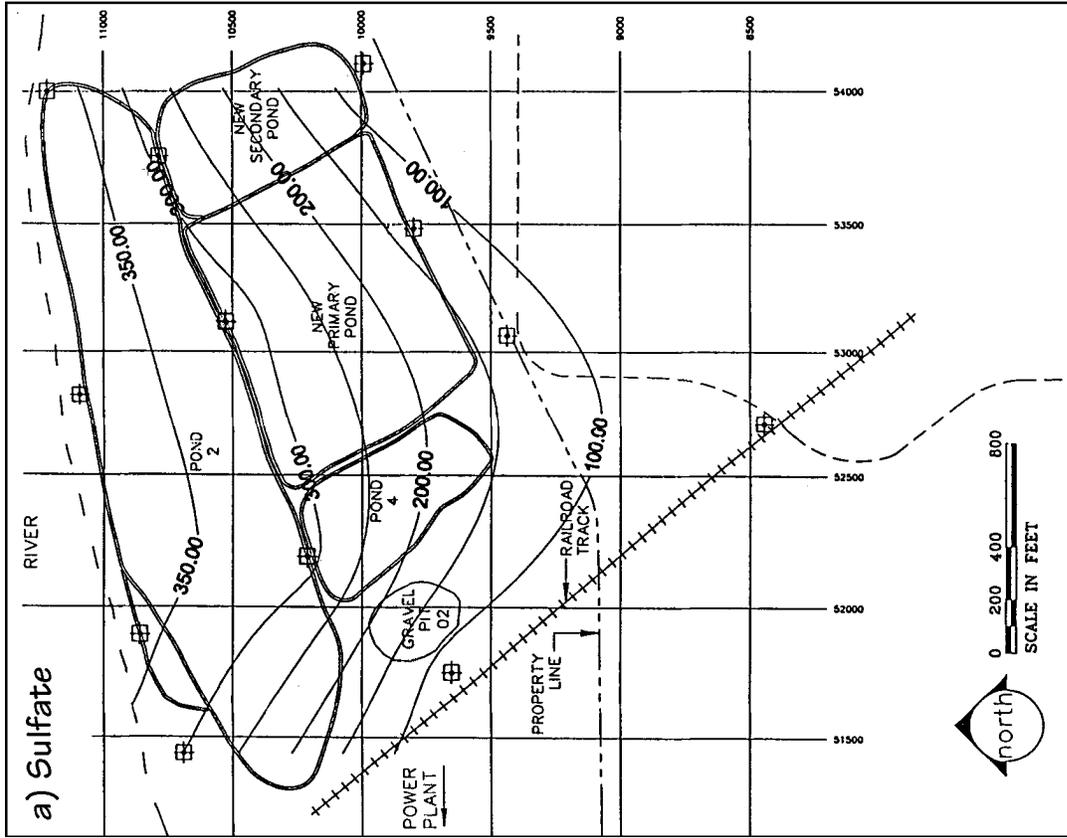


Figure 3-4  
Groundwater concentrations in November 1995 at HN Site for a) sulfate and b) boron

**Table 3-6  
Groundwater Composition Data from Site L**

	<b>Background Wells</b>	<b>Ash Wells</b>	<b>Downgradient Wells</b>
pH	5.25 - 6.29	4.01 - 4.17	4.75 - 7.2
Ca	3.6 - 8.8	408.4 - 400.8	0.80 - 72.1
Mg	1.7 - 3.2	18.2 - 60.3	5.8 - 18.2
SO <sub>4</sub>	1.4 - 11.0	1110 - 1630	45 - 71
Sr	0.023 - 0.12	0.56 - 0.58	0.012 - 0.31
Fe	<0.04 - 0.14	120 - 250	<0.04 - 11.0
Mn	0.07 - 0.23	7 - 90	0.024 - 6.2
As	<0.005	<0.005	<0.005
Ni	<0.02	0.027 - 0.66	<0.02
Pb	<0.05	<0.05	<0.05
Zn	<0.02 - 0.039	0.12 - 0.66	<0.02 - 0.2

Units are mg/l, except for pH.

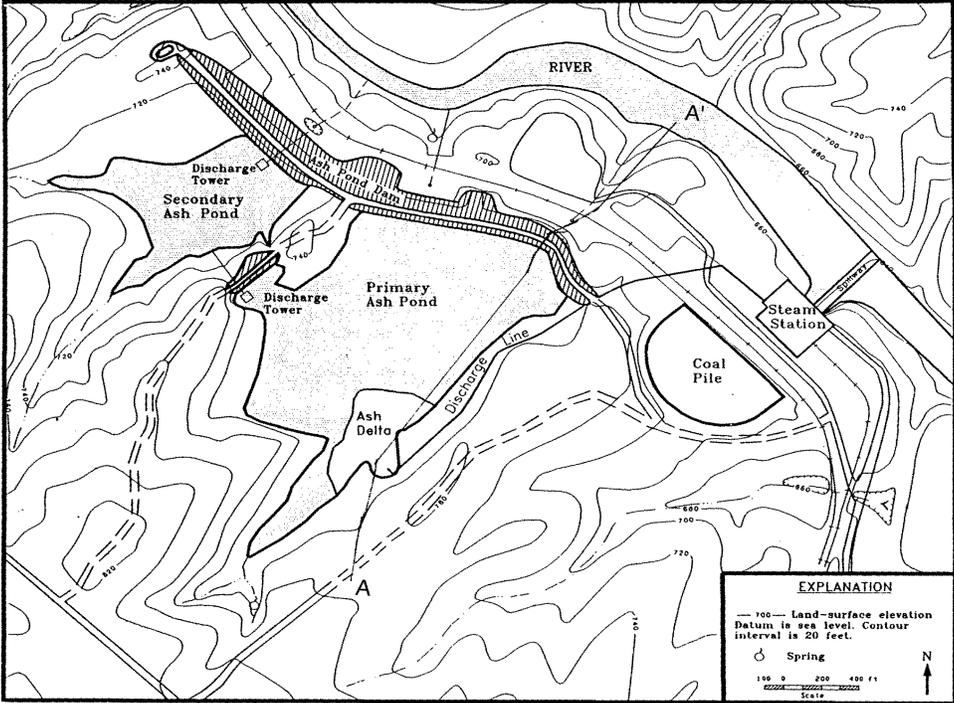
Data are from EPRI Report EN-7545 (1991).

This site is a 400-MW coal-fired power plant located in the southeast (EPRI, 1991). Fly ash and bottom ash were sluiced to two unlined impoundments built in 1973. The total surface area of the impoundments is 60 acres. In addition to ash, mill rejects, demineralizer regenerant, and boiler cleaning wastes were discharged to the impoundments. The mill rejects consist of coal, shale, and pyrites, and were generated at an estimated rate of 37 tons/yr, compared to about 1.09 million tons/yr of coal ash (EPRI, 1991).

The impoundments are located in an area with alluvium, saprolite, and weathered bedrock, underlain by low-grade to moderate metamorphic rocks. The impoundments were formed by building a dam across a bedrock valley (Figure 3-5). The general groundwater flow is toward a large river at the base of the impoundments (Figure 3-6). The seepage velocity ranges from 36.5 ft/yr to 14,600 ft/yr with an average of about 328 ft/yr.

Porewater in cores taken from within the ash delta showed elevated iron and sulfate, i.e., 1,150 to 1,280 mg/l sulfate and 70 to 180 mg/l ferrous iron. The ash porewater showed alkaline pH. The porewater in a core sample from the soil directly beneath the ash also had elevated iron and sulfate at 318 mg/l and 1,190 mg/l, respectively. The pH was acidic (3.9), which may be due to the exchange of Fe(II) ions for H<sup>+</sup> ions in the saprolite. The pH of the upgradient soil was also relatively low (5.9). However, porewater in the deeper soil cores had no measurable Fe(II) and had low sulfate concentrations (25 mg/l).

a) Areal View



b) Geologic Cross-Section

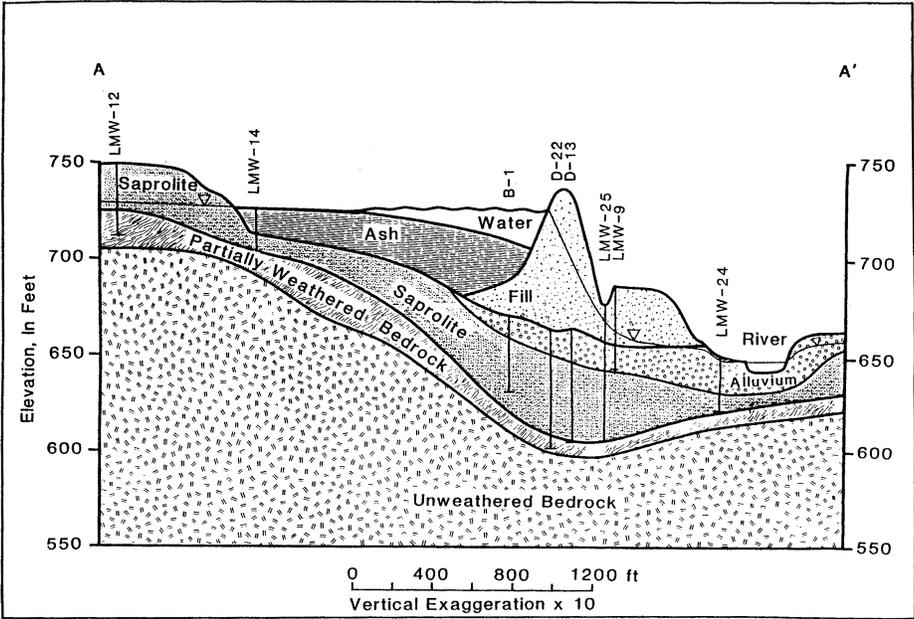


Figure 3-5  
Setting of ash impoundment at Site L (EPRI, 1991).

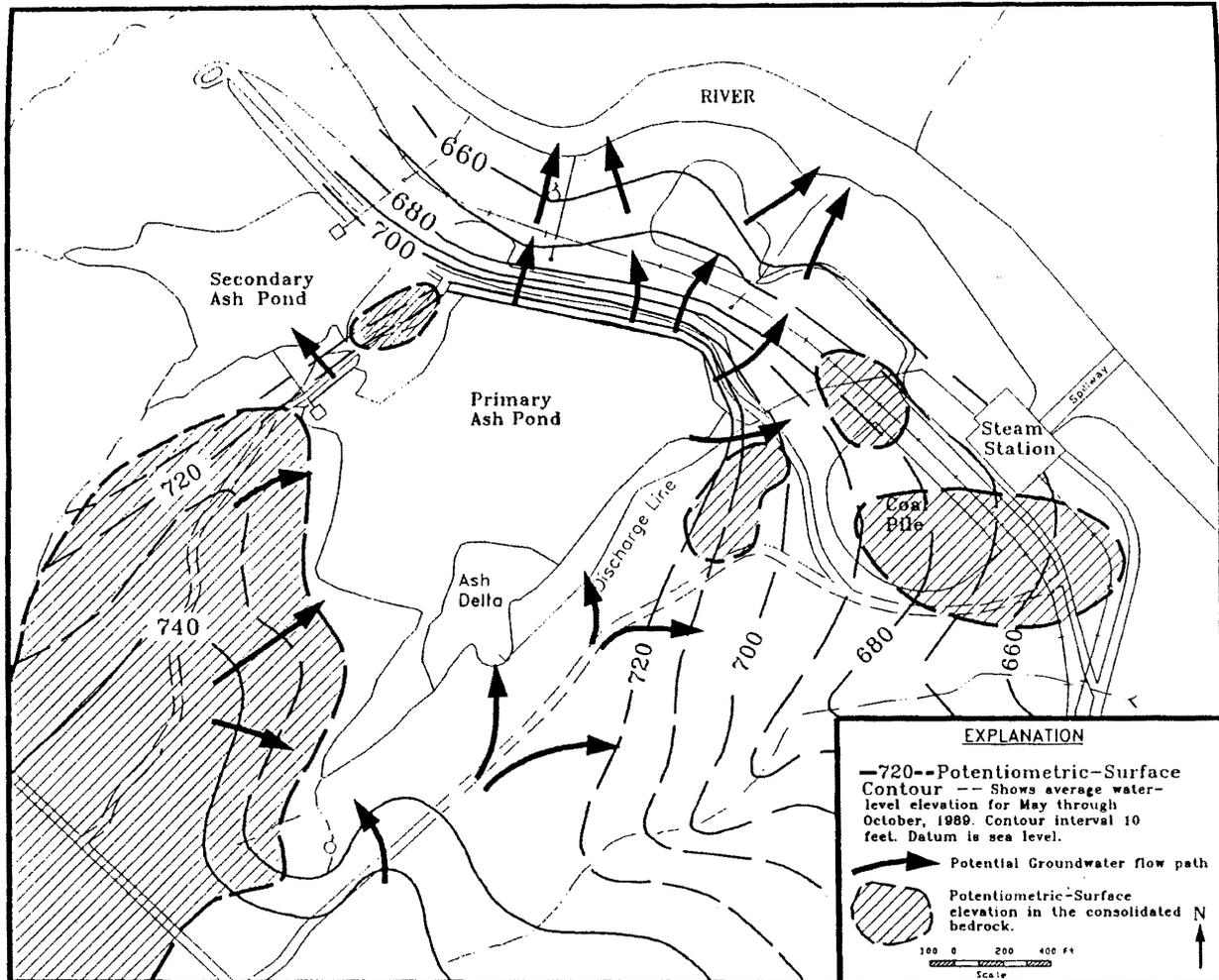


Figure 3-6  
Potential groundwater flow paths at the L-Site

Twenty-four wells were installed and sampled in 1988 and 1989. Comparison of upgradient and downgradient wells showed elevated calcium, sulfate, magnesium, and strontium. For example, in the background wells sulfate concentrations were 1.4 to 11 mg/l, while the sulfate concentration in the downgradient wells was 45 to 171 mg/l. Both upgradient and downgradient sulfate concentrations were below the EPA secondary standard for drinking water of 250 mg/l. The pH was 5.2 to 8.3 in the background wells, compared to 4.1 to 8.4 in the downgradient wells. Two wells screened in the ash pond had elevated sulfate (1,110 to 2,060 mg/l), iron (110 to 280 mg/l), manganese (7 to 120 mg/l), and nickel (0.027 to 0.66 mg/l), and low pH (4.0 to 4.4) (Table 3-6). The elevated iron and manganese concentrations within the ash pond were attributed to the oxidation of pyrites in the mill rejects (EPRI, 1991). Periodic exposure of mill rejects could have occurred in the ash deltas. Sulfate, iron and manganese concentrations in the downgradient wells, however, were much lower than the ash pond wells, as seen in Table 3-5, but were higher than the background wells. Trace elements including antimony, arsenic, boron, cadmium, copper, lead, selenium, silver, thallium, and vanadium were below the detection limit in all groundwater monitoring wells (EPRI, 1991).

## **Case Study BR**

This case study provides an example of comanagement of mill rejects containing pyrites with coal ash in several basins (Figure 3-1). Some of these basins have been closed for periods ranging from 7 to 20 years as of 1992. Field investigations identified the existence of acidic leachates containing higher levels of solubilized constituents in the unsaturated zone in Basins 1 and 3. However, the deeper saturated zone showed near neutral pH and relatively low concentrations of most trace metals. The low pH of the porewater in Basin 3 combined with high concentrations of iron and sulfate in the unsaturated comanaged materials indicate that pyrite oxidation has been occurring in this zone. In contrast, the saturated zone porewater chemistry in Basin 3 indicates that pyrite oxidation is currently not occurring in this deeper, relatively anoxic and high  $\text{Fe}^{2+}$  containing zone. Pyrite oxidation may have occurred during the operating years when pyrites were exposed to air during placement of ash and mill rejects in the basins. A physical barrier in the form of a slurry wall around Basin 3 was constructed to control the lateral migration of the acidic leachate. A low permeability cap was installed to reduce infiltration and diffusion of oxygen to minimize further oxidation of pyrites in the shallow zone.

This site is located in eastern Pennsylvania on a flat area along a large river. Two small creeks separate the "island part" from the mainland. The power plant was built between 1958 and 1961. It currently has three pulverized coal units with a combined peak capacity of 1,500 MW. The plant burns bituminous coal from western Pennsylvania with a heating value of 12,500 Btu/lb, total sulfur of 1.7 percent, and 8.5 percent ash. Two of the units are fitted with electrostatic precipitators, while the other unit has a mechanical fabric filter for the collection of particulate matter from the flue gas and to control emissions to the atmosphere. Annual production of ash is about 400,000 tons. Fly ash is mixed with water and sluiced to impoundments. Mill rejects and bottom ash are retrieved from the hoppers and also sluiced to impoundments. A series of seven impoundments, shown in Figure 3-7, have been used since the plant began operation. Once filled, the ponds are retired. As of 1992, Basins 1, 2, 3 and 5 have been retired.

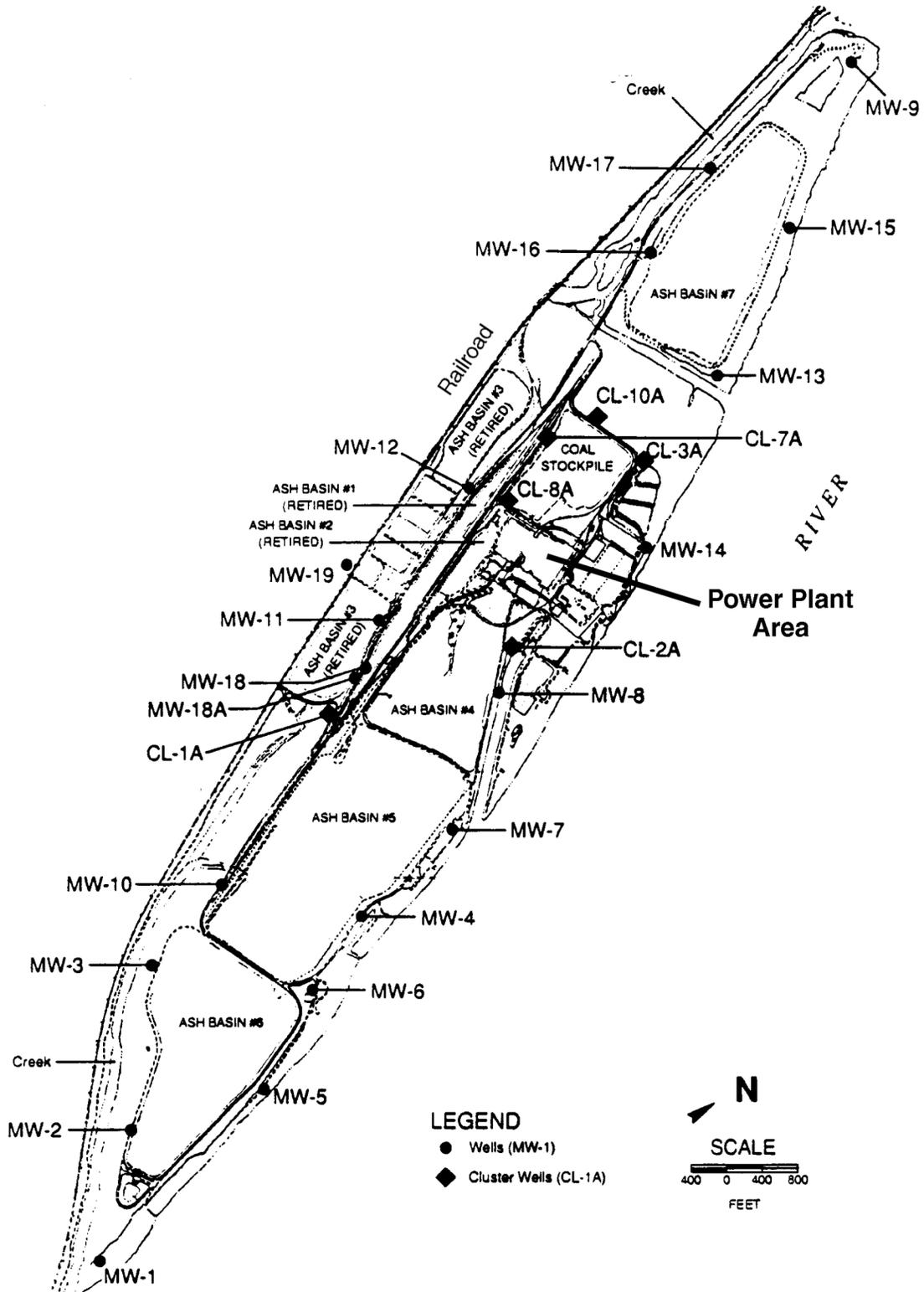


Figure 3-7  
Map of BR site showing ash basins and monitoring wells

The natural geologic formations at the site are 20 to 40 ft of alluvium consisting of silty sands in the shallower depths and sands and gravels at deeper depths near the bedrock interface (Figure 3-8). A thin layer of unconsolidated alluvium and weathered, fractured bedrock underlies the impoundments. The bedrock is primarily sandstones and shales of Triassic age. The shallow alluvium and weathered bedrock system is considered one unconfined aquifer; it is not used for drinking water on the island.

Collaboration between the utility company and EPRI led to a geochemical investigation of pyrite comanagement with sluiced fly ash in the three older basins (Basins 1, 2, and 3). The objectives of this work were to conduct field and laboratory studies to investigate the sources of acidity in these basins, identify possible remediation options, and conduct groundwater modeling to predict effectiveness of the possible remediation options. The field investigation included drilling and sampling of 14 exploratory borings, later completed with piezometers; drilling and sampling of four cores for analysis of solid-phase and porewater concentrations, later completed as monitoring wells; and sampling of existing wells and surface waters around the basins. The location of these borings/wells and a typical cross-section through the largest basin (Basin 3) is shown in Figure 3-9. Methods used for the field and laboratory procedures are described in a separate report (EPRI, 1995).

Ash in Basin 1 varied from about 15 to 25 ft deep. Basin 3 had up to 30 ft of ash. Mill rejects were found to be dispersed in layers throughout Basins 1 and 3, rather than segregated. Basins 1 and 3 had low pH in the unsaturated zone in the upper 10 ft. Basin 2 wastes were generally of higher pH (see Figure 3-10) and were mostly ash and reconstruction soils. The pH values of the porewaters in Basins 1 and 3, generally increased and the redox potential decreased with depth. The sulfate, iron, and calcium concentrations were high in porewaters in the saturated zone (below 9 feet depth) of Basin 3, compared to the unsaturated zone (Table 3-7). The porewaters from Basin 3 showed increasing iron and sulfate concentrations in the upper section of the saturated zone where the redox conditions changed from oxidizing to reducing (Figure 3-11). The iron in the porewaters was mostly  $\text{Fe}^{2+}$ . Copper, nickel, and zinc, were present in the acidic porewaters in the unsaturated zone (above 9 ft, Figure 3-12) but were at detection limits in the near neutral porewater in the saturated zone. There were a few exceptions where Ni and Zn were found at almost 1 mg/l level in near neutral conditions. Arsenic concentrations varied from 0.03 mg/l to 2.2 mg/l with higher concentrations observed in porewaters under reducing conditions in the deeper saturated zone. The concentrations of these metals and iron decreased in the weathered bedrock below the ash. In fact, arsenic, chromium, copper, molybdenum, nickel, and zinc were below detection in the deep saturated zone within the weathered bedrock. The higher sulfate and iron concentrations observed in the porewaters in the saturated zone in Basin 3 have been attributed to the oxidation of pyrite in the past when the mill rejects now in the deeper saturated layer were exposed to an oxygen-rich environment. The acidity generated was neutralized by the calcium and magnesium minerals present in the ashes and/or from interaction with the alumino-silicate minerals in the ash.

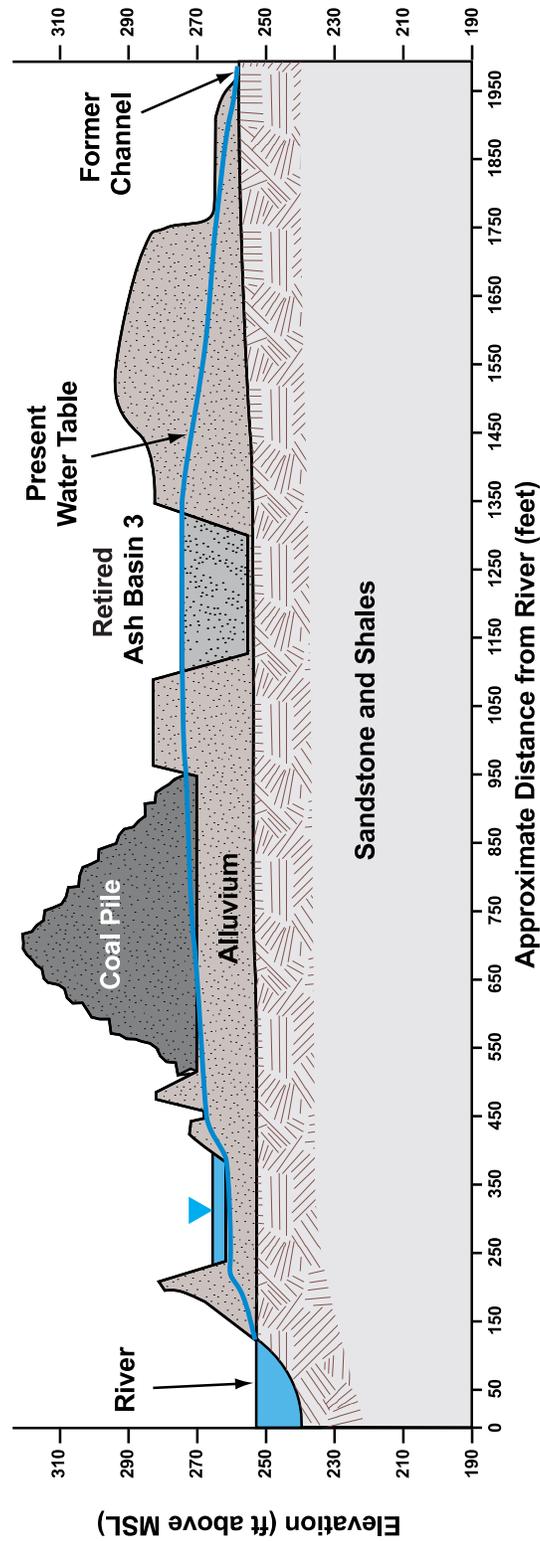


Figure 3-8  
Generalized geologic cross-section at BR site

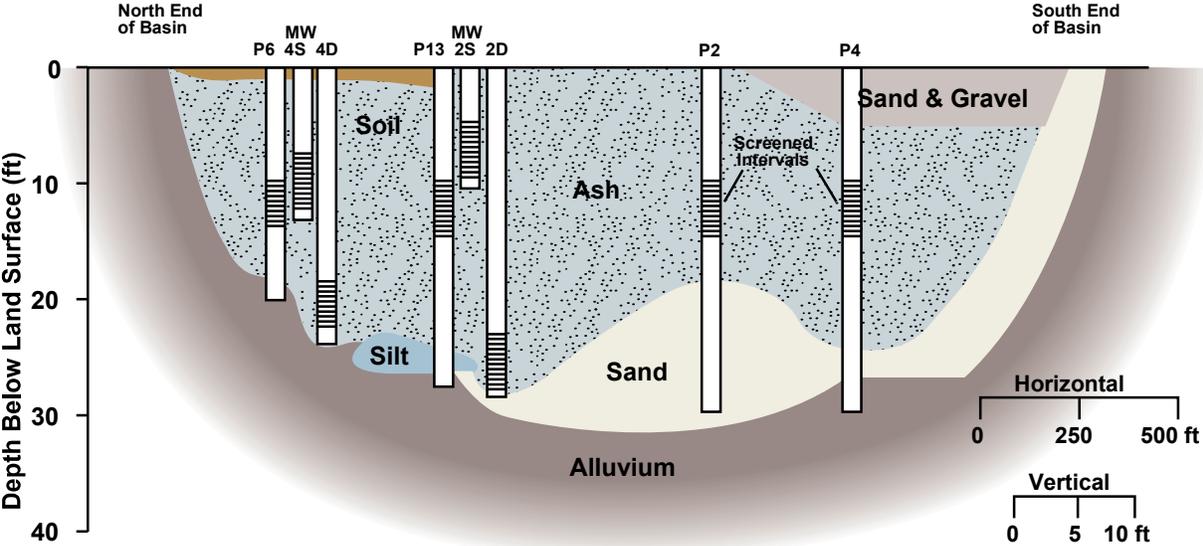
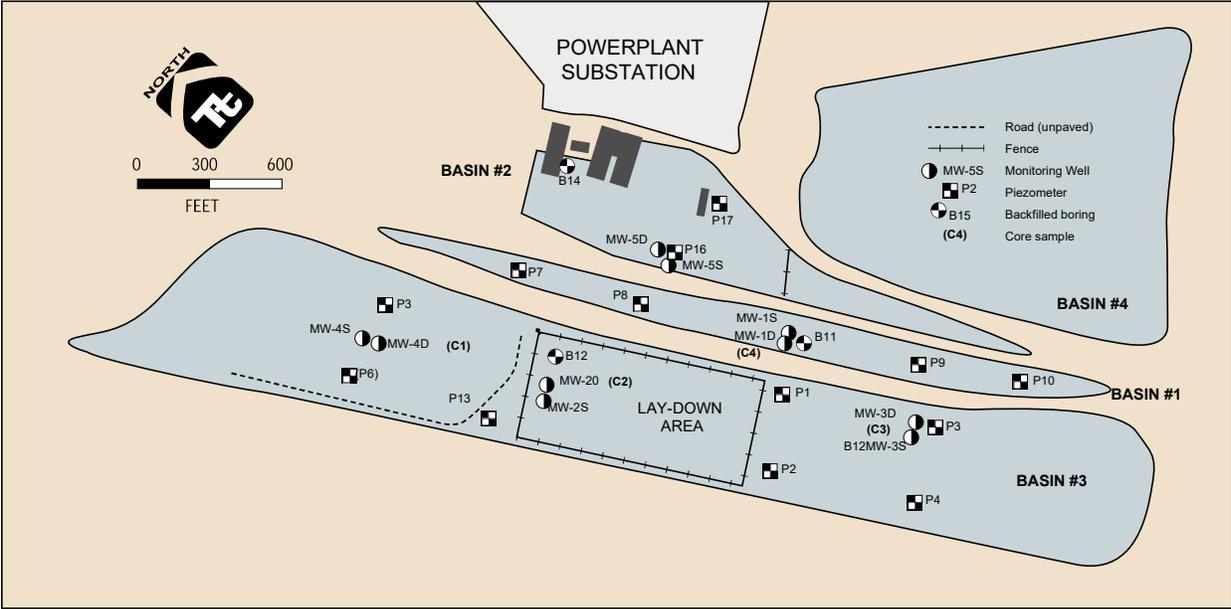
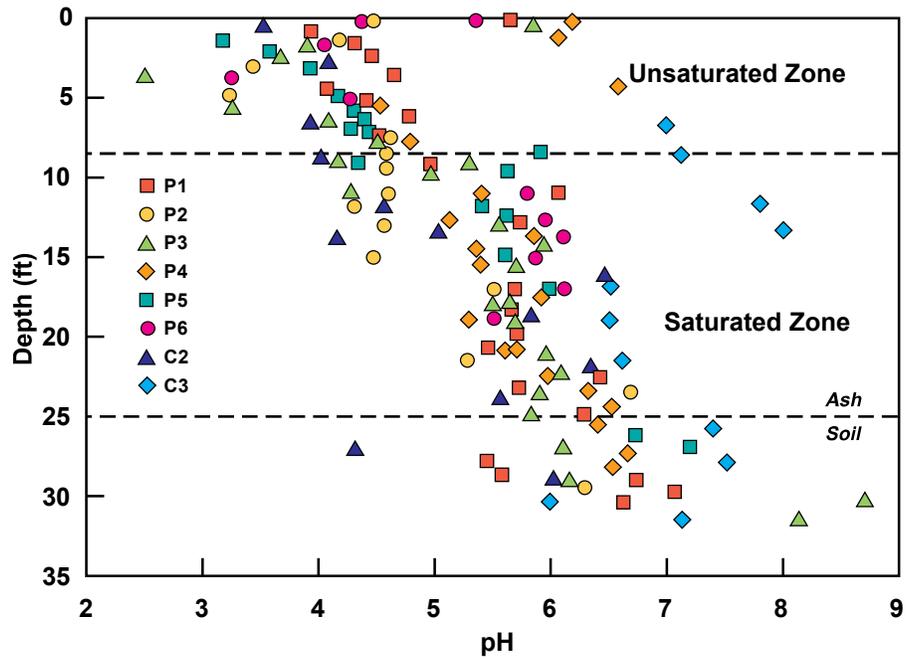


Figure 3-9  
Map showing well locations and typical depth at Basin 3

a) Basin 3



b) Basin 2

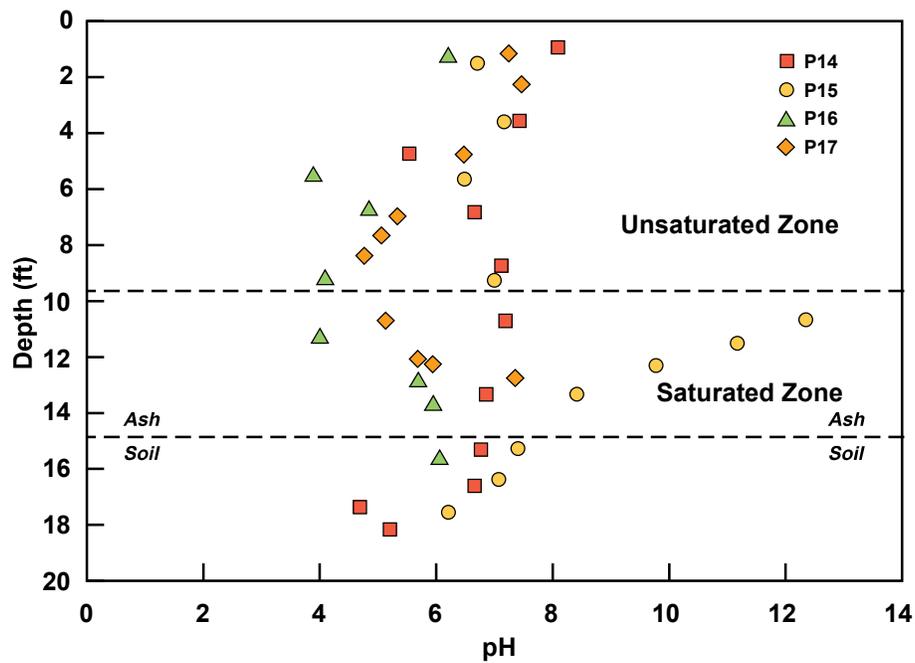


Figure 3-10  
pH versus depth in cores from a) Basin 3, b) Basin 2, and c) Basin 1

c) Basin 1

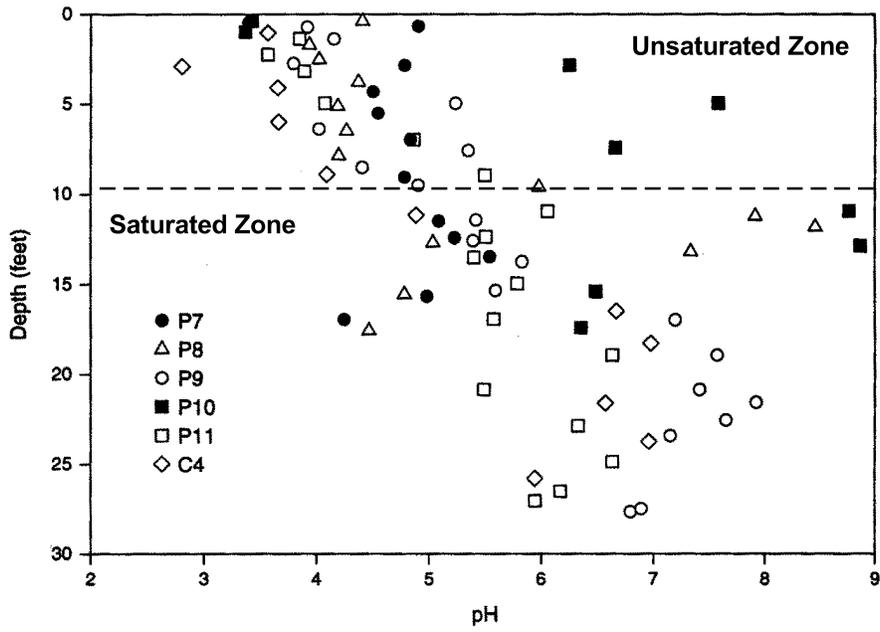


Figure 3-10 (continued)  
pH versus depth in cores from a) Basin 3, b) Basin 2, and c) Basin 1

**Table 3-7  
Porewater Composition from C2 in Basin 3**

Element <sup>a</sup>	Depth (ft)														
	0.5	1.75	3.0	4.5	6.75	8.75	11.75	13.50	13.75	16.25	18.75	22.0	24.0	27.0	29.0
Al	53.7	6.6	13.1	46.8	84.0	23.0	1.3	1.5	24.0	1.7	0.9	1.1	1.7	10.0	2.2
As	<0.0005	0.03	0.004	<0.0005	<0.02	0.022	2.29	5.13	ND	0.873	1.616	0.550	1.080	ND	ND
B	0.8	<0.24	0.4	0.6	1.5	3.1	5.4	8.2	6.9	4.6	6.0	6.1	6.9	8.7	7.3
Ba	0.67	0.72	0.72	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ca	12.3	2.75	34.2	537	526	496	472	496	554.0	484.0	480.0	490.0	511.0	634.0	771.0
Cd	0.075	0.075	0.075	0.075	<0.1	<0.1	<0.1	<0.1	0.4	0.3	0.4	0.4	0.4	0.4	0.2
Cl	1.65	0.52	0.32	10.46	5.17	3.91	2.82	1.74	2.17	3.71	2.8	5.12	4.57	5.36	5.59
Co	0.23	0.23	1.15	0.23	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.0	<0.1	<0.1	<0.1	<0.1
Cr	ND <sup>a</sup>	ND	ND	ND	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cu	0.1	0.1	5.78	0.65	0.6	1	<0.1	0.5	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe <sup>2+</sup>	0.15	43.74	17.34	39.38	476	737.8	1686	2616	1436	1441	1916	1319	1961	830.9	14.56
Fe <sup>3+</sup>	0.17	1.73	1.02	2.38	19.5	30.1	24	42	45	24	23	24	42	30.8	1.75
Fe (total)	0.525	53.3	21.8	49.3	460	760	1650	2540	1520	1400	1840	1870	1990	902	5.7
K	4.2	15.9	1.8	10	30	80	70	80	80	70	70	70	50	30	10
Mg	7.0	3.1	1.7	4.9	24	73	142	180	176	111	146	152	182	356	181
Mn	0.9	0.5	0.3	0.4	1.7	5.3	10.2	13.9	14.1	7.9	11.0	17.0	19.0	9.2	22.0
Mo	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Na	3.1	2.6	3.7	3.6	11	19	27	33	32	28	34	36	41	66	68
Ni	1.1	1.0	1.1	0.6	<0.1	1.8	0.6	<0.1	1.2	1.6	1.9	<0.1	<0.1	<0.1	<0.1
SO <sub>4</sub>	387.2	188.5	236.5	1799	2691	3069	4599	6023	5313	4240	5243	5344	5264	9821	2417
Sr	0.9	1.3	1.7	3.6	4.8	8.9	7.2	6.8	7.8	7.2	8.1	7.7	11.0	14.0	9.1
Zn	<0.02	<0.02	0.08	0.08	1.1	4.8	0.8	0.2	0.8	3.3	<0.5	<0.5	<0.5	0.7	<0.5
pH	3.50	3.94	4.05	4.06	3.92	4.00	4.55	5.02	4.13	6.44	5.81	6.32	5.53	4.29	6.01
Eh (mv)	500	461	459	462	376	404	339	295	423	101	127	82.7	188	388	344
pe	8.45	7.79	7.75	7.80	6.35	6.82	5.73	4.98	7.15	1.71	2.15	1.40	3.18	6.55	5.81
EC (µmhos/cm)	1207	1422	1126	2764	3440	4520	5600	6690	6450	5030	5320	5550	5780	ND	4340

Data are from EPRI, 1995.

<sup>a</sup> As, Cd, Co, Cu, Ni, and Zn results were determined by AA other chemical data were determined by ICP.

<sup>b</sup> Not determined.

<sup>c</sup> Depths above 27 ft are ash; below was weathered bedrock.

Concentrations are in mg/L unless otherwise noted.

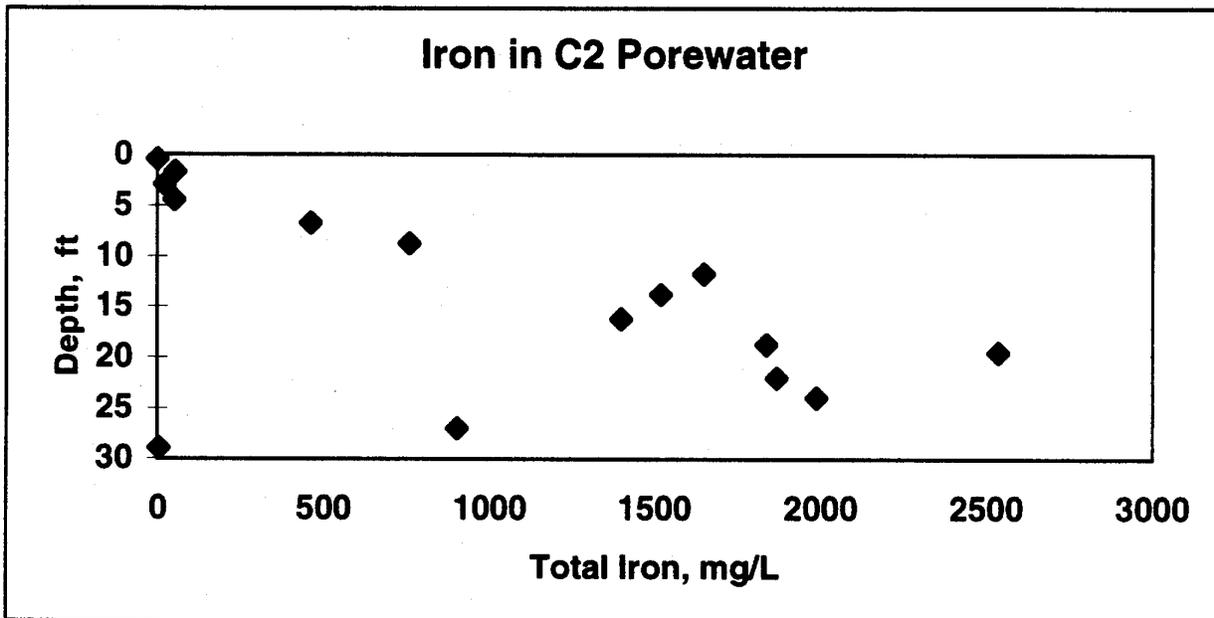
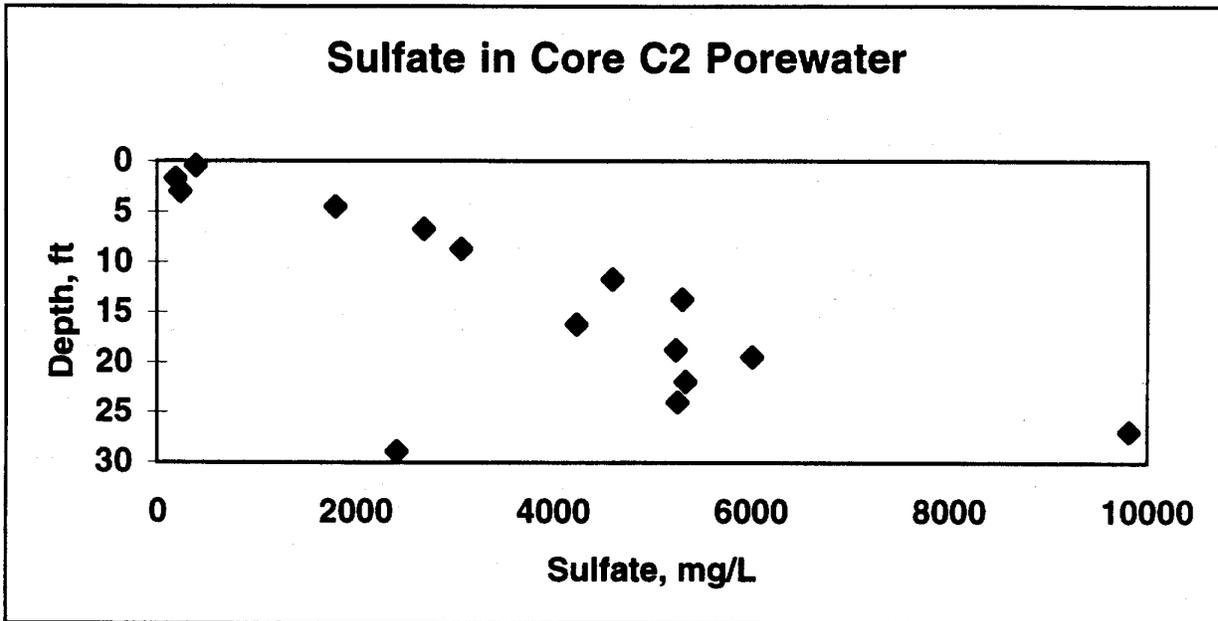


Figure 3-11  
Sulfate and iron concentrations in porewater from C2 core in Basin 3

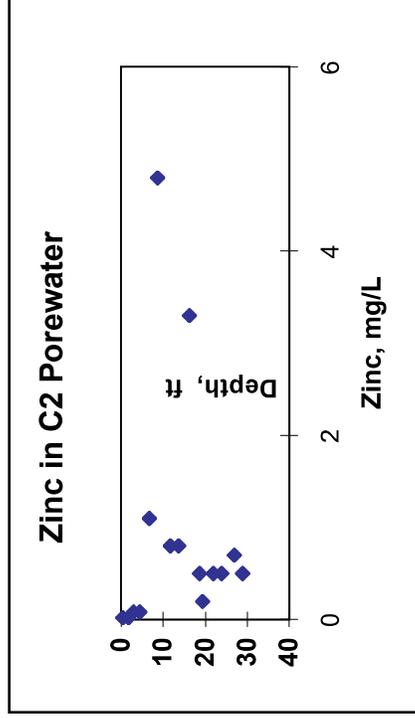
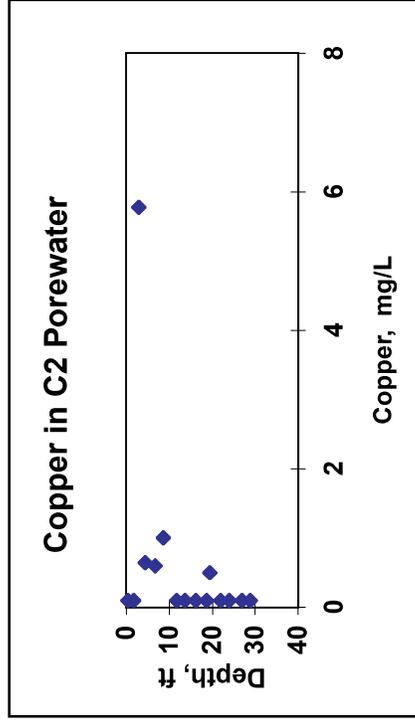
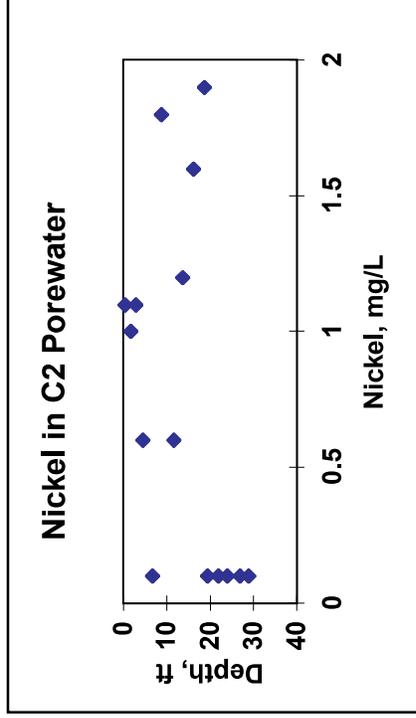
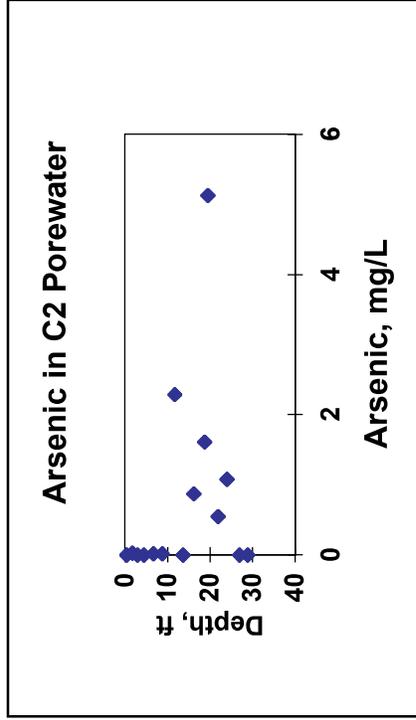


Figure 3-12  
Porewater concentrations of selected metals in C2 core from Basin 3

The water table in all the basins was 6.5 to 10 ft below the land surface. The general groundwater flow direction from the basins is east toward the river, with a secondary flow direction near the ends of Basin 3 toward the two creeks. Groundwater downgradient of Basin 3 had elevated sulfate (1,242 to 3,520 mg/l, Figure 3-13a) compared to around the ash-only basins (118 to 510 mg/l). Iron and arsenic concentrations were also elevated in the shallow groundwater downgradient of Basin 3 (Figures 3-13b and 3-13c). Sulfate, iron, and arsenic were lower in a well further downgradient of the basin (Figures 3-14a, 3-14b, and 3-14c). Most trace elements in the deeper groundwater were low, however, due to the increase in pH (6.2 to 6.6), compared to acidic conditions in the shallower groundwater (3.8 to 4.5).

Monitoring at upstream and downstream stations on the river showed no differences due to NPDES discharges from the power plant or seepage from the groundwater. There were noticeable effects on the two small creeks near Basin 3 due to groundwater seepage and direct seepage from Basin 3. This seepage was high in sulfate, iron, and manganese; trace metals were low. One of the creeks also received discharges from a sewage treatment plant.

The present pyrite oxidation rate in the saturated zone of the closed, dewatered former impoundment is believed to be very slow due to the near-neutral pH, relatively anoxic conditions, and high  $\text{Fe}^{2+}$  concentrations. Amounts of sulfate-S and sulfide-S in ash were estimated by analyzing a few selected samples from the unsaturated and saturated zones. These results indicate that a considerable amount of pyritic sulfur is still present in the ash basins; and unoxidized pyrite grains were visible in some core samples from the saturated zone in Basin 3. The low pH and relatively higher concentrations of minor elements in the unsaturated zone porewater indicate that pyrite oxidation is occurring in this zone. However, the significantly lower concentrations of soluble salts in upper 2-3 ft compared to the deeper porewaters indicate that lateral drainage from unsaturated zones is also occurring.

The BR case study has identified two main sources of acidity in Basins 1 and 3: the unsaturated zone, a direct source, and the saturated zone, an indirect source. The upper unsaturated zone has low pH as a result of acidity produced from the active oxidization of pyrites. Neutralizing the acidity in this zone will reduce further oxidation of pyrites. Finely crushed calcite or limestone could be added as the treatment in the unsaturated zone. The EPRI study performed titrations of unsaturated zone materials and assessed the amount of base needed to neutralize existing acidity to pH 7.5. The initial pH of the two samples was 3.92 and 3.65. The results showed that more than 85% of the acidity could be rapidly neutralized (Figure 3-15) and estimated that 35 to 66 tons of  $\text{CaCO}_3$ /acre would be needed to neutralize the acidity in 1 m of Basins 1 and 3 (EPRI, 1995).

The lower saturated zone has near-neutral pH but contains high amounts of Fe(II). When this leachate comes in contact with atmospheric oxygen, the Fe(II) is oxidized to Fe(III) which then precipitates as  $\text{Fe}(\text{OH})_3$ , solid, and generates acidity and, therefore, is an indirect source of acidity. No in situ neutralization methods have been identified to address this indirect source of acidity. In addition, the high levels of soluble salts observed deep in the saturated zone cannot be effectively remediated by the use of calcite or lime in the unsaturated zone.

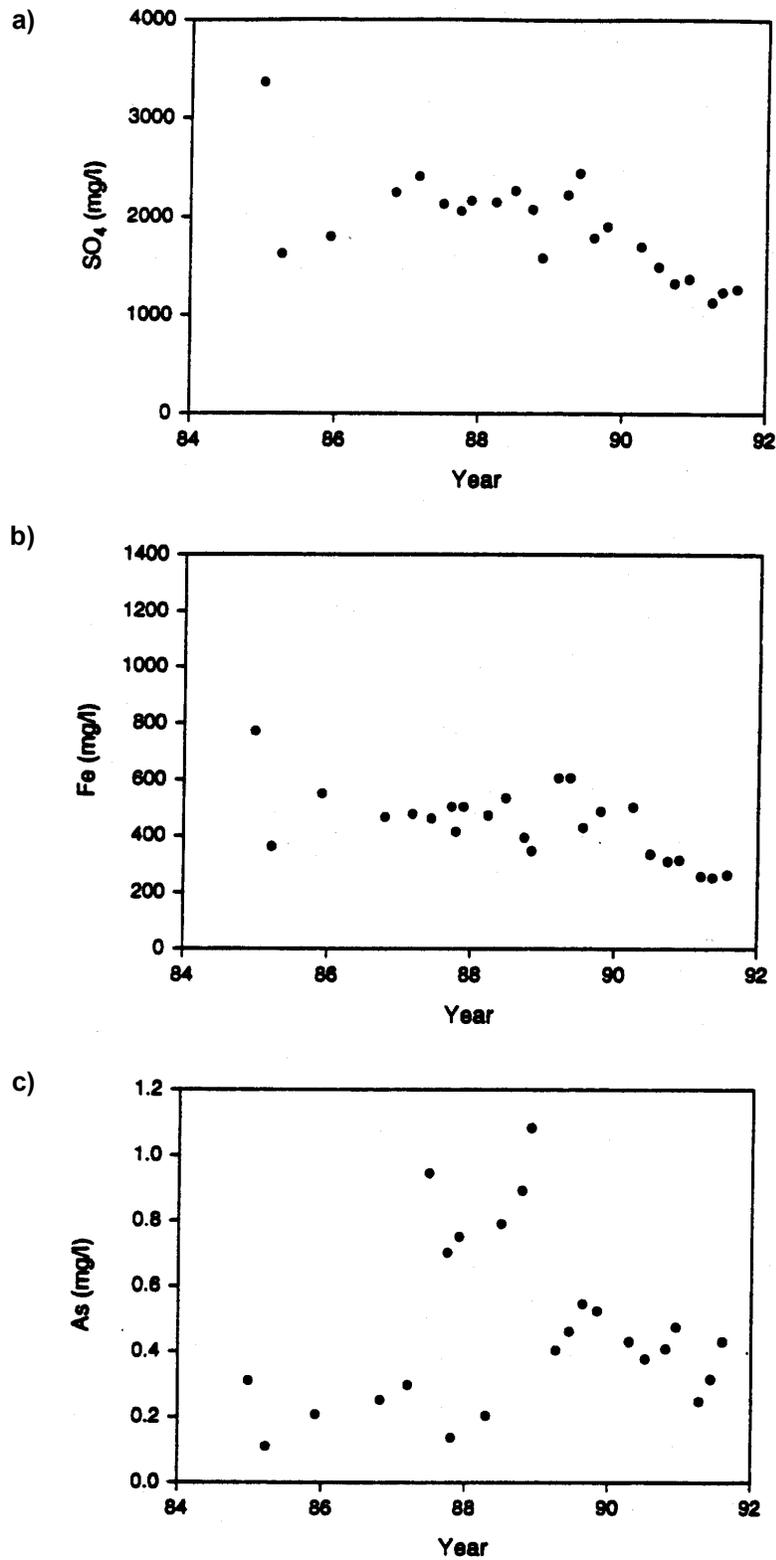


Figure 3-13  
Downgradient groundwater concentrations of sulfate, iron, and arsenic in MW12 near Basin 3

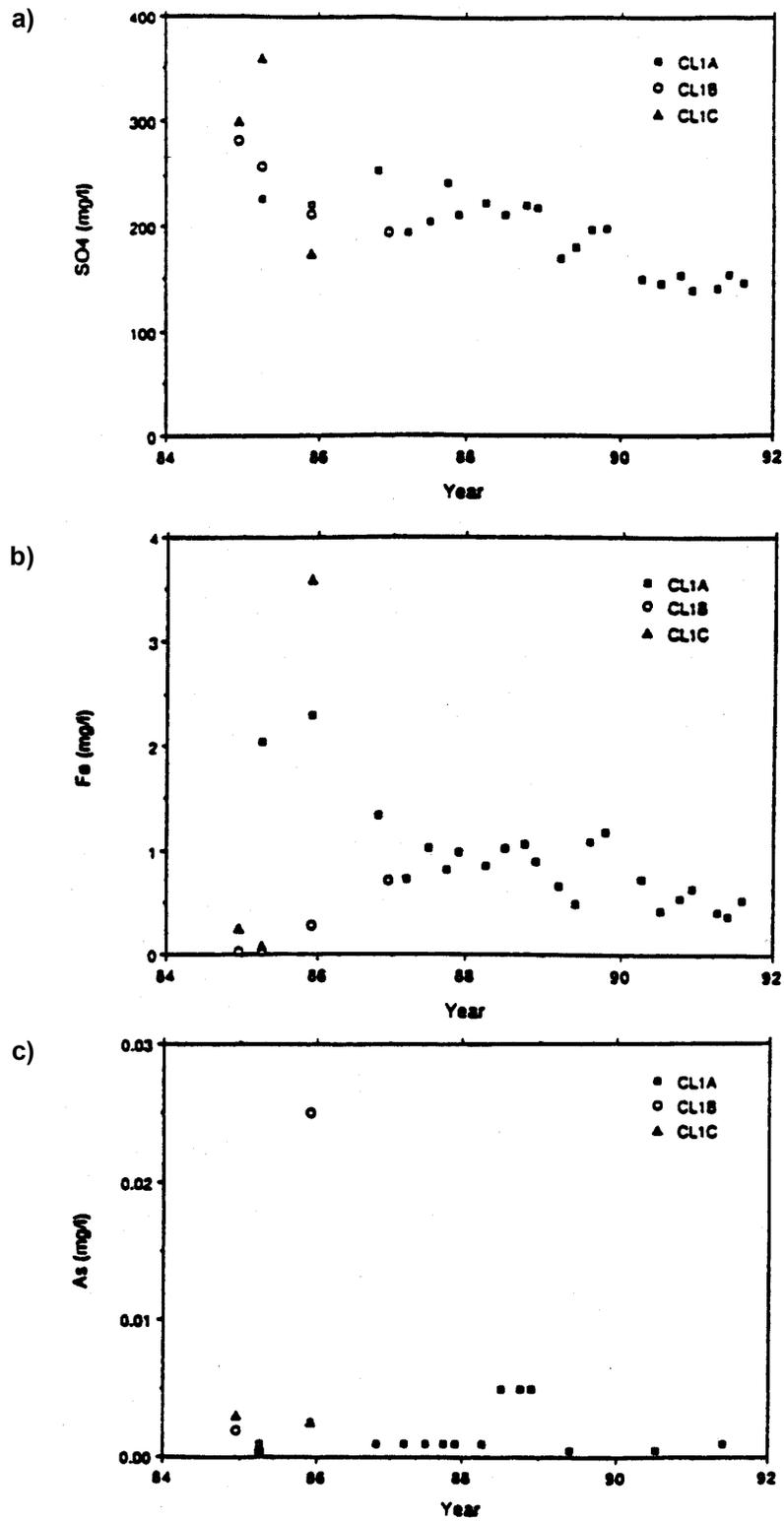


Figure 3-14  
Downgradient groundwater concentrations of sulfate, iron, and arsenic in CL1 at the south end of Basin 3.

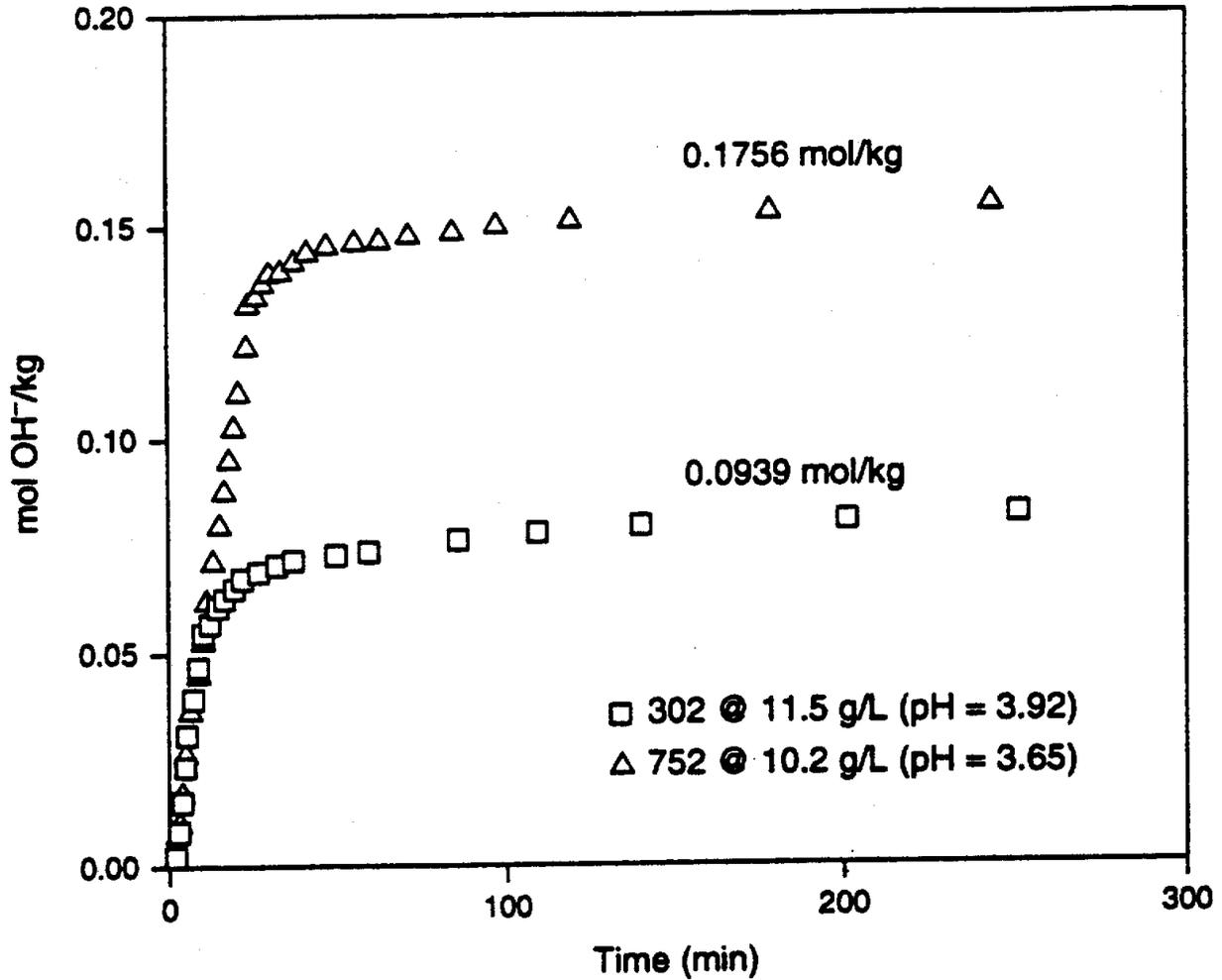


Figure 3-15  
 Base consumption by Basin 1 and Basin 3 unsaturated  
 zone materials (EPRI, 1995).

The utility selected an environmental control approach that combined hydrologic, chemical, and physical methods to reduce the formation, release, and migration of leachates from past and future pyrite oxidation. A cap was installed on Basin 3 to reduce infiltration and diffusion of oxygen to decrease pyrite oxidation and leachate formation in the unsaturated zone. A slurry wall was installed around Basin 3 to prevent lateral movement of the saturated zone water to the nearby creeks and the downgradient wells. Groundwater monitoring to demonstrate the effectiveness of these postclosure control measures is continuing at the facility.

## **Case Study MO**

This site is an example of an ash impoundment where alkaline coal fly ash was disposed first followed by the disposal of bottom ash and mill rejects containing pyrites. These CCBs and mill rejects are managed in a segregated manner. Field investigations revealed that the pyrites have oxidized in the pond and have generated acidic leachates with elevated concentrations of iron, sulfate, arsenic and other constituents. The underlying alkaline flyash, however, has effectively neutralized the leachate and reduced dissolved concentrations of iron, arsenic, sulfate and the other constituents. Because a slurry wall around the impoundment was built to control general seepage, the leachate has had minimal effect on the surrounding environment.

This site is also located in eastern Pennsylvania. The plant has two units with a total generating capacity of 1,500 MW. Unit 1 began operation in 1972, while Unit 2 began in 1973. The units burn central or southwestern Pennsylvanian bituminous coal in dry bottom pulverized coal furnaces. At full capacity the plant burns 12,800 tons of coal per day. The coal has about 2 percent sulfur and 12 percent ash. Originally, the plant had a wet ash-handling system and electrostatic precipitators. An unlined 144-acre impoundment was built to manage the ash. The impoundment was constructed by excavating to bedrock and using the excavated materials to form dikes around the facility tied into a bedrock hill on the northeast side. After construction, two interior dikes were built to divide the basin into three subbasins referred to as A, B, and C (Figure 3-16). Subbasin C functions as a settling basin prior to routing pond overflow to a permitted discharge to a nearby creek. The plant converted to a dry fly ash handling system in 1982, and since then fly ash has been disposed of in several landfills near the plant. In 1984, a soil-bentonite slurry wall was constructed in the outer dike of the impoundment on the western side of the basin to control seepage. In 1987, a similar slurry wall was added to the remainder of the outer dikes, except for the hill area.

Mill rejects are collected from each unit using water, discharged to a pyrite transfer tank, and then sluiced to Subbasin B, where a delta has formed. Subbasin B also contains fly ash and bottom ash. The amount of mill rejects generated is about 10,000 to 20,000 tons per year. Agricultural lime is periodically spread on the exposed mill rejects to help neutralize the acidity.

Multiple borings were installed in the ash basin for collection of cores for solid-phase and porewater analyses. Figure 3-17 depicts a cross section through the ash basin showing the major mill reject area. The ash basin is underlain by residual soil, weathered shales, and bedrock consisting of folded Paleozoic shales, siltstones, and sandstones. The predominant formations are the Mahantago Formation and the Marcellus Formation, consisting of claystones, siltstones, sandstones, and some shales. The boundary between these formations is located along the northeastern edge of the basin. The Marcellus shale contains some dispersed pyrites. There are two aquifers at this site; a shallow aquifer in the weathered bedrock, and a deeper aquifer in the fractured bedrock. The general flow direction in the shallow groundwater near the basin is toward the east to a creek.

The ash basin recharges the shallow aquifer at this site. However, because the basin has slurry walls, radial flow out of the basin is restricted. The water quality around the basin is quite variable depending on well location and screened interval, as is the background groundwater

quality in the weathered shale bedrock aquifer. Sulfate concentrations in two wells downgradient of the entire basin averaged about 250 and 310 mg/l since installation of the slurry wall.

Oxidation of pyrites has occurred in Subbasin B only where the mounded mill rejects are exposed to the atmosphere. As described in the BR Case Study, exposure to air in the presence of moisture increases the pyrite oxidation rate. This pyrite oxidation resulted in elevated porewater concentrations of sulfate, iron, and some trace metals such as arsenic, copper, nickel, manganese, boron, and zinc (Table 3-8). However, the alkaline fly ash in the deeper part of Subbasin B was effective in lowering the iron and sulfate concentrations (Figure 3-18) as well as lowering the concentrations of copper, nickel, zinc and arsenic in porewaters (Figure 3-19a). Arsenic concentrations data for the porewater samples in core C2 were normalized as a ratio of the highest measured value and then plotted as a function of the pH measured in those samples. Figure 3-19b shows that the increase in pH precipitously reduces the normalized ratio for arsenic in porewater. Most likely, arsenic coprecipitated with the iron as a result of increasing pH that reduces solubility of both iron and arsenic.

The pH of the mill reject zone in the three cores was less than 4.5 in most samples. This increases the solubility of iron and cationic trace metals such as cadmium, nickel, and zinc. After the leachate had passed through about 5 ft of fly ash, the pH had increased to over 6 due to neutralization by the alkaline materials present in the ash, chiefly calcium and magnesium. The effect of the increased pH is to reduce acidity, which is desirable in itself, but the increased pH also results in decreased solubility of cationic metals. When the pH of leachate is above about 5.5, most cationic metals, e.g., cadmium, copper, nickel, and zinc, have decreased solubility. Thus, because of natural chemical reactions that can occur in alkaline conditions provided by the fly ash, the mill rejects have not significantly affected water quality outside the basin.

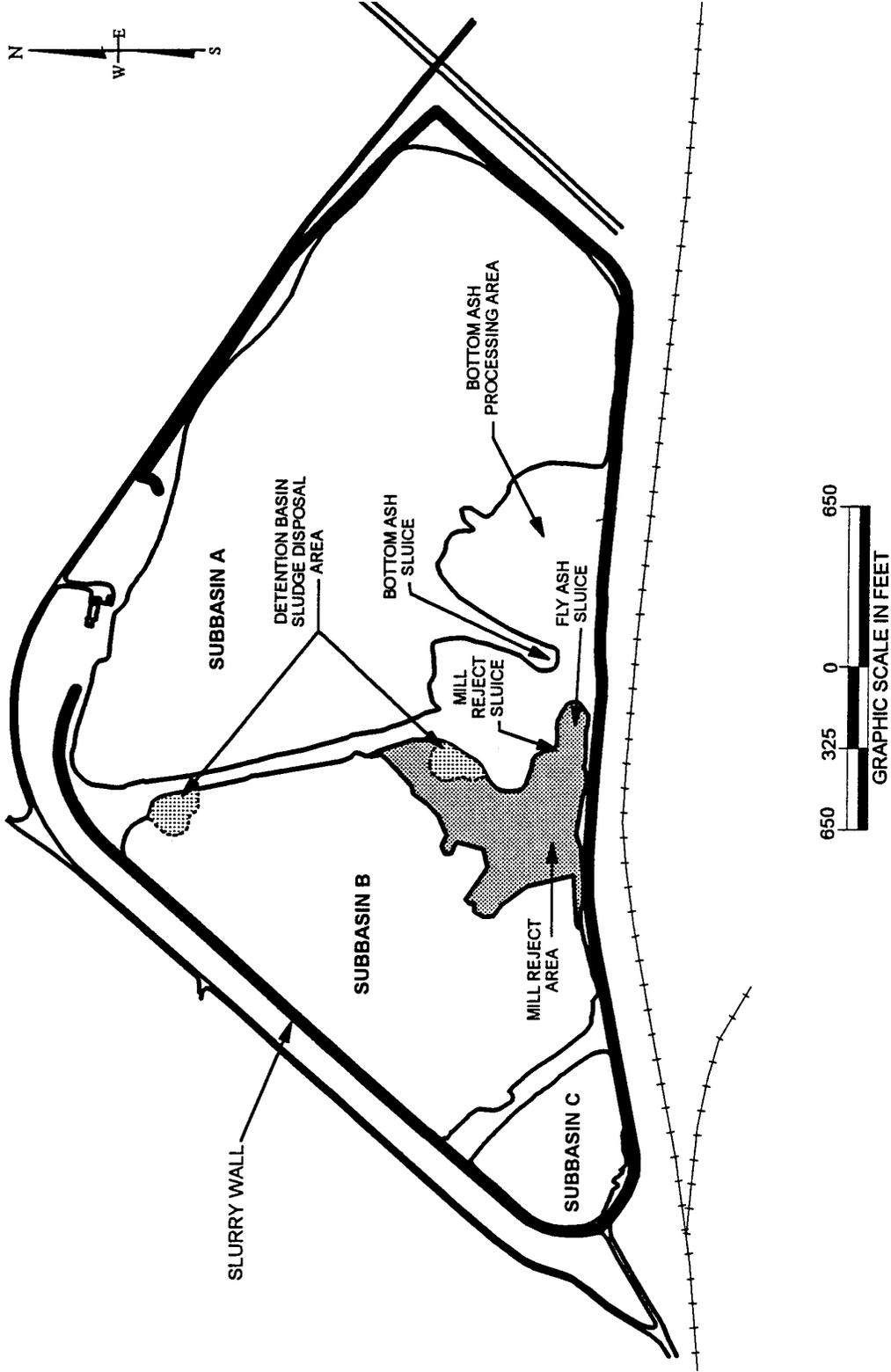


Figure 3-16  
Ash basin at MO plant (after EPRI, 1997b)

Case Studies Related to Mill Rejects

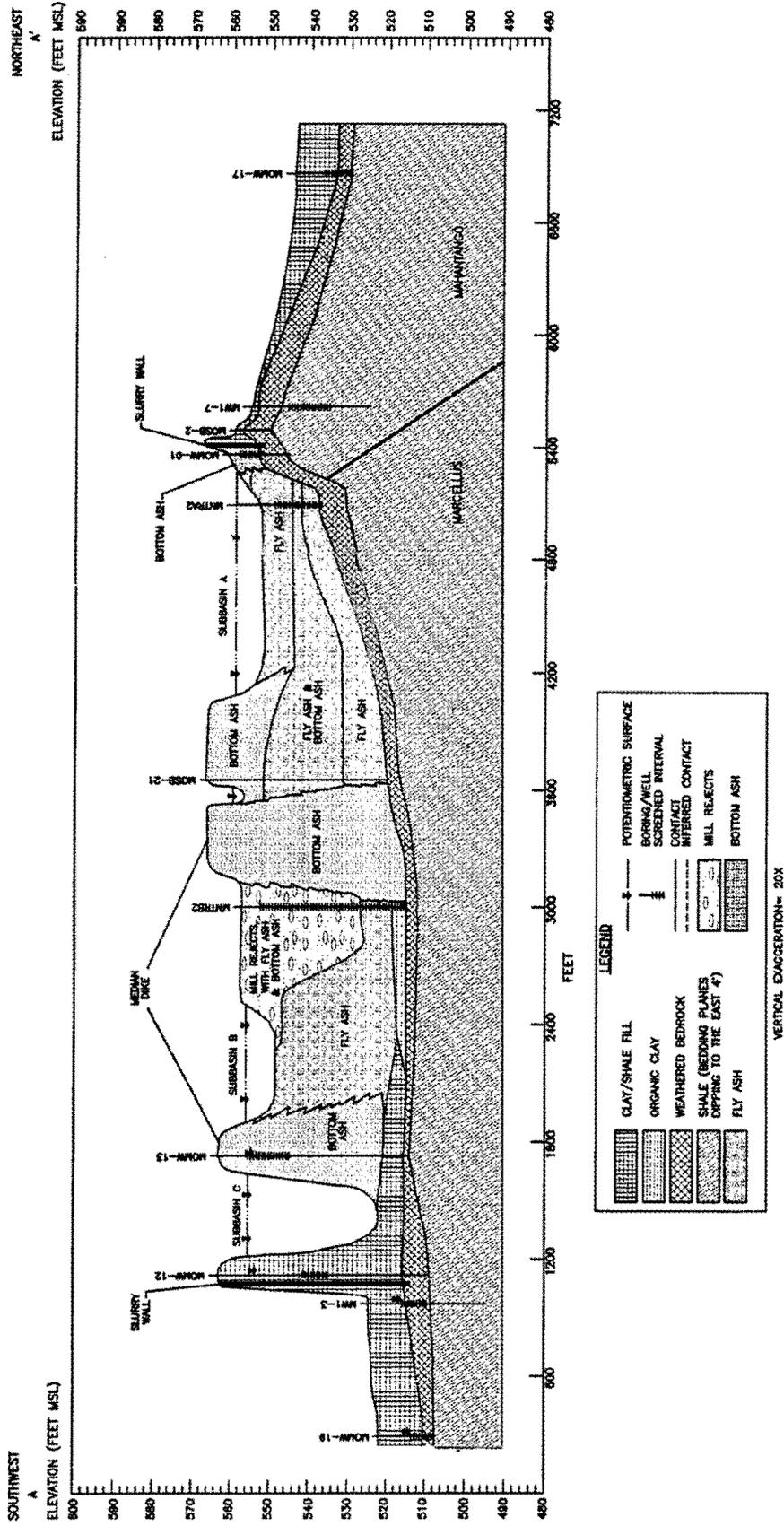


Figure 3-17 Geologic cross-section through ash basin at MO plant (after EPRI, 1997b)

**Table 3-8**  
**Porewater Concentration Ranges at MO site**

Analyte	Unit	Mill Rejects	Bottom Ash/Rejects	Fly Ash
CA	mg/L	479 – 610	102 – 555	104 - 158
SO <sub>4</sub>	mg/L	4050 – 64,400	275 – 1475	242 – 372
Fe	mg/L	646 – 25,400	<0.05 – 41.9	0.05 – 0.09
Mn	µg/L	11,100 – 1,570,000	154 – 8630	<2.5 – 13.3
As	µg/L	55.2 – 86,000	25.9 – 83.7	215 – 855
B	µg/L	9500 – 66,400	<50 – 170	<50 – 590
Cu	µg/L	61.2 – 7610	<10	<10
Ni	µg/L	1890 – 23,000	10.5 – 36.7	<5
Zn	µg/L	2050 – 49,100	<25 – 370	<25
pH	s.u.	1.1 – 3.8	6.56 – 8.03	8.66 – 9.65

Data from EPRI, 1997b.

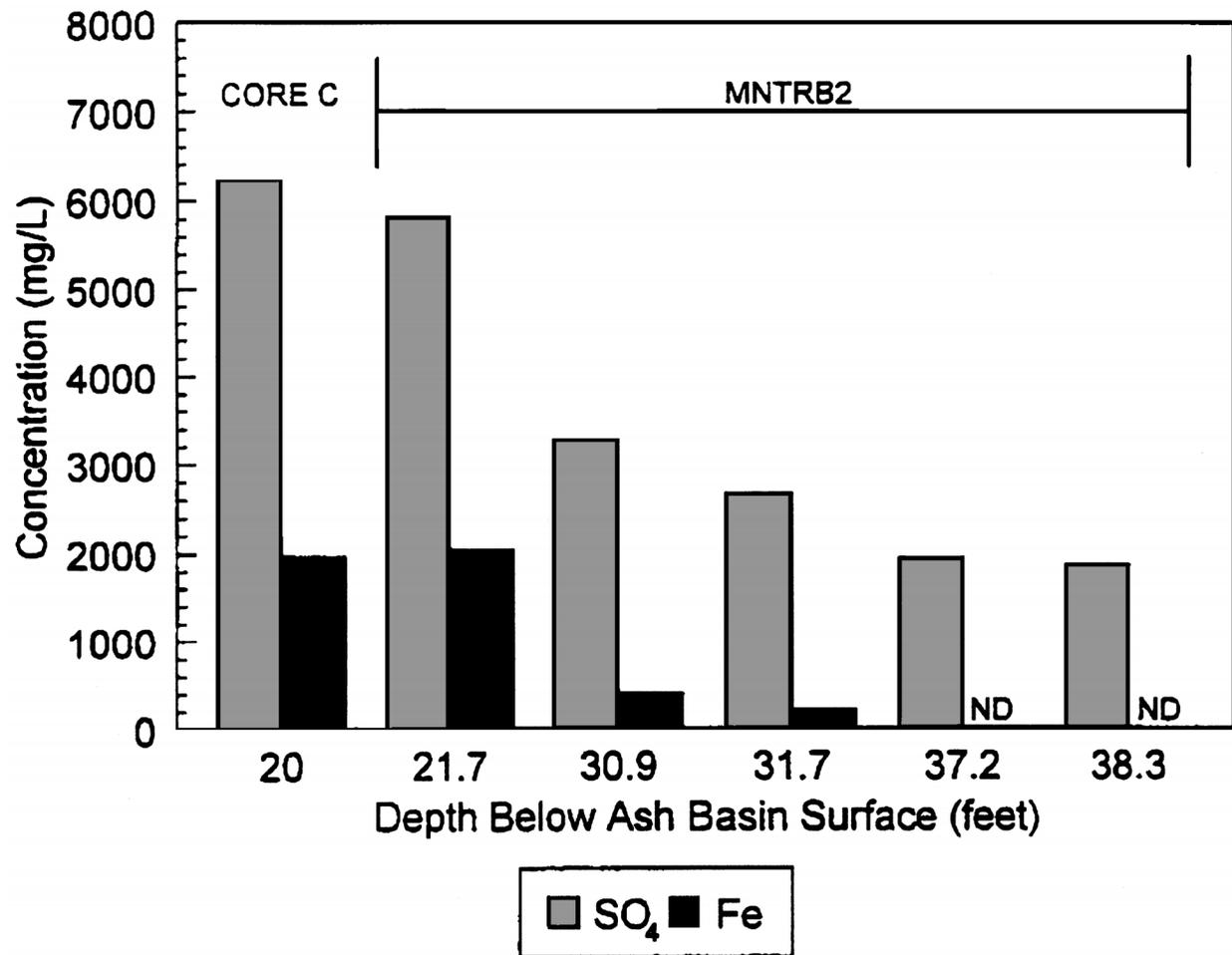
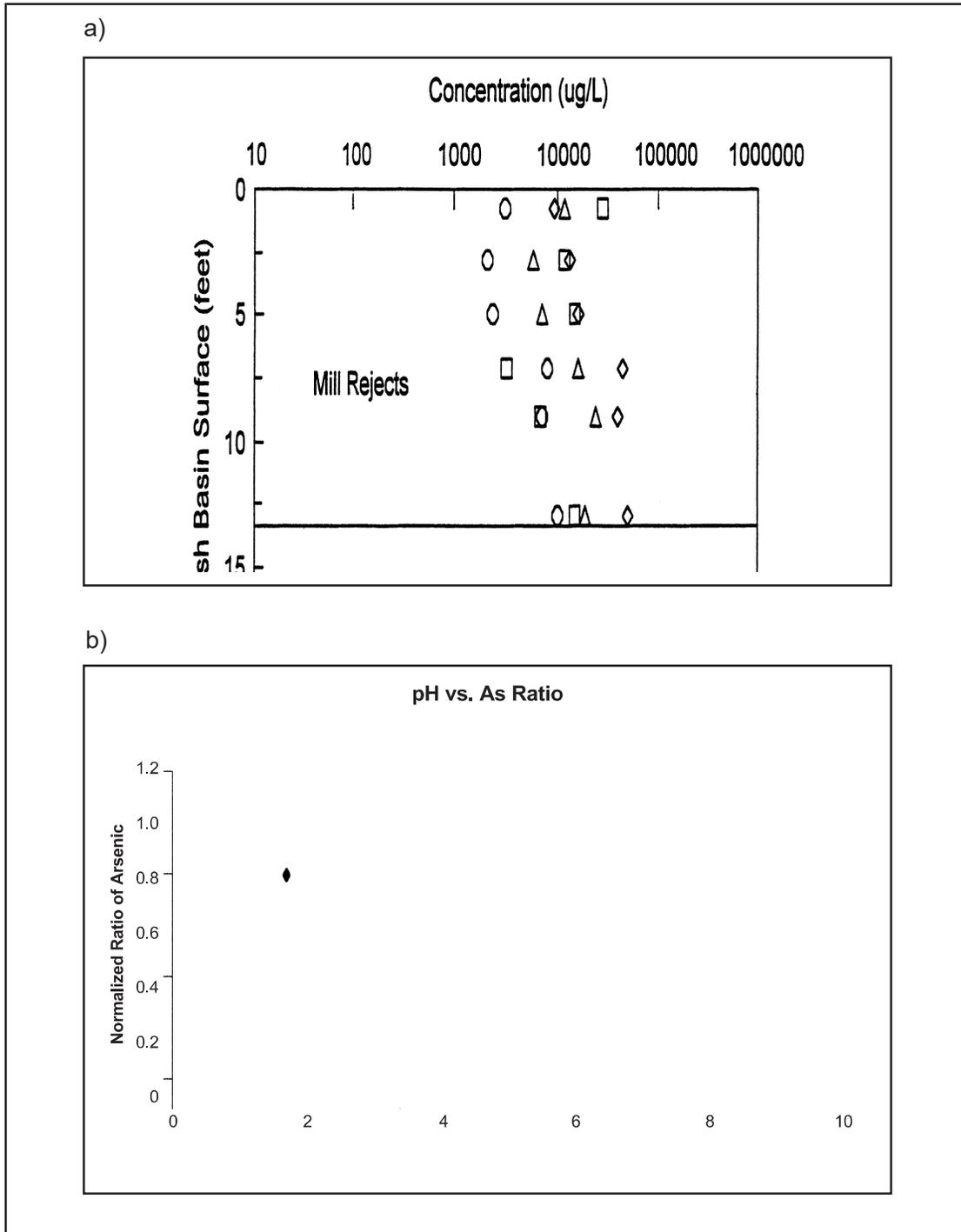


Figure 3-18  
SO<sub>4</sub> and Fe concentrations in fly ash porewater underlying mill rejects in Subbasin B at MO Site (EPRI, 1997b).



**Figure 3-19**  
 Measured As, Co, Ni, and Zn concentrations a) in porewater from Core C and b) the change in As ratio with pH in Subbasin B at MO Site (EPRI, 1997b).

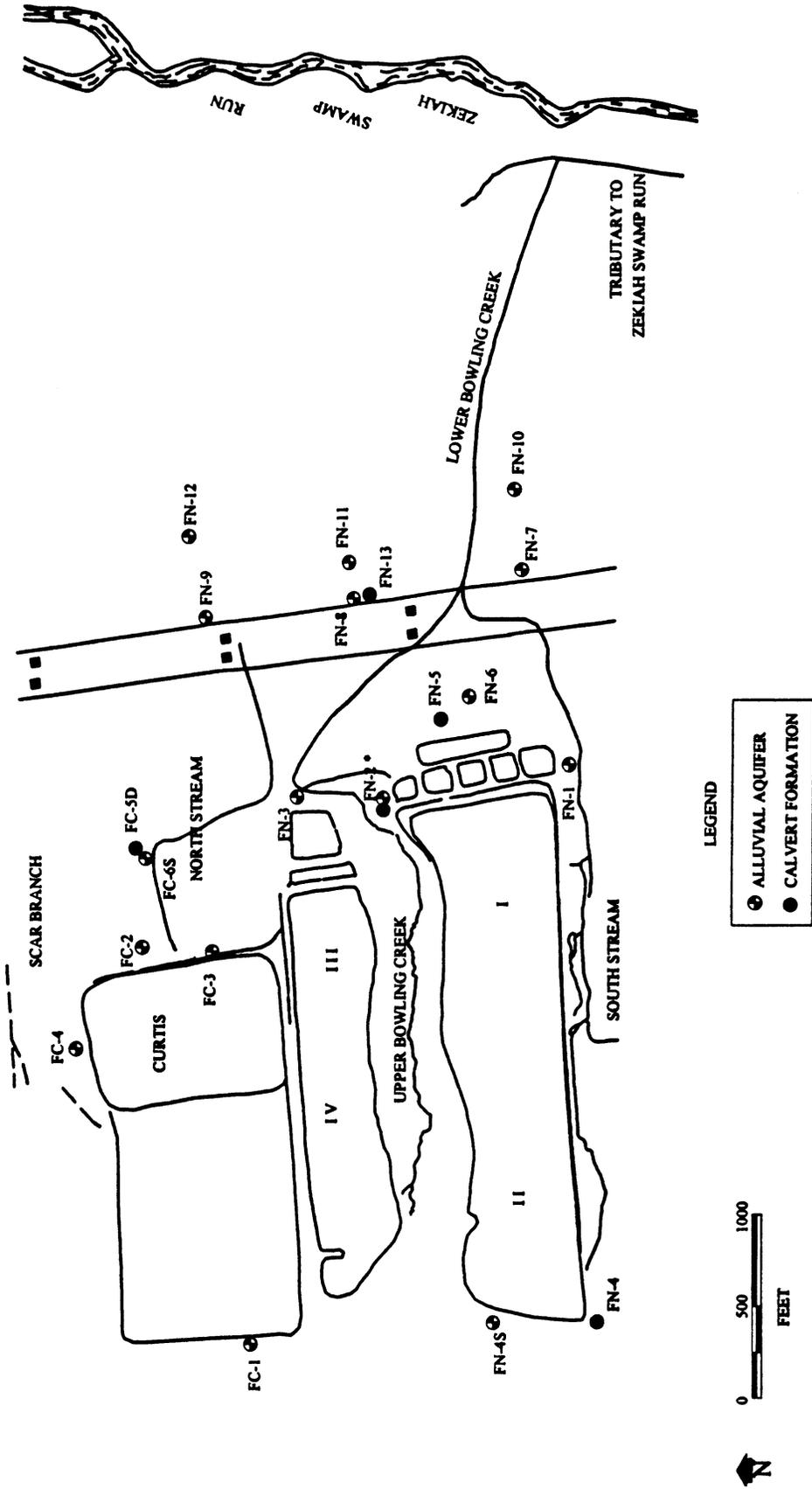
## **Case Study FA**

This site is an example of an ash storage facility where mill rejects were placed in an ash landfill containing acidic ash from bituminous coal. Oxidation of pyrites appears to have occurred, and the acidic ash appears to have also contributed to generating an acidic leachate with elevated levels of iron and sulfate concentrations that affected the nearby surface streams and shallow groundwater. The utility has proactively taken steps (e.g., physical barrier installation, impermeable cap placement, collection and treatment of leachate) to mitigate and restore water quality in the surrounding areas.

### ***Site Description***

This site is a fly ash storage facility, with bottom ash and mill rejects, located in Maryland about 6 miles north of the coal-fired power plant in a rural area on the western edge of a swamp (Figure 3-30). The power plant was built in the late 1960s and has a peak capacity of about 1100 MW. It burns bituminous coal from western Maryland, western Virginia and western Pennsylvania with a heating value of about 11,000 BTU/lb, total sulfur content of 1.6 to 3 percent and 8 to 15 percent ash. The plant has two pulverized coal units with electrostatic precipitators and produces about 250,000 tons of fly ash, annually. Fly ash is handled dry and transported to the fly ash storage facility by truck. Bottom ash is sold. In the past, mill rejects were disposed with fly ash in the Phase I/II fill, but now mill rejects are managed separately at the power plant. The utility company initiated ash storage operations in 1970. Phases I/II and III/IV, comprising 132 acres, were developed sequentially and completed in 1989/1990. Ash storage in the adjoining 49 acres of land known as Curtis Phase began in 1989/1990 and has an anticipated life until the end of year 2005.

The natural topography of the site slopes downward toward the east with elevations ranging from about 160 ft at the western end to about 25 ft at the eastern end of the site. The top of the Phase I/II fill ranges from about 177 ft at the western end to about 100 ft at the eastern end. Upper Bowling Creek separates the Phase I/II fill from Phase III/IV fill (Figure 3-20). To the south of Phase I/II is a creek designated as South Stream. A series of six collection and treatment ponds are located at the eastern end of the Phase I/II fill. One large stormwater/leachate management pond is located at the end of Phase III/IV. The Phase III/IV fill has a drain system beneath it that discharges into this large pond.



\* FN-2 replaced 11/1994 -- Originally screened in Calvert Formation now screened in Alluvial Aquifer.

**MONITORING WELLS**

**Figure 3-20**  
Map showing FA ash storage areas, wells, and nearby streams

Borings completed in 1993 in the Phase I/II fill area indicated a soil cover of 2 to 3 ft, and fly ash ranging from about 21 to 56 ft thick. About 3-4 ft of bottom ash was found below the fly ash and above the native material. In some borings, bottom ash containing pyrites/mill rejects approximately 22 ft thick was encountered underneath about 20 ft of fly ash. This is consistent with utility accounts that a mound of pyrites/mill rejects may have been placed near the boundary between Phases I and II.

Borings in the Phase III/IV fill indicate a soil cover of 3 to 4.5 ft, and fly ash about 30 to 35 ft thick underlain by a layer of bottom ash approximately 2.5 ft thick. The fly ash encountered in Phase I through IV can be generally classified as a fine sandy silt with a hydraulic conductivity of approximately  $10^{-4}$  cm/sec. Bottom ash is a coarser material and can be classified as a coarse sand.

### ***Geology and Hydrology***

The FA site lies within the Atlantic Coastal Plain Physiographic Province of Maryland. The Coastal Plain consists of gently dipping beds of sands, silts and clays deposited on an eroded bedrock surface. The surficial sediments beneath the site are Pleistocene Age Terrace Deposits consisting of yellow and dark grayish and greenish-yellow orange undifferentiated sands, clays and gravels. Beneath the Terrace Deposits is the Miocene Age Calvert Formation, which consists of pale olive to pale brown sandy or silty clays to fine silty to clayey sands. The Terrace Deposits range in thickness from 0 to 50 ft, whereas the Calvert Formation ranges in thickness from 30 to 170 ft. Borings completed in 1993 indicated the presence of Terrace Deposits under the ash fill varying in thickness from about 12 to 35 ft. The Calvert Formation was encountered below the Terrace Deposits where borings were terminated at a depth of 90 ft.

The Coastal Plain formations consist of sequences of aquifers and aquitards. The uppermost water-bearing zone is usually under unconfined conditions while the successively deeper aquifers tend to be under confined conditions. The groundwater in the Terrace Deposits can fluctuate three to eight feet, and it is typically higher in spring and lower in summer and fall. A schematic geologic cross-section of the shallow stratigraphy beneath FA site is shown in Figure 3-21 and a water table contour map for the alluvial aquifer is shown in Figure 3-22. Groundwater flows generally west to east. However, groundwater also discharges locally into the on-site streams.

Based on the slug tests conducted at the site, the hydraulic conductivity in the alluvial aquifer is estimated to range from 32.9 to 100.8 ft/day. The Calvert Formation on the other hand has a hydraulic conductivity range of 0.004 to 0.2 ft/day. Taking the hydraulic gradient into account and an assumed porosity of 0.4, a seepage velocity of 0.5 to 2.0 ft/day was calculated for the alluvial aquifer. The Calvert Formation's seepage velocity is three to four orders of magnitude lower than that of the alluvial aquifer.

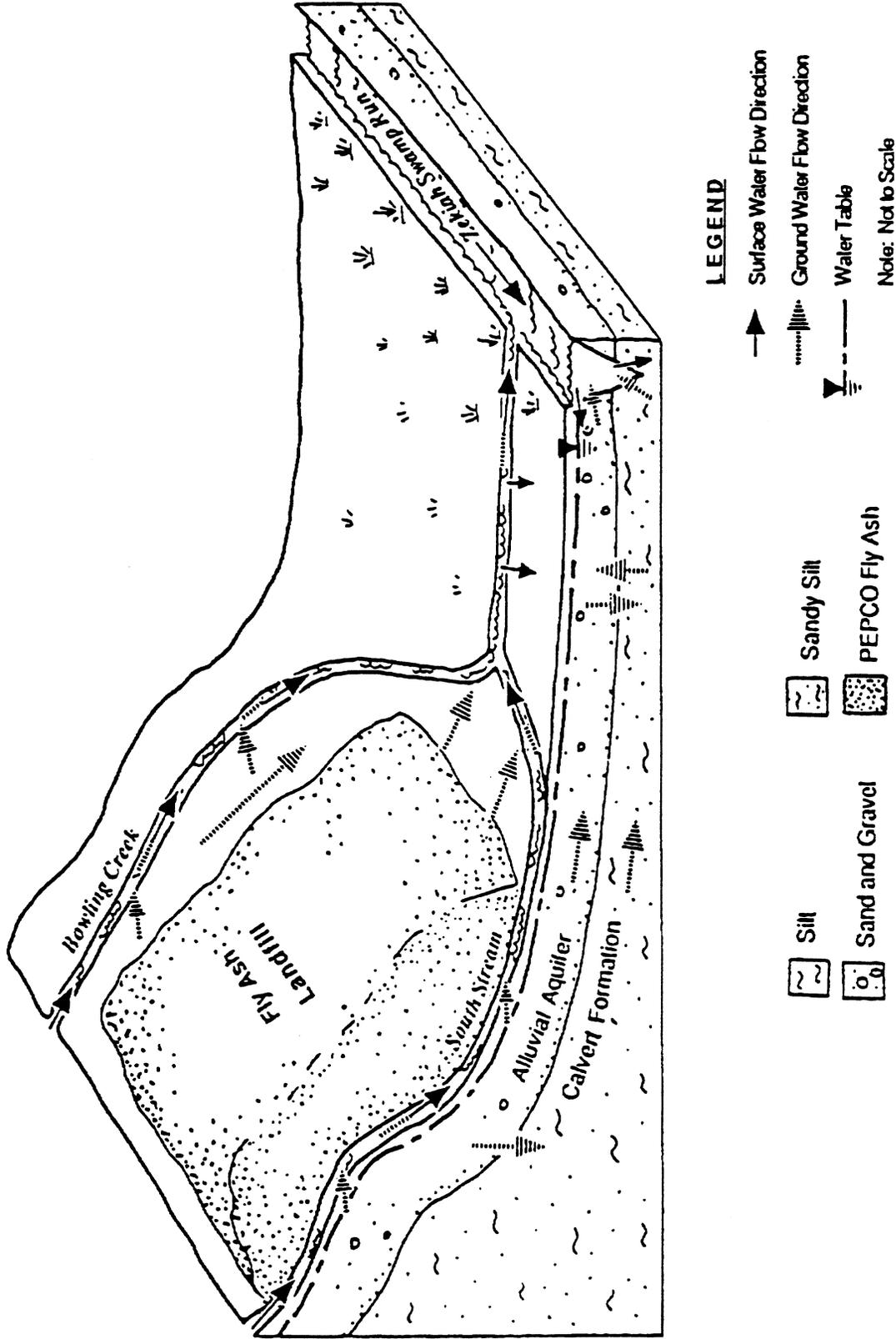


Figure 3-21  
Conceptualized hydrologic conditions at the FA facility

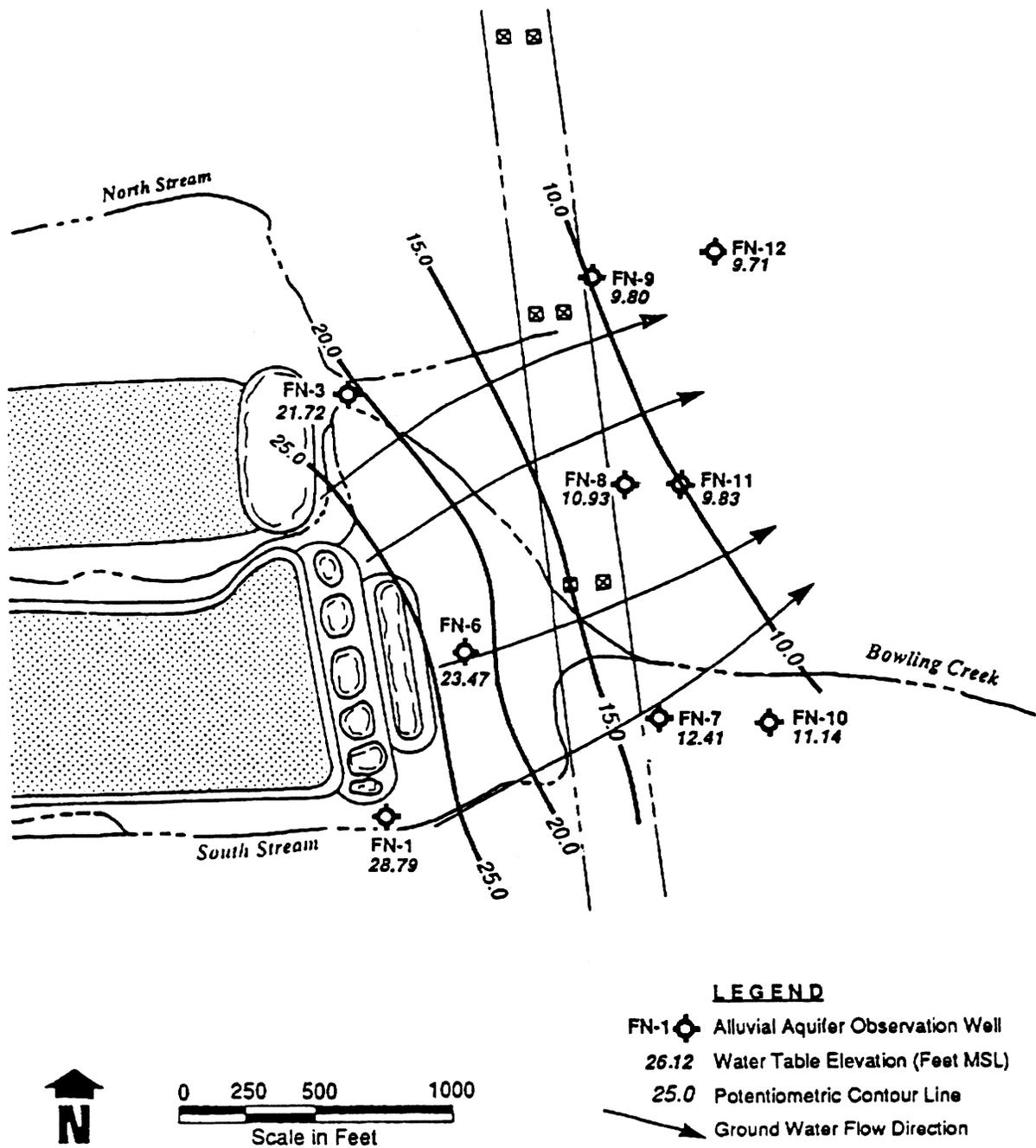


Figure 3-22  
Water table contour map for the alluvial aquifer

### ***PPER Study in 1988-1989***

The FA facility has a State NPDES permit whereby the Maryland Department of the Environment (MDE) reviews and retains groundwater and surface water quality data collected at the ash storage facility. The Maryland Power Plant and Environmental Reviews Division (PPER) has sponsored studies for assessing the effects of the FA facility on groundwater and surface waters. A 1983 PPER study indicated that leachates were affecting shallow groundwater quality beneath the facility. Water quality in the intermittent streams adjacent to and downgradient of the facility was impaired by the discharges from the affected shallow groundwater. The groundwater in the deeper aquifers was not affected by the leachates. The 1983 study also concluded that leachate constituents were not affecting the chemical character of the nearby Zekiah Swamp.

Renewed interest in the effects of the FA facility on the quality of the waters raised questions about the downgradient extent of leachate constituent migration leading to a PPER study in 1988-89. In 1991, the PPER published a report entitled "Assessment of Water Quality Impacts from the FA Facility". A summary of the PPER study is given below.

The 1988-89 PPER study consisted of field investigations which included well installation, aquifer testing, soil testing and groundwater and surface water quality sampling. Seven new groundwater wells were installed to bring the total number of wells to 13. Four of these wells were screened in the Calvert Formation and the remaining nine were screened in the alluvial aquifer. Soil testing included analysis of 11 soil samples for cation exchange capacity (CEC) and a number of other parameters. Results of acid-base accounting tests indicated that the native soils at the FA site have limited to no neutralizing capacity. Surface water was sampled and analyzed for pH, specific conductance and temperature from approximately 50 locations. In addition, several surface water samples were also analyzed for major cations, anions and trace metals. Groundwater pH and conductivity were measured in the field and other chemical parameters were analyzed in the laboratory. Groundwater elevations were measured during each sampling round.

### ***Surface Water Quality Results (1988-89 Study)***

Low pH and high specific conductance values were observed in Bowling Creek and South Stream in May 1988 (Figure 3-23). The lowest measured pH value was 2.65, and the highest specific conductance was 8000 mmhos/cm. Table 3-9 shows the chemical analysis results for Pond-2 water downgradient of Phase I/II, and surface water samples from Bowling Creek and South Stream. These results suggest that the surface waters in these intermittent streams are being affected by the leachates from the Phase I/II ash fill. High acidity, elevated levels of sulfate and chloride, high TDS and high specific conductance were typical characteristics of affected surface waters. The Pond 2 water chemical characterization data also showed elevated sulfate, chloride, TDS, specific conductance and iron and acidic pH, offering a signature that corresponds to the observed surface water quality impacts in the two intermittent streams.

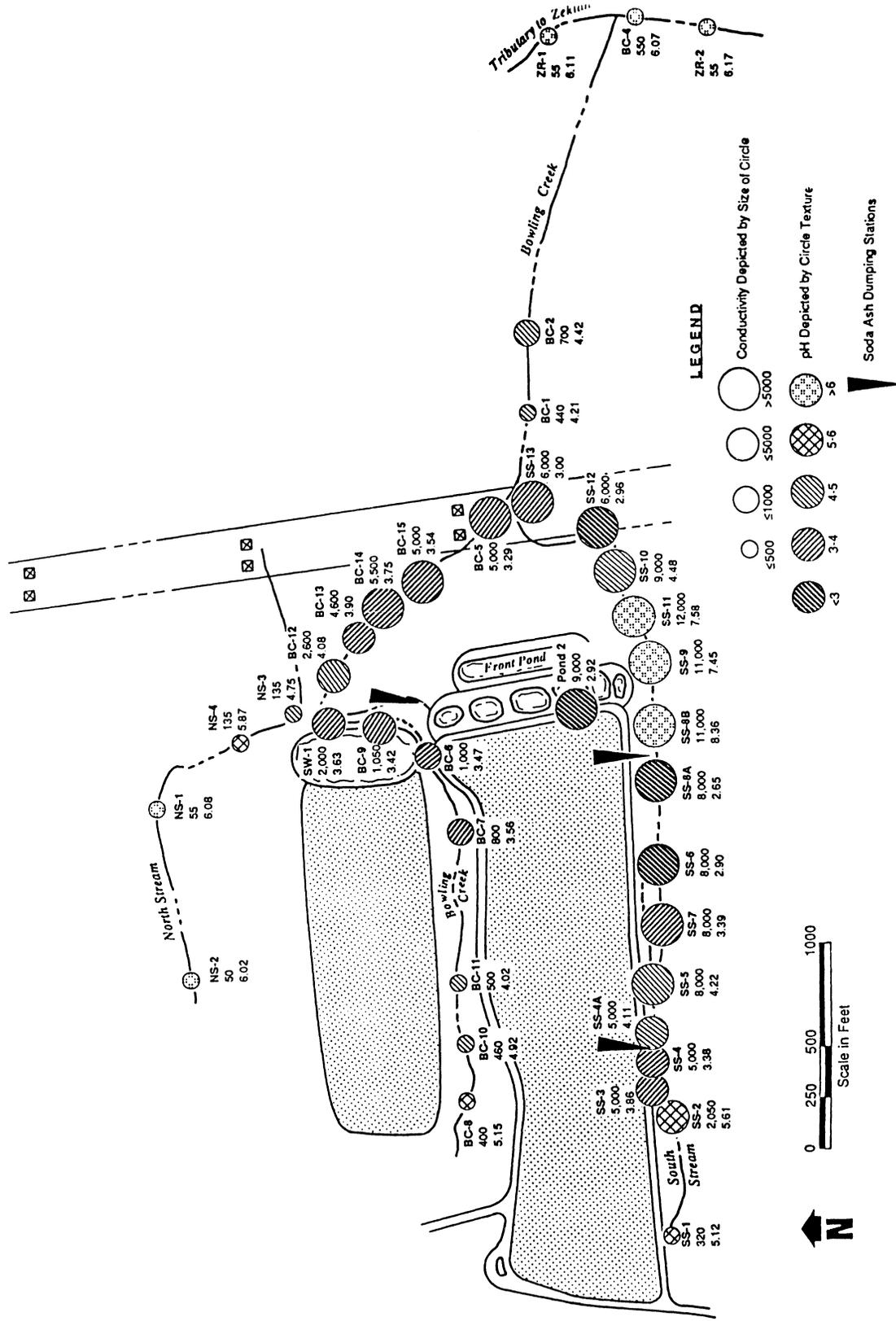


Figure 3-23 Specific conductance and pH of on-site surface waters (May 1998)

**Table 3-9**  
**Mean Concentrations and Standard Deviations of Major Constituents in the Pond Water and Bowling Creek**

Parameters	Pond	Bowling Creek					South Stream				
		BC-8	SW-1	BC-5	BC-1	BC-2	BC-4	SS-1	SS-2(f)	SS-9	SS-12
<b>Anions</b>											
Sulfate	2587 ± 974	146 ± 48	307 ± 65	1207 ± 938	510 ± 550	285 ± 230	24 ± 1.8	146 ± 101	2780	958 ± 384	1083 ± 873
Chloride	1179 ± 526	191 ± 80	205 ± 45	588 ± 384	265 ± 251	147 ± 115	12 ± 9	88 ± 25	720	457 ± 273	516 ± 392
Fluoride	4.1 ± 4.2	0.7 ± 0.4	0.9 ± 0.4	3.3 ± 4.0	0.9 ± 1.2	0.8 ± 0.9	0.3 ± 0.3	0.6 ± 0.4	0.1	1.5 ± 2.1	3.7 ± 4.5
Bromide	10.9 ± 10.5	0.6 ± 0.4	1.8 ± 0.8	5.8 ± 7.0	0.9 ± 1.2	0.7 ± 0.8	—	1.2 ± 1.0	— (c)	2.5 ± 1.2	1.8 ± 1.6
<b>Cations</b>											
Calcium	287.0 ± 115.3	42.3 ± 39.6	49.0 ± 10.5	137.2 ± 100.7	62.9 ± 60	43.3 ± 31.9	6.7 ± 3.4	23.8 ± 16.7	299	90.8 ± 35.7	103.6 ± 69.8
Magnesium	276.7 ± 98.5	23.3 ± 8.2	36.5 ± 8.5	128.7 ± 79.7	54.0 ± 60.5	33.5 ± 27.7	2.6 ± 2.1	18.8 ± 10.7	279	90.3 ± 39.2	109.8 ± 10.9
Sodium	634.4 ± 362.8	113.8 ± 41.8	115.1 ± 27.0	385.1 ± 292.8	157.6 ± 177.1	97.6 ± 75.8	6.9 ± 4.6	56.3 ± 30.3	1280	331.5 ± 253.9	354.9 ± 26 7.4
Potassium	164.6 ± 94.2	6.3 ± 2.3	13.9 ± 3.4	63.0 ± 59.9	22.9 ± 30.0	12.1 ± 11.8	1.8 ± 0.9	8.3 ± 6.3	177	24.2 ± 10.5	15.8 ± 8.7
<b>Metals</b>											
Aluminum	18.0 ± 15.6	1.6 ± 0.8	6.5 ± 2.3	12.2 ± 7.3	7.2 ± 8.8	4.6 ± 3.9	0.2 ± 0.2	0.1 ± 0.1	66.7	53.9 ± 1.6	16.6 ± 10.9
Iron	69.6 ± 106.2	0.4 ± 0.3	3.0 ± 2.0	2.7 ± 2.9	2.7 ± 4.6	1.7 ± 2.0	0.4 ± 0.3	0.6 ± 0.3	102	5.9 ± 2.8	8.0 ± 5.4
Manganese	10.4 ± 4.7	0.7 ± 0.3	2.6 ± 0.5	3.8 ± 1.2	2.9 ± 2.3	2.5 ± 1.9	0.3 ± 0.1	0.05 ± 0.5	12.5	0.36	0.23 ± 0.16
Nickel	0.29 ± 0.03	0.04 ± 0.04	0.09 ± 0.01	0.16 ± 0.02	0.08 ± 0.13	0.04 ± 0.06	—	0.06 ± 0.08	—	0.53	0.52 ± 0.42
Zinc	0.52 ± 0.06	0.10 ± 0.02	0.17 ± 0.05	0.31 ± 0.08	0.19 ± 0.20	0.17 ± 0.13	—	—	0.5	—	—
<b>General Indicators of Water Quality</b>											
Alkalinity	—	2 ± 2	—	—	—	—	5. ± 1	3 ± 3	—	3 ± 5	—
pH	3.58	4.8	3.59	3.46	3.83	3.92	5.26	4.87 (d)	3.95	3.31	3.11
Specific Conductance	5470 ± 2410	620 ± 150	1060 ± 260	3190 ± 2000	1450 ± 1590	960 ± 820	70 ± 30	630 ± 200	8000	2620 ± 1010	3070 ± 2660
Total Dissolved Solids	5780 ± 2360	580 ± 170	810 ± 140	2910 ± 2340	98 ± 1070	690 ± 540	100 ± 40	420 ± 230	6190	2305 ± 1265	2360 ± 1820

Mean concentrations calculated from all monitoring events.

All concentrations reported as mg/l, except specific conductance reported as µmhos/cm.

Constituent not detected above the detection limit.

Mean pH calculated as -log (mean hydrogen ion concentration).

The low pH conditions in Bowling Creek and South Stream were considered as potentially detrimental to aquatic organisms in these streams. The extremely low pH values (<3.0) measured in South Stream are associated with the precipitation of iron that was evident by the orange stains in South Stream, but not in Bowling Creek. Evidence of iron precipitation was also provided by the decreasing dissolved iron concentrations, as well as visible orange staining of the stream bottom. Since low pH and elevated dissolved iron concentrations in leachates were observed and the presence of mill rejects containing pyrites in Phase I/II fill was confirmed, it was inferred that the high acidity in the leachates was caused by the oxidation of pyrites in the ash fill. Additional field investigations during 1993 by the utility provided information showing that high conductivity values corresponded to the suspected location of the mill rejects/pyrite mound towards the South Stream. Therefore, it was concluded that the water quality impacts along South Stream may be due to the oxidation of pyrites in the mill rejects placed in Phase I/II area.

### ***Groundwater Quality Results (1988-89 Study)***

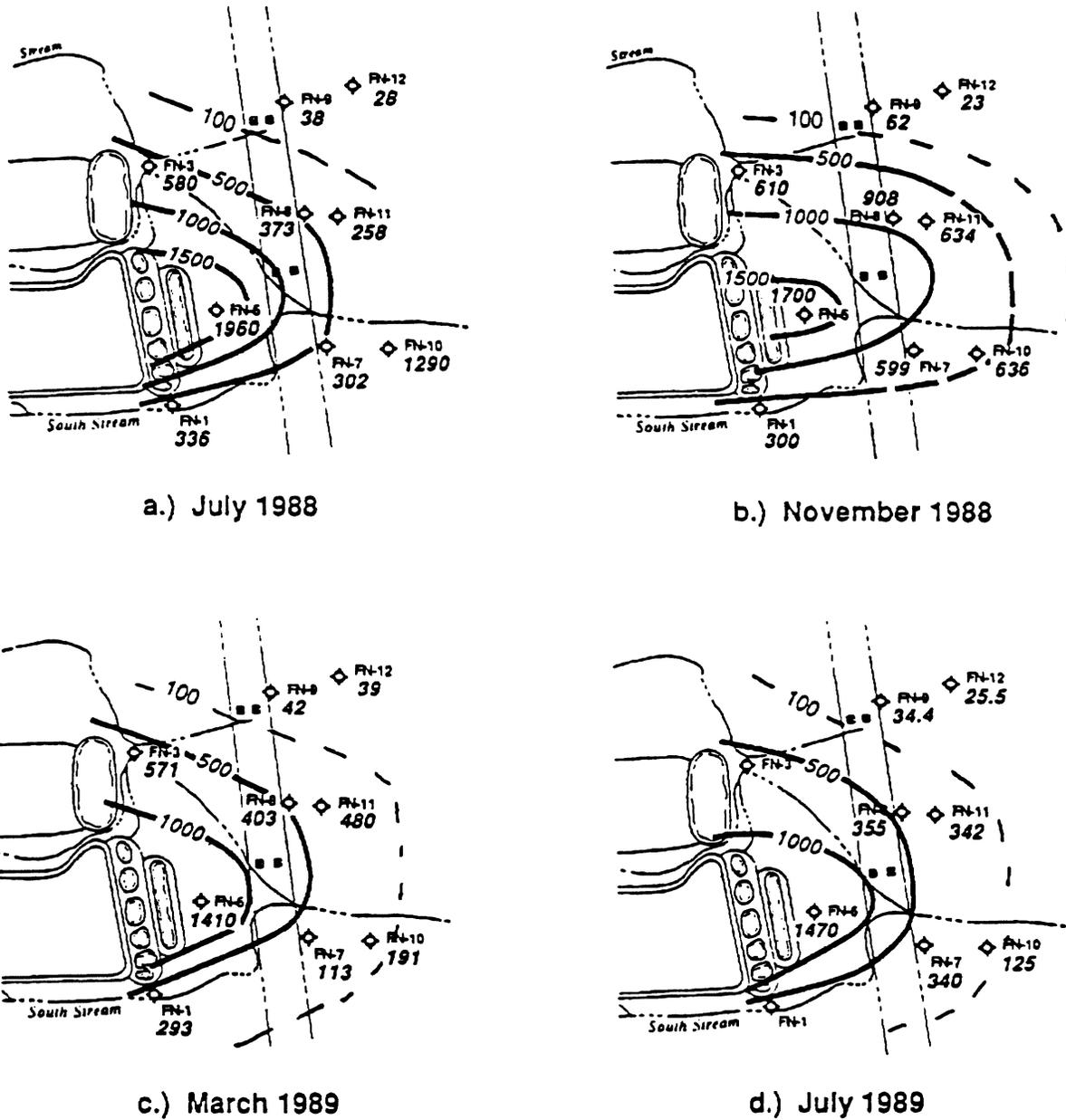
Groundwater quality results for the alluvial aquifer indicate that a plume of elevated sulfate concentration extends east from the sedimentation ponds in the alluvial aquifer as shown in Figure 3-24. Other leachate constituents such as calcium, TDS, iron, nickel and zinc have similar plume behavior. In general, the dissolved concentrations of leachate constituents decrease downgradient of the Phase I/II ash fill. The pH in these shallow groundwater wells also is acidic with elevated specific conductance values. These results suggest that leachates from the Phase I/II fill have migrated into the shallow aquifer resulting in a plume extending some 1500 ft downgradient to the east.

### ***Remedial Action by the Utility***

The utility company proactively decided to undertake remedial/mitigation actions with the immediate objective of protecting the South Stream. During 1993 and 1994 investigations were completed to design a leachate collection system and a cement-bentonite slurry wall installation around the pond system at the east end of the Phase I/II ash fill. In 1994-1995 the utility installed geomembrane and slurry wall barriers between South Stream and Phases I and II, along with a subsurface drain system to carry leachate to the treatment ponds. A clay-bentonite cap to reduce the overall volume of leachate generation was also completed. Finally, a wetland underlaid with limestone was constructed in South Stream. The clay bentonite cap was completed in the spring of 1997 and the drain became fully operational in early September 1997; partial operation was achieved in June 1995.

### ***Further Monitoring (1995-1999) and Assessment Studies***

The utility conducted a comprehensive monitoring program from March 1995 to August 1997 to (1) evaluate the overall impact of the site activities on water quality and biota in the intermittent streams draining the site and in the main stream Zekiah Swamp Run, and (2) evaluate changes in South Stream adjacent to the area where the mitigation measures were implemented.



**LEGEND**

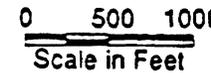
- ◆ Observation Well
  - 580 Sulfate Concentration (mg/l)
  - 1500— Sulfate Isoconcentration Line (mg/l), Dashed where Inferred
- 

 Scale in Feet

Figure 3-24 Sulfate isoconcentration map of the Alluvial Aquifer at FA site for four sampling events: a) July 1988, b) November 1988, c) March 1989, and d) July 1989

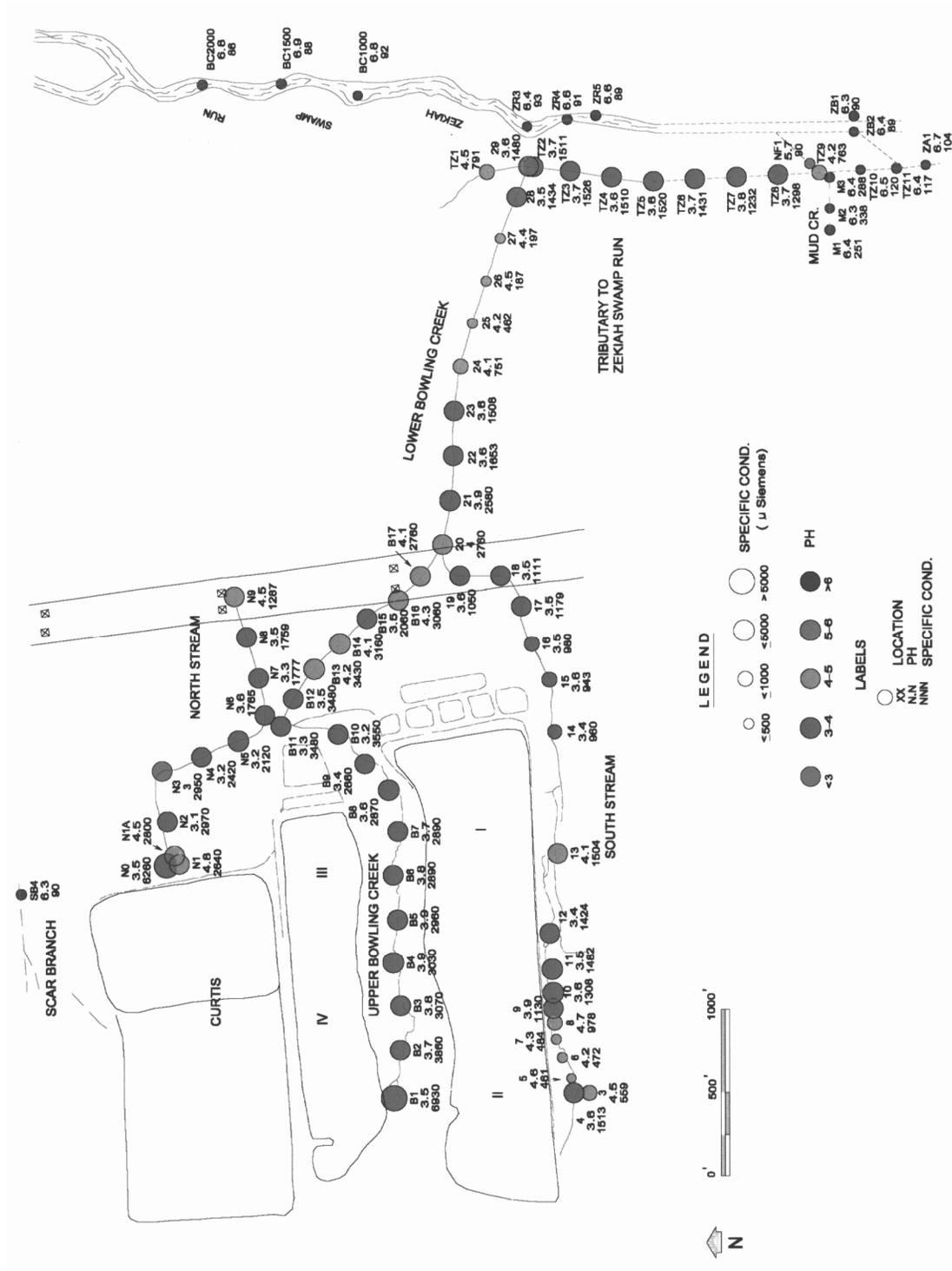
Figures 3-25 and 3-26 show the pH and specific conductance values for the surface water locations measured in May 1996 and in April 1997. These results indicate that there was a substantial extension, in 1996-1997, of the area of leachate influence from what was observed in 1988. North Stream, Tributary of Zekiah Swamp Run, and Mud Creek, which were unaffected in 1988, have since been affected. The utility postulates that the effects on the North Stream and the Tributary of Zekiah Swamp Run are related to the site expansion for ash storage (1997 utility report).

Quarterly groundwater monitoring data for the FA ash-storage site are now available from 1989 through January 1999 and have been used in completing further evaluation of the groundwater quality impacts at the site. Six chemical parameters have been used in statistically summarizing the quarterly groundwater monitoring data for the ten-year period. The statistical summary is shown in Table 3-10. This summary table indicates that the deeper Calvert Formation wells FN-4 and FN-2D are unaffected by the ash storage operations. This Calvert Formation groundwater is low in dissolved constituents with near neutral pH. Similarly, the shallow alluvial aquifer wells FC-1 and FN-4S located upgradient of the ash-storage show an ambient groundwater that contains low levels of chloride, sulfate and TDS with acidic pH conditions and moderate amount of total iron and total manganese. The chemical composition of both the shallow upgradient wells and the deep aquifer wells has remained constant throughout the monitoring period.

FN-1, FN-2S and FN-3 are groundwater monitoring wells located downgradient nearest to the Phases I through IV ash storage area. These wells are screened in the shallow alluvial aquifer. Time series plots for several parameters for each of these wells are included in the Appendix C to this report. Figures 3-27 to 3-30 show the time series plots for pH, sulfate and manganese respectively for these three wells. Based on these graphs and the statistical summary table, it is apparent that both FN-2S and FN-3 are acidic compared to well FN-1. However, these downgradient wells all show an increasing trend in sulfate concentrations over time. The sulfate levels in these wells are elevated as compared to the background wells. The statistical summary Table 3-10 also indicates that these wells have elevated concentrations of chloride, total iron, total manganese and TDS, implying that the Phases I-IV have impacted the groundwater quality downgradient of the ash storage area.

Similar time series graphs are shown in Figures 3-30 through 3-32 for groundwater wells FC-2 and FC-3, which are screened in the alluvial aquifer downgradient of the new Curtis phase. These time series plots and the statistical summary (Table 3-10) show elevated concentrations of sulfate, TDS and chloride with a highly acidic pH. Total iron and total manganese concentrations are only moderately elevated. The utility has indicated that no mill rejects containing pyrites have ever been placed in the Curtis phase of the FA facility. Therefore, these evaluations of the monitoring results indicate that the alluvial aquifer downgradient of Phases I through IV and the Curtis Phase are all impacted by the acidic fly ash leachate with no discernable signature of pyrite oxidation from Phases I and II. In fact, the available chemical composition data for the various leachates (Table 3-11) from the FA facility show similar chemical characteristics as is seen in the groundwater quality data in these five wells.





**Table 3-10**  
**Statistical Summary of Up and Downgradient Wells at FA Site**

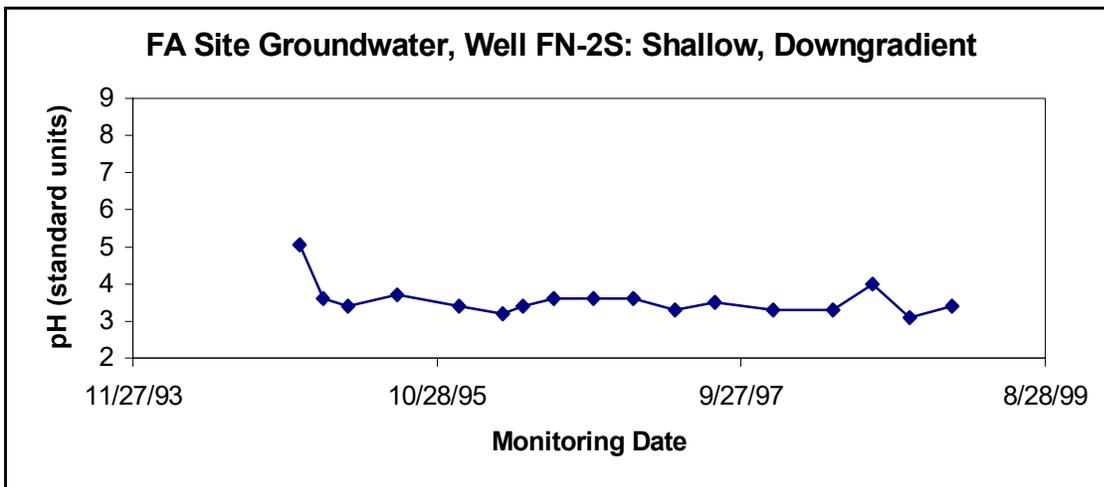
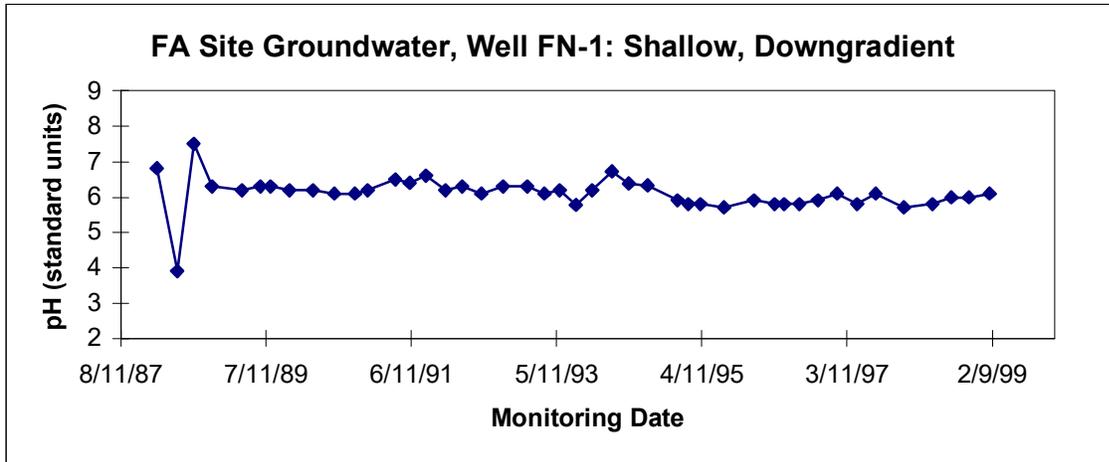
	<b>Chloride mg/L</b>	<b>Total Iron mg/L</b>	<b>Total Manganese mg/L</b>	<b>Sulfate mg/L</b>	<b>TDS mg/L</b>	<b>pH S.U.</b>
<b>Upgradient Wells:</b>						
<b>FC-1:</b>						
Count	12	6	7	12	12	11
Mean	38.5	84.8	0.56	2	109	4.9
(Min-Max)	(25-65)	(40-160)	(0.05-1.1)	(0.5-4)	(68-150)	(4.4-5.8)
<b>FN-4S:</b>						
Count	7	7	7	9	7	9
Mean	26.4	1.7	0.05	4	117	5.7
(Min-Max)	(22.-31)	(0.2-3.6)	(0.04-0.06)	(3-6)	(98-130)	(5.2-6.4)
<b>FN-4:</b>						
Count	42	37	38	43	43	42
Mean	3.1	1.8	0.05	3	188	7.6
(Min-Max)	(0.25-6)	(0.08-24.1)	(0.02-0.15)	(0.5-11)	(100-250)	(7-8.3)
<b>Nearest downgradient:</b>						
<b>FN-1:</b>						
Count	45	39	40	44	45	44
Mean	503.8	11.3	1.22	1004	2490	6.1
(Min-Max)	(95.7-950)	(0.17-82.5)	(0.18-7)	(150-1750)	(732-4174)	(3.9-7.5)
<b>FN-2S:</b>						
Count	18	12	13	18	18	17
Mean	183.9	163.8	2.47	1521	2395.0	4
(Min-Max)	(110-330)	(65.8-250)	(1.57-3.1)	(890-2000)	(1510-3000)	(3.1-5.1)
<b>FN-3:</b>						
Count	45	39	40	45	45	44
Mean	363.9	52.5	2.42	416	1185	4.1
(Min-Max)	(24.1-740)	(0.4-130)	(0.9-5.4)	(140-1300)	(566-2600)	(3.4-4.8)
<b>FC-2:</b>						
Count	12	6	7	12	12	11
Mean	1038.3	3.7	3.63	935	2842	3.8
(Min-Max)	(470-1400)	(1.6-7.4)	(1.8-13)	(340-1900)	(1500-4500)	(3.5-4.1)
<b>FC-3:</b>						
Count	12	6	7	12	12	11
Mean	1833.3	8.9	4.41	2283	5783	3.9
(Min-Max)	(1100-2800)	(3.7-19)	(3.5-5.6)	(1400-3400)	(4100-8600)	(3.7-4.2)

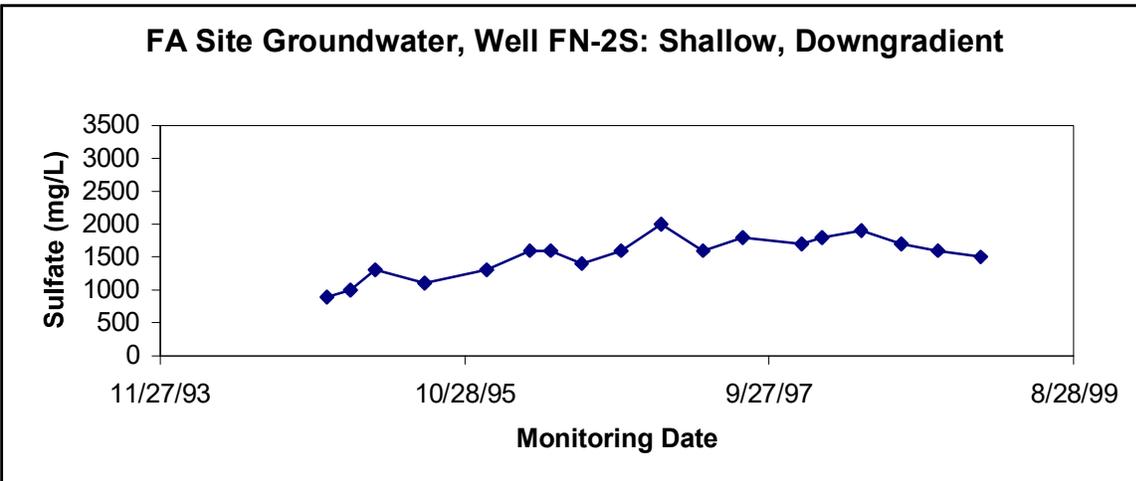
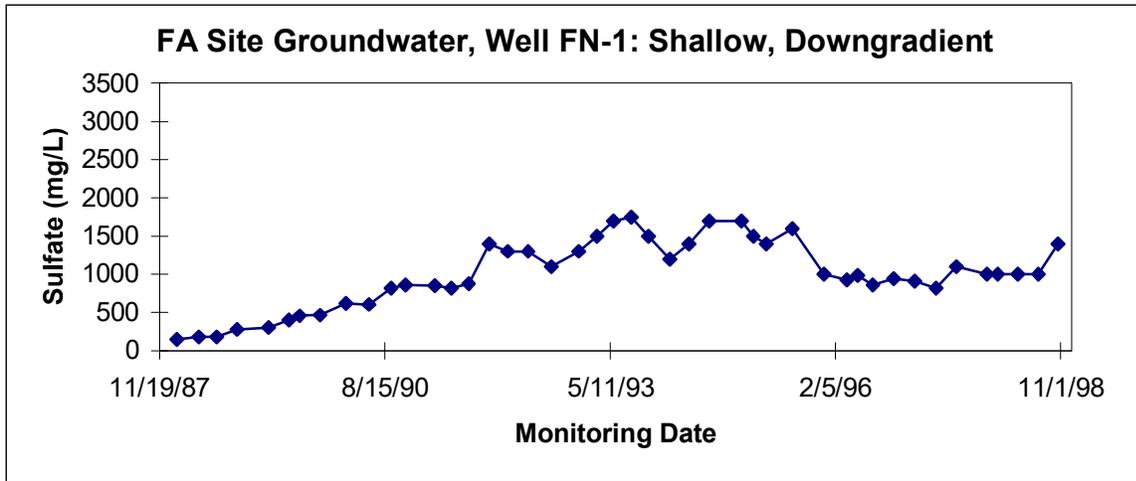
\* Wells located in calvert aquifer. All other wells are located in the alluvial aquifer.

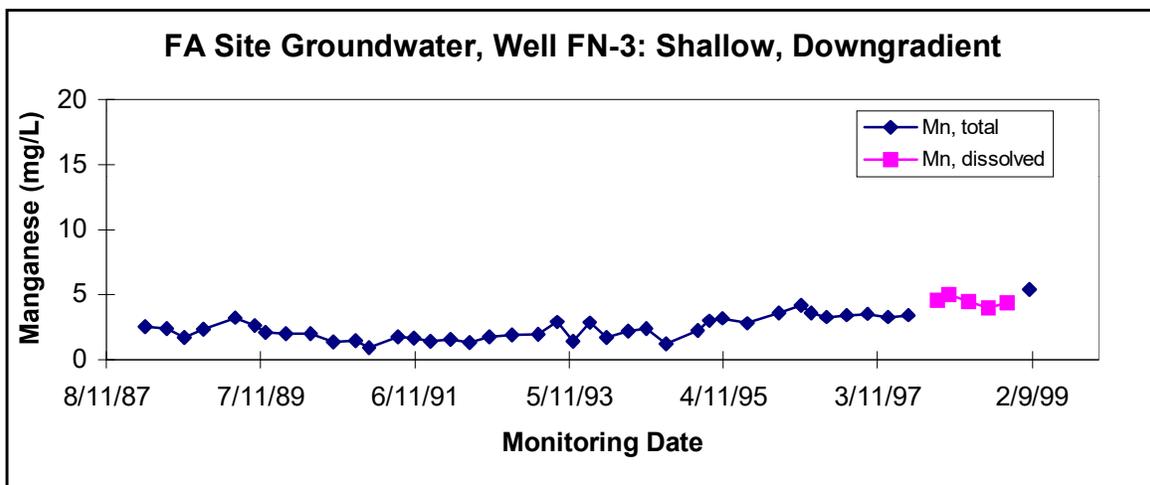
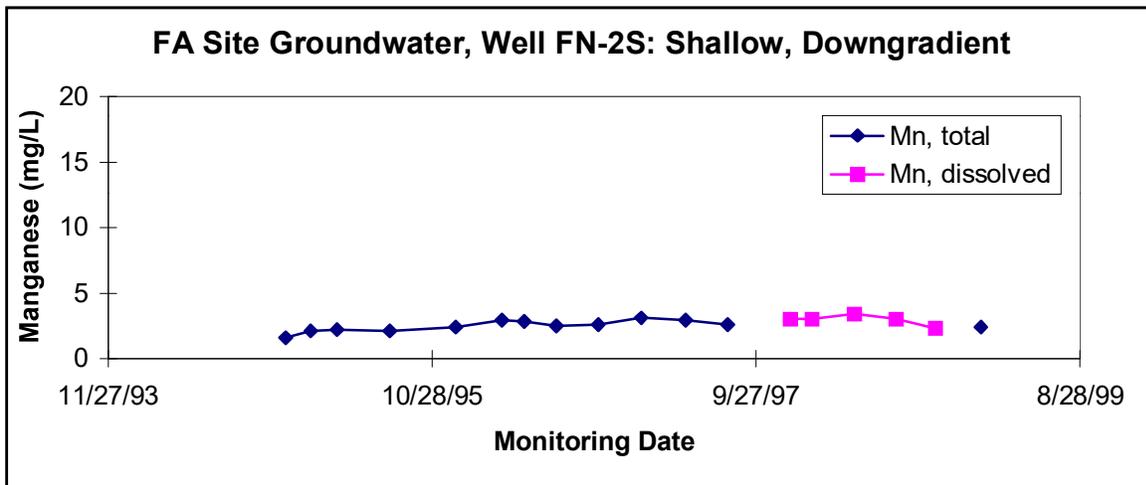
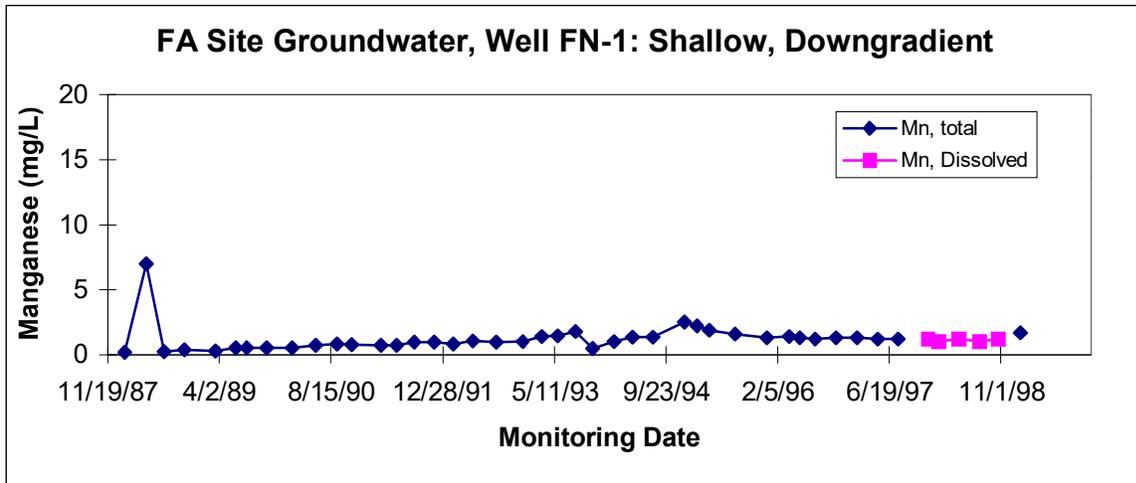
**Table 3-10 (Continued)**  
**Statistical Summary of Up and Downgradient Wells at FA Site**

	<b>Chloride mg/L</b>	<b>Total Iron mg/L</b>	<b>Total Manganese mg/L</b>	<b>Sulfate mg/L</b>	<b>TDS mg/L</b>	<b>pH S.U.</b>
<b>Nearest Downgradient: (continued)</b>						
<b>FC-4:</b>						
Count	12	6	7	12	12	11
Mean	110.7	0.2	0.09	134	445	5.0
(Min-Max)	(48-220)	(0.05-0.3)	(0.05-0.16)	(35-260)	(180-800)	(4.6-5.4)
<b>FN-2D*:</b>						
Count	25	25	25	25	25	25
Mean	2.6	5.4	0.04	7	242	7.4
(Min-Max)	(1.0-5)	(0.025-80.5)	(0.005-.17)	(0.5-18)	(206-272)	(6.9-8)
<b>Further Downgradient:</b>						
<b>FN-6:</b>						
Count	44	38	39	44	44	43
Mean	792.9	50.3	5.14	1739	3879	4.6
(Min-Max)	(160-1200)	(2.3-200)	(2.8-7.22)	(200-2400)	(720-5256)	(3.4-6.0)
<b>FC-6S:</b>						
Count	7	7	7	9	7	9
Mean	94.4	38.6	0.28	16	226	4.6
(Min-Max)	(44-140)	(6.3-110)	(0.16-0.45)	(12-24)	(160-310)	(4.2-5.2)
<b>Furthest Downgradient:</b>						
<b>FN-10:</b>						
Count	7	7	7	9	7	9
Mean	99.9	9.2	2.86	348	483	5.0
(Min-Max)	(18-310)	(4.6-17)	(1.2-5.4)	(45.-1300)	(120-1300)	(4.1-4.8)
<b>FN-12:</b>						
Count	7	7	7	9	7	9
Mean	99.3	17.1	3.20	101	340	5.4
(Min-Max)	(76-120)	(6.6-31)	(2.4-3.9)	(68-170)	(310-400)	(4.7-5.5)

\* Wells located in calvert aquifer. All other wells are located in the alluvial aquifer.







**Figure 3-29**  
Time-series plot for manganese at FN-1, FN-2S, and FN-3 wells

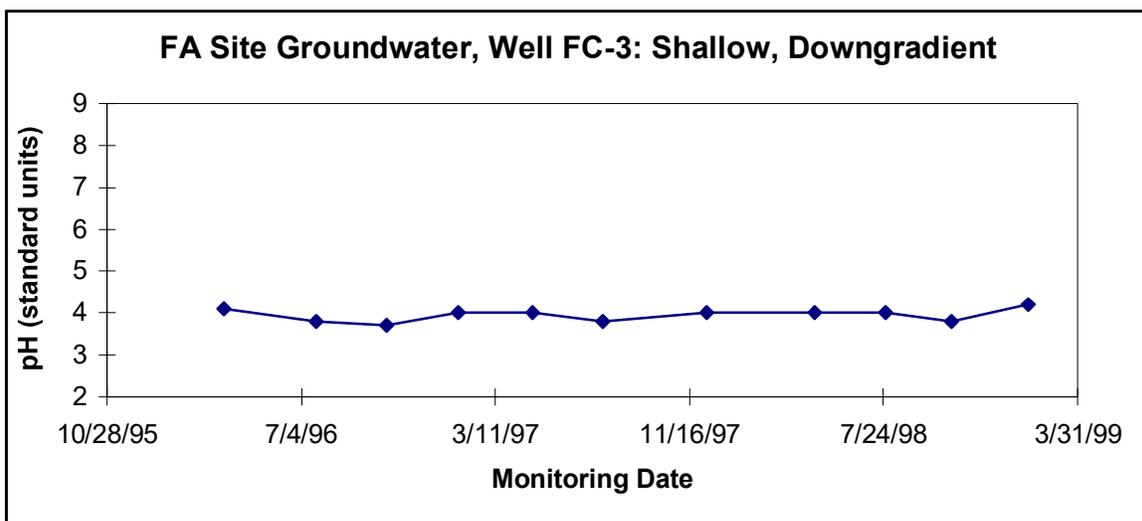
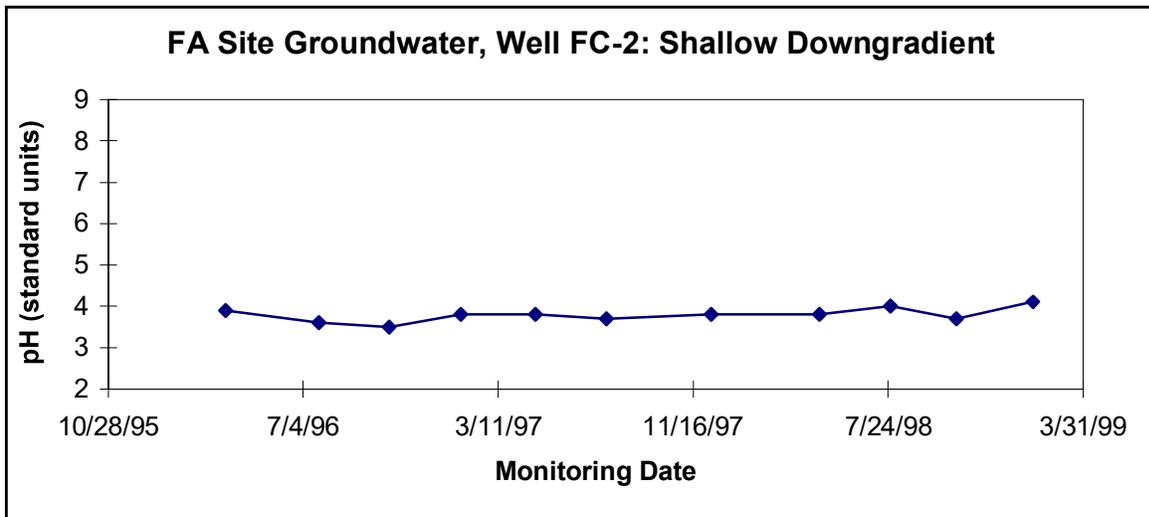


Figure 3-30  
Time-series plot for pH in FC-2 and FC-3 wells

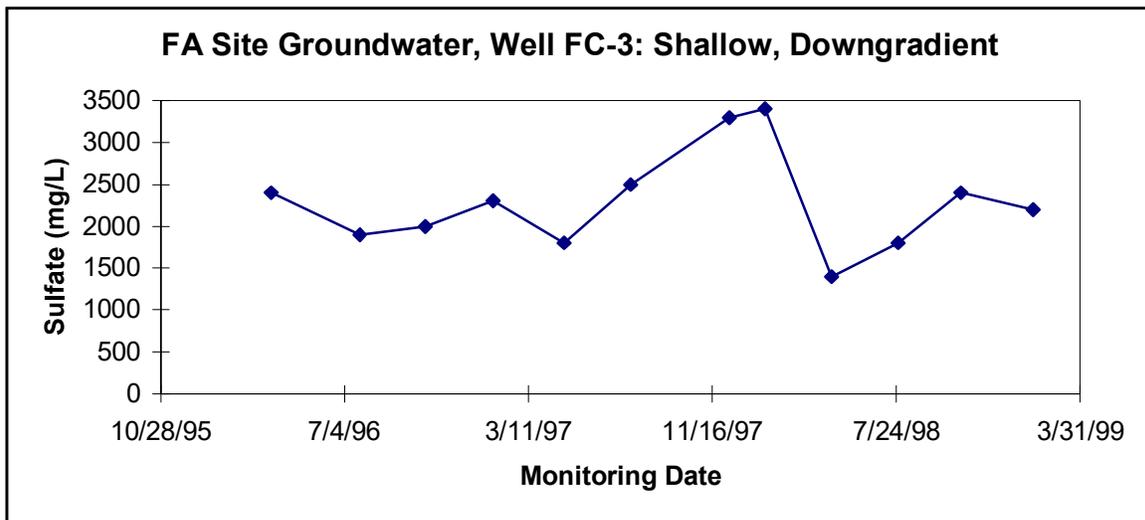
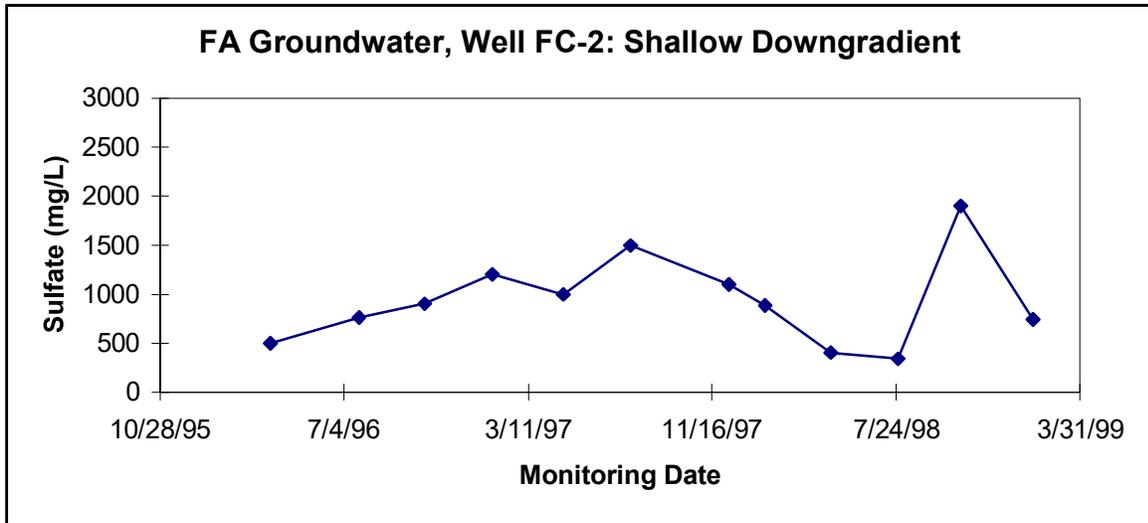
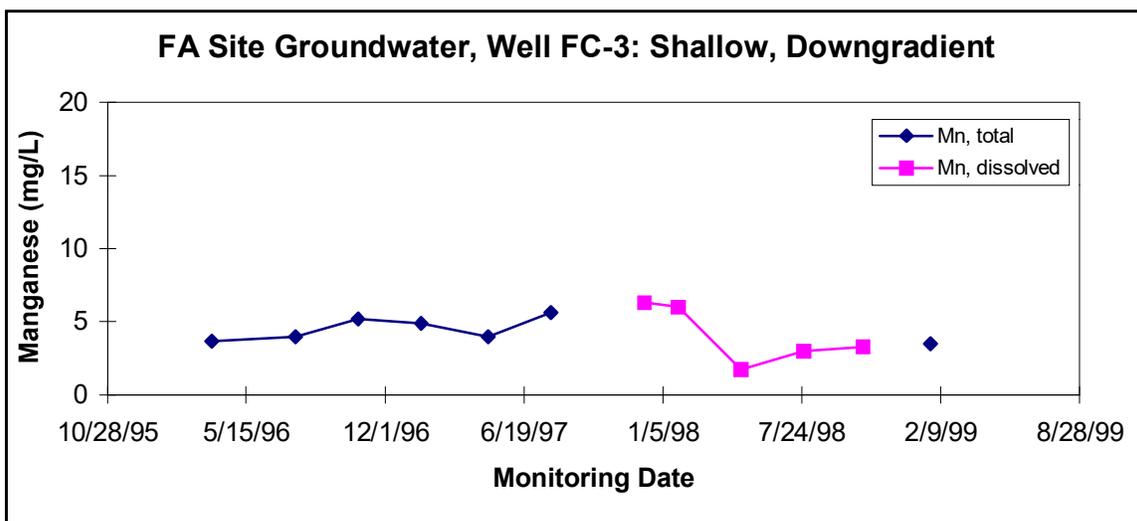
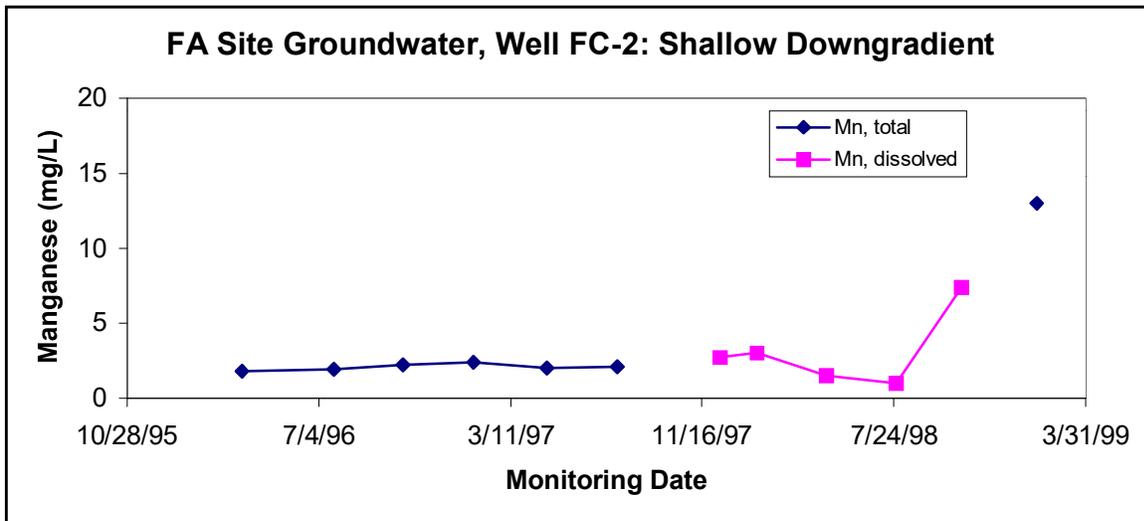


Figure 3-31  
Time-series plot for sulfate at FC-2 and FC-3 wells



**Figure 3-32**  
Time-series plot for manganese at FC-2 and FC-3 wells

**Table 3-11**  
**Leachate Analysis Results for FA Site**

Date	1981	1988-891	Unknown	Dec. 1996	Sept. 1997
	EP Test On Fly Ash	Pond 2 Water	ASTM Water Leach Test	Phase I/II Leachate Drain	Curtis Leachate Drain
<b>Parameters</b>					
Sulfate	182-211	2587	–	3500	–
Chloride	<.08 - 211	1179	–	650	–
Fluoride	20-28	4.1	–	–	–
Bromide	–	10.9	–	–	–
Calcium	–	287	–	–	–
Magnesium	–	276.7	–	–	–
Sodium	–	636.4	–	–	–
Potassium	–	164.6	–	–	–
Aluminum	–	18	–	38.3	20
Iron	0.017-0.28	69.6	–	450	42(29)*
Manganese	0.16-0.19	10.4	–	15.8	14
Nickel	–	0.29	0.074	0.58	–
Zinc	–	0.52	–	–	–
Alkalinity	–	–	–	–	<1
Acidity	–	–	–	–	320
PH	–	3.58	4.15	–	–
Spec. Cond.	–	5470	–	5140	–
TDS	–	5780	–	–	–

\* Total Fe (Fe<sup>2+</sup>); - data not available.

All concentrations reported mg/l; specific conductance reported as  $\mu$ mhos/cm.

The statistical summary table (Table 3-10) and the time series graphs shown in Appendix C for downgradient wells FN-6, FN-10 and FN-12 also show acidic pH and increased levels of chloride, sulfate, TDS, manganese and iron. These increases in the further downgradient wells are of lesser magnitude, indicating that leachates from the FA Phase I-IV have resulted in impacts on the alluvial aquifer. The new Curtis phase ash leachate impacts are restricted to a much shorter downgradient distance.

### ***Summary and Conclusions for FA Site***

During initial investigations, it was assumed that the acidic conditions in the groundwater and the surface water along with the elevated levels of sulfate, iron, manganese and TDS were due to the oxidation of pyrites in the Phase I and II ash storage area. However, the long term groundwater quality monitoring results indicate that the acidic ash leachates may be the source of the groundwater and surface water impacts observed at the site with very little or no contribution from pyrite placed in the Phase I/II ash fill.

The utility has employed significant resources in undertaking mitigation and restoration efforts for improving the water quality in the surrounding areas. Continued monitoring and further mitigation measures are being implemented to document the effectiveness of the restoration actions.

# 4

## ACID-BASE ACCOUNTING AND NEUTRALIZATION POTENTIAL

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### Methods for Estimating Acidity and Neutralization Potential

A number of test methods have been developed to estimate acid generation potential and acid neutralization capacity of solids. These methods fall into two categories, namely: static tests and kinetic tests. Many of these methods have been developed by the coal and metal mining industry for identifying the geochemical nature of mining wastes and for assessing their potential for oxidation of sulfide minerals resulting in acid mine drainage. Several examples of these methods are discussed in this section. The application of these methods to coal ash and mill rejects is also illustrated. Acid-base accounting is intended as a screening method for estimating the amount of acid that can be generated and the quantity of acid that a material can neutralize.

#### *Static Methods*

One of the early methods of acid-base accounting was developed by Sobek et al. (1978) for coal overburden materials and mine spoils. Sobek's method requires the measurement of total sulfur and the available neutralizing bases. The neutralization potential is estimated using a hot hydrochloric acid extraction and NaOH titration and is expressed as calcium carbonate equivalents. The total sulfur is measured and then converted to equivalents of calcium carbonate needed to neutralize the inferred acidity, assuming that all the sulfur is in the pyritic form and could potentially oxidize. This conversion is based on a relationship of 1 weight percent sulfur needing 31.25 tons of  $\text{CaCO}_3$ /1000 tons of material for neutralization. The neutralization potential based on the hot acid extraction and titration is then subtracted from the amount needed to balance the acidity to determine the deficiency. If the deficiency or net acid producing potential (NAPP) is more than 5 tons of  $\text{CaCO}_3$ /1000 tons of material, the generation of acidic leachates is considered possible. However, the criteria of 5 tons NAPP was tested on Pennsylvania coal mines, and found not to be a good predictor of acidic leachate. A qualitative method of prediction using the same inputs as Sobek's method was then developed, classifying acidic strata as strata with more than 0.5 percent sulfur and less than (15.6 tons of  $\text{CaCO}_3$ /1000 tons of material) of neutralization potential (Brady and Hornberger, 1990).

More recently, the relationship of 1 weight percent sulfur to 31.25 tons of calcium carbonate was thought to underestimate the total acidity eventually generated (Cravotta et al., 1990). It was suggested that instead of using a relationship of 1 g of sulfur to 3.125 g  $\text{CaCO}_3$  based on 1 mole of  $\text{FeS}_2$  being neutralized by 2 moles of  $\text{CaCO}_3$ , the relationship should be based on a need for 4 moles of  $\text{CaCO}_3$  for neutralization to provide a buffer. Both approaches were tested by Brady et al. (1994) on Pennsylvania coal mines. The best prediction of acidic leachates was based on

using a 31.25 multiplier with total sulfur. Strata with a NAPP of 5.1 tons of  $\text{CaCO}_3$ /1000 tons of material or less did not produce acidic leachate. The comparison of predictions and actual data showed that strata with 1 to 3 percent carbonates did not generate acidity. Suggested reasons include the reduced rate of bacterial oxidation at more alkaline pH values and the lower solubility of  $\text{Fe}^{3+}$  in higher pH solutions.

Other classification methods have used a ratio of acid generating capacity to neutralization potential to estimate the likelihood of acidic leachate. A fixed ratio defining when acidity is likely has not proven accurate in the field (Morin and Hutt, 1994). Part of the reason for differences between field results and predictions are the assumptions associated with the underlying approach. These include the following: 1) all sulfur occurs as sulfide, 2) sulfide oxidizes completely to sulfate, 3) pyrite is the only mineral that is oxidized, 4) molecular oxygen and water are the only oxidants, 5) all iron oxidizes to the ferric state ( $\text{Fe}^{3+}$ ), and 6) all ferric iron then precipitates as  $\text{Fe}(\text{OH})_3$ . These assumptions do not always hold true. Moreover, another factor that influences neutralization potential is the presence of weatherable minerals containing bases such as feldspars. Effectiveness of common feldspars to neutralize acidity was determined by Morin and Hutt (1994). Their work showed that dissolution of feldspars could provide more neutralization capacity than calcite does for the same amount of material.

Field data from several Canadian mines were used to compare the prediction of static tests based on ratios of cations (Ba, Ca, Mg, Mn, and Sr) to sulfate with the results of kinetic tests (Morin and Hutt, 1994). The results of kinetic tests using humidity cells for extended periods of 18 to 90 weeks were conducted showing that ratios of 1.3 to 4.2 (cations to sulfate) were required at these mines to maintain neutrality for long periods, compared to predicted ratios of 1 to 2. At some sites, cations were more readily leached, compared to the oxidation rate of the sulfides.

Another comparison of acid-base accounting predictions and laboratory results was conducted by Renton et al. (1988). The authors also pointed out problems relating to the underlying assumptions of the simplified acid-base accounting approach, namely that 1) all sulfur is present as the iron disulfide minerals, i.e., pyrite or marcasite, 2) all these minerals will react to form acid, and 3) all the carbonate minerals will react to provide neutralization. Siderite ( $\text{FeCO}_3$ ) is an example of a carbonate mineral that does not provide neutralization in the long-term (Williams et al., 1982) but can still provide short-term neutralization, especially when finely disseminated as cements or coatings (Morrison et al., 1990).

Another simple static test to estimate the acid generation potential is to measure the saturated paste pH and conductivity of representative samples of crushed solids. The crushed solids are saturated with enough distilled water to create a paste and equilibrated for a period of 12 to 24 hrs. Both the pH and the EC of the paste are then determined. A material with a paste pH of less than 4 indicates that the material is naturally acidic (Environment Australia, 1997).

Recently, a new static test has been advanced. This method estimates the net acid generation potential directly. A strong oxidizing reactant, such as hydrogen peroxide, is added to the test material and the oxidation reaction is allowed to be completed. The solution pH and acidity are then measured. If the measured pH is greater than 4, then the material is classified as non-acid forming. If the measured pH is less than 4, then the material has the potential for acid generation.

It should be noted that all these static test methods are not sufficiently definitive and, therefore, are best used as screening tools for acid-base accounting.

### ***Kinetic Methods***

Geochemical kinetic tests are intended to simulate weathering and oxidation of materials over time when exposed to air and moisture. Columns and humidity cells are methods most often used in laboratory-based kinetic tests. These kinetic tests typically take 8 to 10 weeks although longer test periods have also been utilized.

Most static acid-base accounting approaches do not consider differences in the rates of acid production versus neutralization. An alternative approach was developed by Renton et al. (1988) using the sulfur content, a rate constant derived from a simulated leaching experiment, and the mass of the material. The method was developed for rocks associated with coal, such as carbonaceous shale waste from a coal cleaning plant. The rate constant for a given material was derived by first leaching a sample for 24 hours with water to remove already weathered products, then sequentially leaching a sample with water for 24 hours and oven drying it for 14 days, with this cycle repeated four times. The leachate after each cycle was analyzed for sulfate. This sulfate was considered to represent a measure of acid generated by oxidation. The lab experiment showed that after a 56-day period 85.6 percent of the sulfur was unreacted. A 257-day small-scale field experiment was also conducted for comparison to the laboratory test. The field test showed that about 35 percent of the iron sulfide minerals had not reacted after 155 days and did not react completely even after 257 days (Renton et al., 1988). The data were used to derive a first-order rate constant for acid production. The rate constant for acid production from the laboratory (-0.0043/day) was comparable to that from the field experiment (-0.005/day). This rate constant means that after 200 days about 37 percent of the sulfur would be unreacted. The method was tested on a larger scale at a 350-ton backfill site. This method only addresses the acid production step.

Another kinetic test method is an extended wet-dry cycle test (Lappakko, 1988). The effects of elevated temperature and particle size on leaching test results have also been evaluated (Lappakko et al., 1995). The wet-dry cycle test required crushing of the sample to -100 mesh. Samples were placed in a two-stage filter unit and stored in a temperature and humidity-controlled environment. Each week the samples were leached with 20 ml of distilled water for a 24-hour period. The leachate was analyzed for pH, alkalinity, conductivity, sulfate, calcium, and magnesium. The tests were continued for 132 weeks. The results were used to estimate neutralization potential using both calcium and magnesium. Most other methods use only calcium. The release rates of calcium, magnesium, and sulfate were plotted. Comparison of the leaching rates in conjunction with the mineralogy can help interpret the observations and their application to field conditions.

Simulated weathering experiments have been used by Hornberger et al., (1981) and Morrison et al., (1990) to estimate acid production and neutralization of coal and overburden materials. A study on coals and shales in Pennsylvania showed that when carbonate content was greater than 0.01 percent, the amount of acidity, sulfate, and iron leached was substantially less (Morrison et al., 1990). For example, coal and shale with less than 3.25 percent sulfur and more than 0.01 percent carbonate generated essentially no acidity at all (Figure 4-1). Samples were also tested

to show the variation in acidity produced depending on the form of the pyrite. For example, less acidity is produced when pyrite is in a crystalline form rather than in a framboidal form.

Guidelines for prediction of acid drainage conditions have recently been developed by Price et al. (1997a,b) for use in coal and heavy metal mines in British Columbia. The guidelines recommend use of a combination of static and kinetic tests along with detailed characterization of materials and environmental conditions. The static tests suggested include measurements of trace elements as total and soluble concentrations; acid-base accounting including measurements of total sulfate, and sulfide sulfur; determination of bulk and carbonate neutralization potential; pH measurement; and characterization of mineralogy. Kinetic tests suggested include pre- and post-weathering characterization, humidity cells, on-site test pads, wall washing stations, and site drainage monitoring. As a screening criteria, Price et al. (1997a) suggested that if the material contains less than 0.3 weight percent sulfide-sulfur and a pH greater than 5.5, there would not be an acid generating concern.

Other criteria have been developed using the neutralization potential to acid ratio (NPR). If NPR is greater than 4, no further testing is needed. Ratios less than 1 indicate potential for acid generation (Price et al., 1997b). Samples with ratios between 1 and 4 are recommended for further testing to determine the relative rates of acid generation and neutralization. Humidity cells are suggested as a method of predicting rates, but these conditions do not duplicate true field conditions, partly due to the increased fine-grained material in most tests.

### ***Application of Methods to Coal Ash and Mill Rejects***

The above methods were designed for use at coal and metal mines. The composition and mineralogy of coal ash and mill rejects differ from these materials in a number of ways. For example, only a portion of the sulfur in coal ash and mill rejects is pyritic sulfur, so use of total sulfur can result in an overestimate of acid generation potential. This is also true for coal mines as was pointed out in the previous pages in this report. All coal ashes contain some sulfur, but many ashes are alkaline and would not, therefore, produce net acidity (Figure 4-2). Mill rejects can generate acidity depending on their pyritic sulfur content and composition. However, as evident from the chemical data presented in Section 2 of this report, not all rejects contain pyritic sulfur (Figure 4-3). Calcite and dolomite were detected in some mill reject samples based on the mineralogical analyses, and calcite is known to be present in coal ash (EPRI, 1986). A substantial amount of neutralization in ash is supplied by the dissolution of calcium and magnesium oxides. Because coal ash has undergone combustion, it is an oxide-dominated system. Availability of calcium and magnesium oxides for neutralization is enhanced by the small particle size of coal ash. Other minerals such as feldspars are also present in both mill rejects and coal ash, and can contribute to neutralization capacity of ash as well.

Mill rejects contain calcium, although the content is variable (Figure 4-4a). In general, bituminous coals have more pyritic sulfur and less calcium; the calcium in the mill rejects does not increase as the sulfur content in the coal increases (Figure 4-4b). As seen in Table 2-11, the

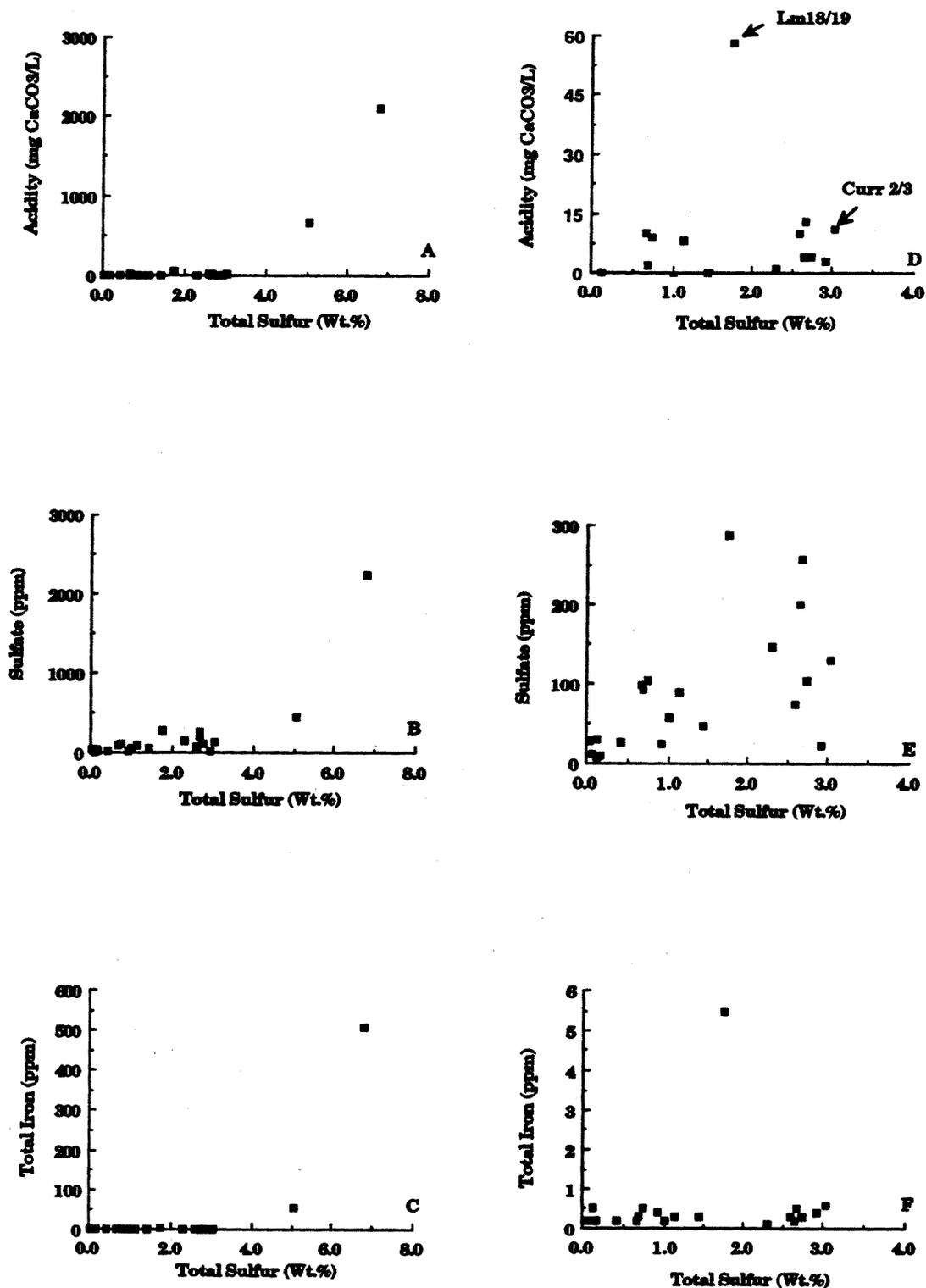


Figure 4-1  
 Examples of relationships between leachate chemistry and total sulfur for shales and coals containing greater than 0.01 percent carbonate carbon (after Morrison, 1988 and 1990).

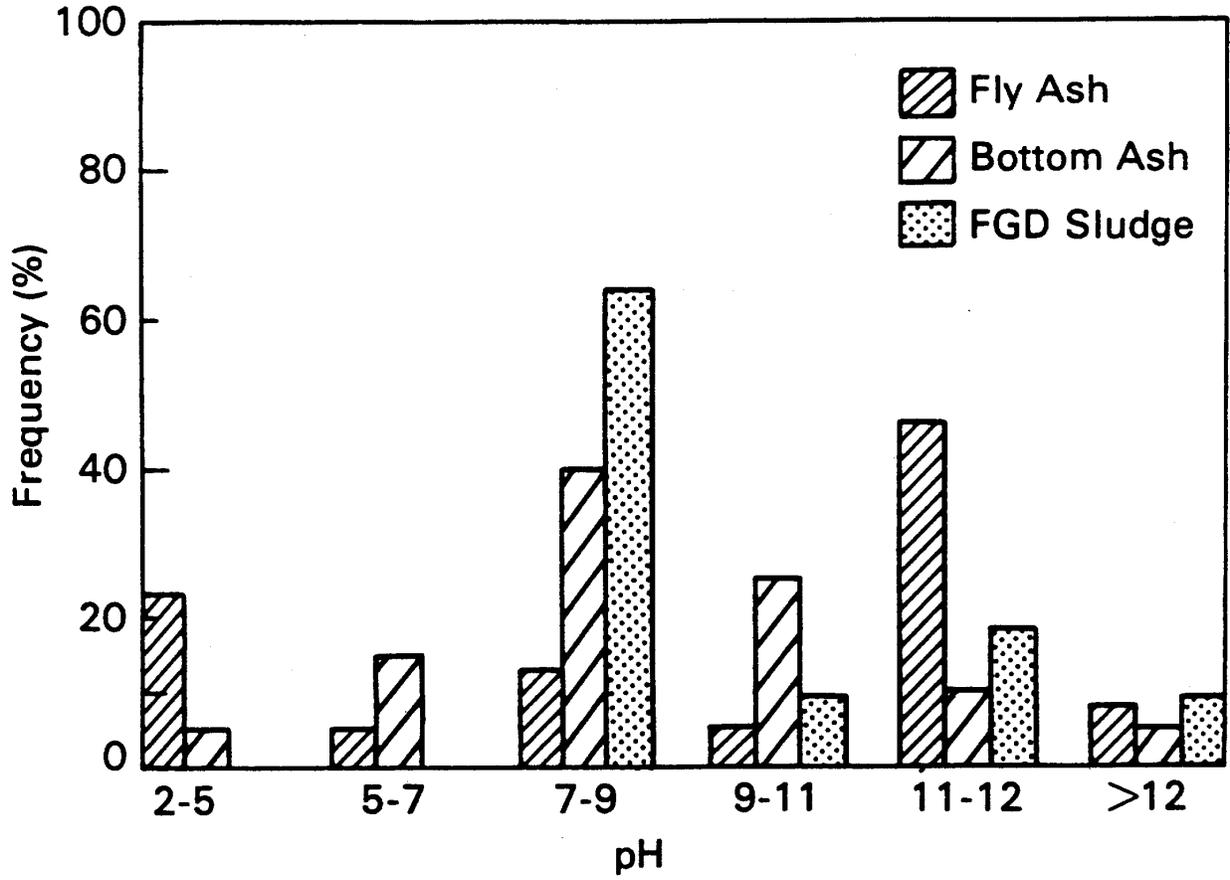


Figure 4-2  
Variation of pH of fly ash, bottom ash, and FGD sludge

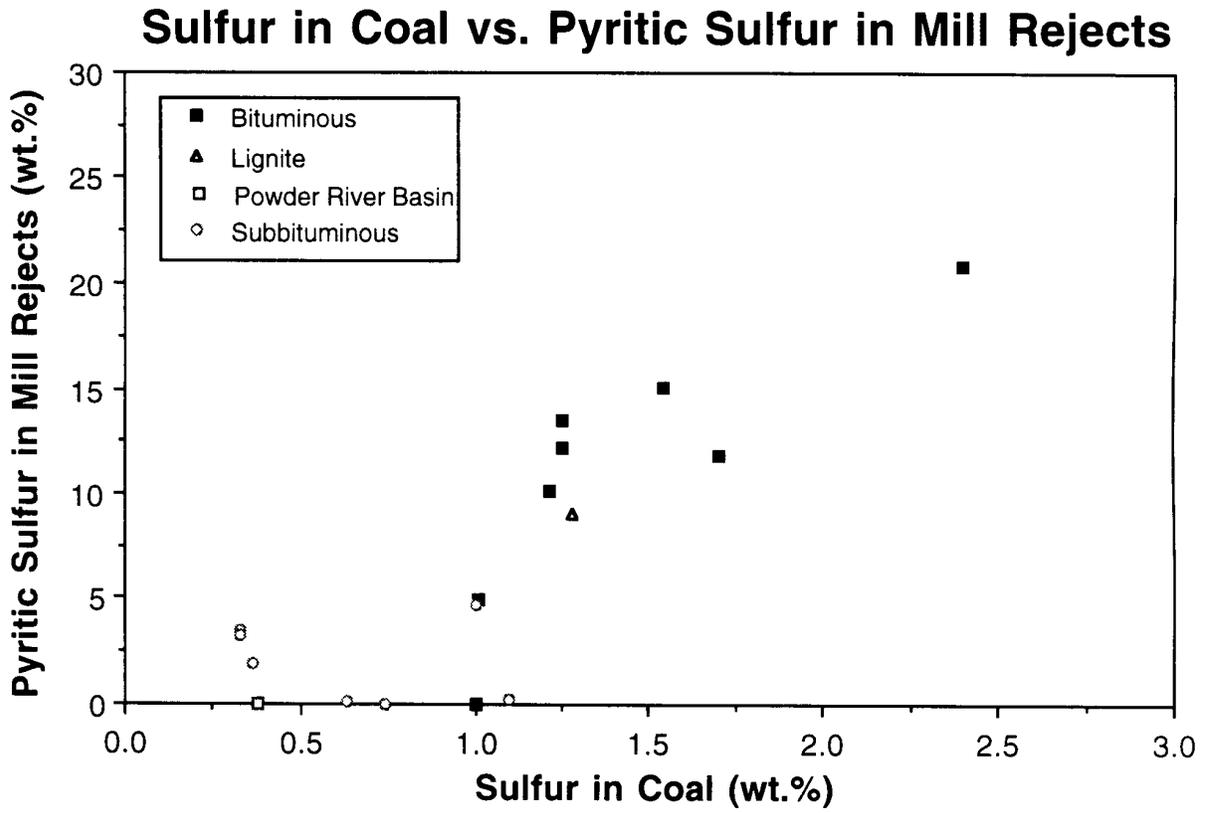


Figure 4-3  
Comparison of sulfur in coal and mill rejects

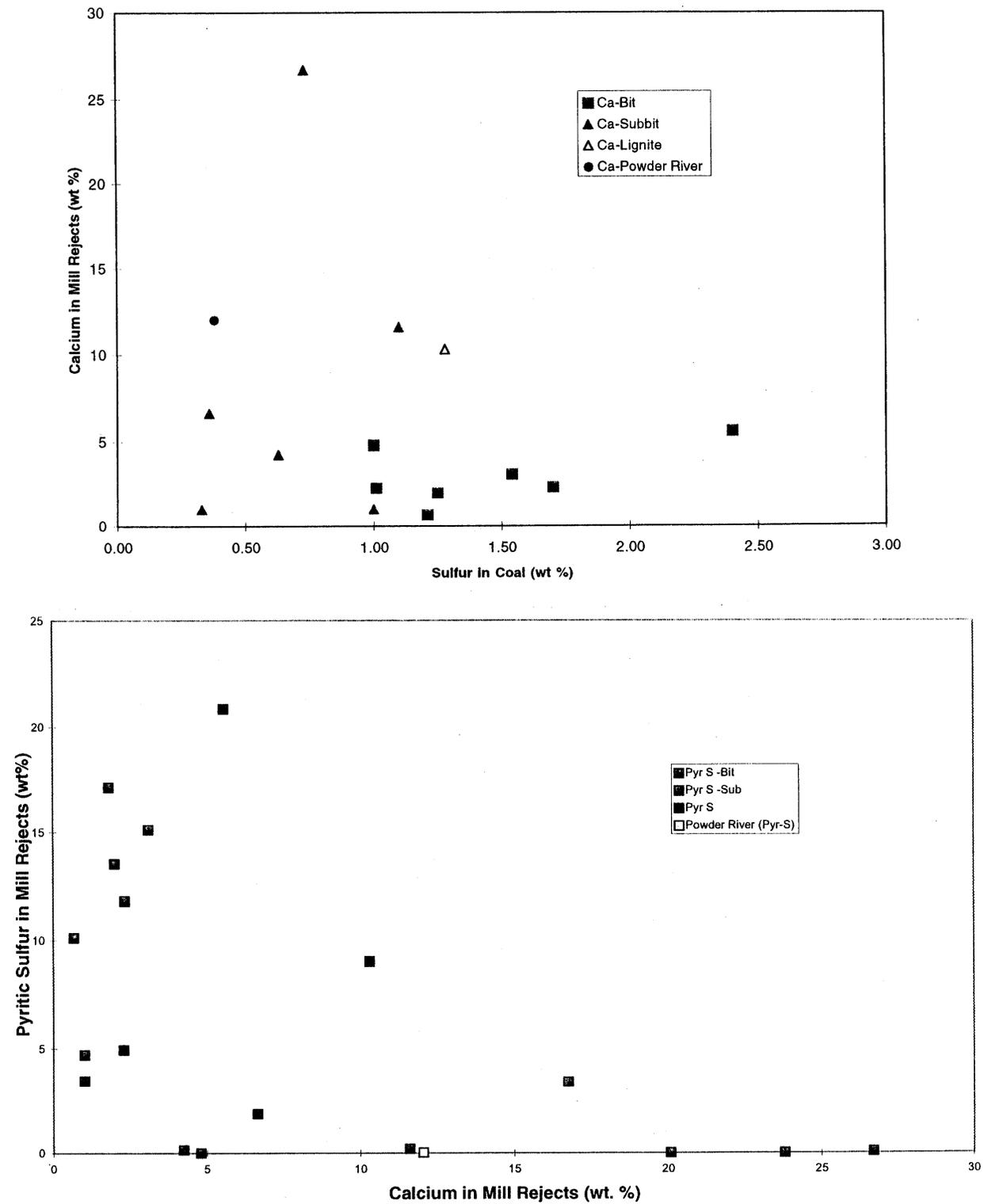


Figure 4-4  
Comparison of calcium and pyritic sulfur in mill rejects

magnesium content in mill reject samples varied from 0.18 to 6.03 weight percent. The mean and median magnesium concentrations in the mill rejects were 1.42 and 0.77 weight percent, respectively. When the mill rejects are comanaged with alkaline coal ash, there is neutralization capacity supplied by the coal ash. Mixing alkaline fly ash with mill rejects has been shown to significantly reduce concentrations of iron, manganese, and sulfate from seepage (Evangelou and Zhang, 1995 and Jackson et al., 1993). Acidic fly ash has a limited amount of available neutralization capacity, although laboratory equilibration tests on an acidic ash designed to simulate an ash pond showed an increase in pH from the initial ash paste value of 4.1 to over 6, after 36 days (Roy and Griffin, 1994).

## **Determining Need for Neutralization of Mill Rejects**

A summary of pyrite oxidation and neutralization reactions with fly ash is depicted in Figure 4-5 for mixing of ash and mill rejects. The same principle applies when lime or limestone is added to the mill rejects or coal ash. The alkalinity from limestone acts as a pH buffer and hydrolyzes most heavy metals. If conditions are changed to oxidizing and the pH is high enough (e.g., 6.5 to 7 or higher), iron can be converted from the ferrous to the ferric form and can precipitate as oxides or hydroxides. Both forms were detected in mill reject/ash porewater (see Table 2-19). The need for neutralization of mill rejects with ash or another material is dependent on the amount of acidity that can be generated if pyrites in the mill rejects are oxidized. As a screening approach to determine the need for neutralization, the estimated potential amount of acidity can be compared to the amount of alkalinity present in the mill rejects itself. If the acidity is greater than the alkalinity, then addition of ash or another neutralizing agent would be beneficial.

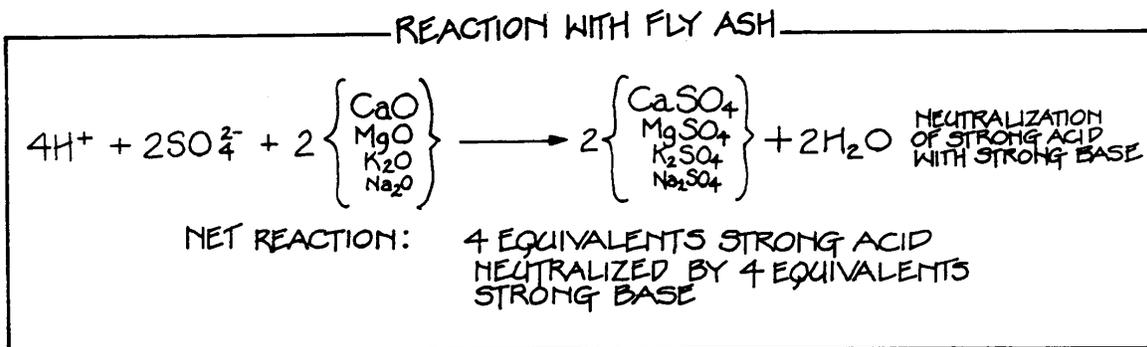
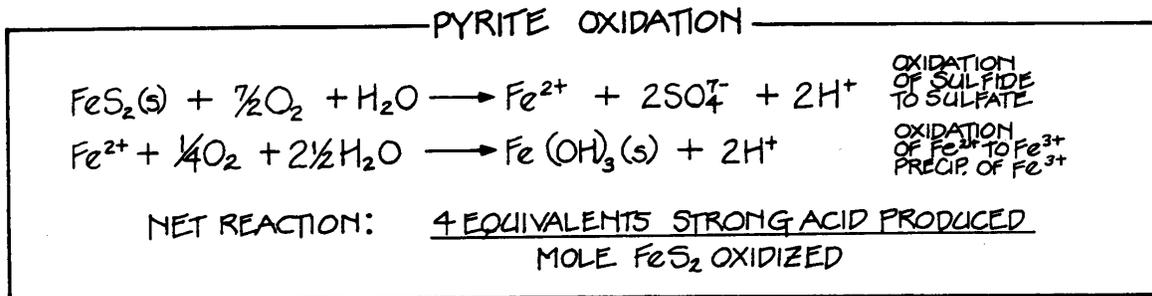
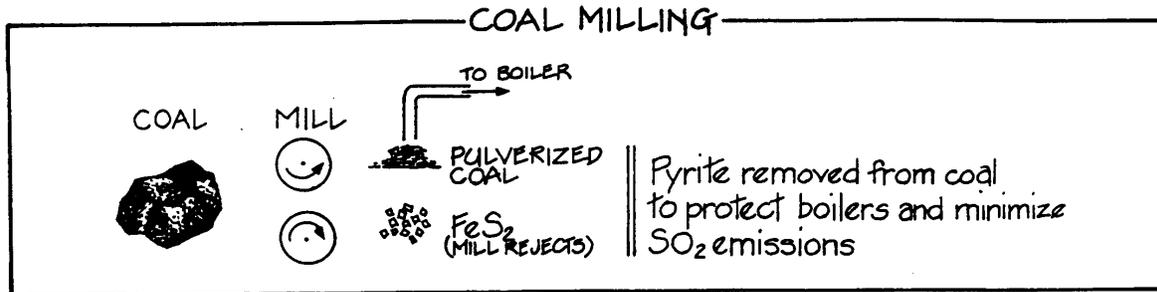
The following method can be used to estimate the potential acidity generated by oxidation of the pyrites in mill rejects. The first step is to estimate the amount of acidity that can be generated. As shown in Figure 4-5, one mole of pyrite ( $\text{FeS}_2$ ) can generate 4 equivalents of acidity and requires 4 equivalents of base ( $\text{CaO}$  or  $\text{MgO}$ ) to neutralize it. This represents a theoretical relationship, which can vary due to composition and mineralogy of the material. Laboratory experiments have shown that 3 percent pyritic sulfur generated 1.2 to 1.9 equivalents of acidity (Bruynesteyn and Hackl, 1982). The measured percent pyritic sulfur in the mill rejects is converted to potential acidity in equivalents using these laboratory results as follows:

$$\text{Potential Acidity (eq/kg)} = (\% \text{ sulfur}) * (0.6 \text{ equivalents/kg acidity}).$$

Acidity in eq/kg can be converted to tons acidity per ton of material by multiplying the acidity in eq/kg by 48.

To estimate the neutralization potential of ash or mill rejects only the calcium and magnesium content are considered, rather than an estimate of the total quantity of bases, and the measured content is modified to use only the readily available portion of these base cations. The amount of acidity that can be neutralized by calcium or magnesium oxide is estimated by first converting the weight percent of these cations to equivalents.

## COMANAGEMENT CHEMICAL CONCEPTS



OVERALL:

$$\Delta A_{IK} = \Delta \Sigma C_B = \Delta \Sigma C_A$$

where

$C_B$  = base cations, in equivalents (Ca, Mg, K, Na)

$C_A$  = strong acid anions, in equivalents ( $SO_4$ , Cl,  $NO_3$ )

Figure 4-5  
Summary of oxidation and neutralization reactions with fly ash

An example for calcium is shown below:

$$\text{Ca}/\text{MW} \times \text{C} \times 1000 = \text{eq/kg}$$

where

- Ca = calcium in weight fraction in mill rejects (1 wt % = 0.01 g/g).
- MW = molecular weight of cation (here molecular weight for calcium is 40.2).
- C = charge of cation (here charge for calcium is +2).

The molecular weight and charge of magnesium are 24.32 and +2, respectively. The proportion of base considered to be available in the mill rejects is 70 percent for calcium and 37 percent for magnesium, based on experiments on ash leaching (EPRI, 1986). The sum of the base equivalents (from calcium and magnesium) is determined and compared to the total acidity potentially generated by oxidation. Fly ash would also provide some additional base from other cations present in ash, such as sodium and potassium. If additional base is needed to neutralize excess acidity, the specific quantity can be determined based on the type of material to be used. An experiment using ash from the BR site showed that 85 percent of the acidity was neutralized within 20 to 40 minutes after addition of calcium carbonate (EPRI, 1995).

An example using the mill rejects data in this report is given below (the chemical composition used is the median of mill rejects samples).

- Pyritic Sulfur: 3.41 weight percent
- Potential Acidity generated: 2.16 eq acid/kg solids
- Calcium: 5.19 weight percent
- Magnesium: 0.77 weight percent
- Potential available Base: 2.05 eq base/kg solids
- Quantity of excess Acidity:  $2.16 - 2.05 = 0.11$  eq acid/kg solids

Additional amount of base containing material needed to neutralize the excess Acidity:

- Based on available results on neutralization capacity of Coal Ash: 44 g/kg solids of Fly Ash
- Based on neutralization capacity of  $\text{CaCO}_3$ : 5.5 g/kg solids of Lime

An analysis was conducted to determine the likelihood that coal ash would contain enough calcium and magnesium oxides to neutralize the acidity generated by the above example using the median chemical composition for mill rejects. Using the ash composition data, the neutralization potential was calculated for selected ash samples from the EPRI database (1987), representing a range of ash types. The computed neutralization potential varied from 0.45 eq/kg to 6.32 eq/kg in fly ash and 0.65 to 3.67 eq/kg in bottom ash (Table 4-1). Thus, there is enough estimated neutralization potential in all these ash samples to neutralize the mill rejects with composition equal to the median case, even if the mill rejects and ash were in equal proportions.

For mill rejects from bituminous coal, the pyritic sulfur can be higher. The maximum amount of pyritic sulfur in the samples analyzed was 20.85 percent. The acidity generated was estimated as 13.2 eq/kg solids and the base available in the rejects was 2.47 eq/kg. The excess acidity was 10.73 eq/kg, which means that the proportion of ash to mill rejects would need to be greater for this case. To provide enough neutralization for this type of mill rejects, lime (536 g/kg) or fly ash (75 to 1050 g/kg, based on the data in Table 4-1) could be used. Mixing mill rejects that have high pyritic sulfur with ash prior to placing them in a comanagement unit increases the efficiency of neutralization, and provides the maximum benefit from the available neutralization capacity in ash.

The static test methods of Sobek et al. (1978) were applied to seven coal ash samples from two power plants. The static test results along with measured paste pH, sulfate-sulfur, sulfide-sulfur, and total sulfur are presented in Table 4-2. The acid generation potential of these ash samples was less than 0.6 tons CaCO<sub>3</sub>/1000 tons of ash (Table 4-2). The neutralization potential ranged from 4.7 to 48.6 tons CaCO<sub>3</sub>/1000 tons of ash (Table 4-2). The lowest neutralization potential value of 4.7 tons CaCO<sub>3</sub>/1000 tons corresponds to a pH value of 5.6 for the sample (Table 4-2), and the highest neutralization potential value of 48.6 tons CaCO<sub>3</sub>/1000 corresponds to a pH value of 9.6 (Table 4-2). The net neutralization potential for the five coal ash samples from Plant A are all positive and lie between 7 and 48 tons CaCO<sub>3</sub>/1000 tons ash (Table 4-2).

These static test results for coal ash are in agreement with pH based classification of these samples as non-acid forming materials with a range of available net neutralization potential of 4.7 to 48 tons CaCO<sub>3</sub>/1000 tons.

### ***Laboratory Titration Results to Determine Alkalinity of Coal Ash Samples***

Six archived fly ash and four bottom ash samples from the EPRI coal ash characterization study in 1987 were retrieved and tested in the laboratory to measure alkalinity by titration. Approximately 0.1 g of ash was suspended in 50 ml deionized water and titrated to pH 4.0 with a 0.05 m H<sub>2</sub>SO<sub>4</sub> solution. All fly ash titrations were conducted in triplicate; the bottom ash titrations were run only once. Each titration took approximately 1 to 6 hours. Representative titration curves are shown in Figure 4-6, and alkalinity estimates are reported in Table 4-3 along with the sample identification number from the 1987 EPRI report. Fly ash alkalinity was calculated from the laboratory titration results using the following equation:

$$\begin{aligned} \text{Alkalinity (mg CaCO}_3\text{/kg ash)} &= (\text{meq of H}_2\text{SO}_4 \text{ required}/ \\ &\quad \text{kg of sample to reach a given pH}) *(50) \\ &= (\text{ml of H}_2\text{SO}_4) * (0.1 \text{ meq/ml}) * (1000 \text{ mg/kg}) *(50) \end{aligned}$$

These laboratory titration results indicate that all six fly ash samples have significant acid neutralization capacity. The alkaline bottom ash samples also show significant acid neutralization capacity. However, the two acidic bottom ashes show zero acid neutralization capacity.

**Table 4-1**  
**Estimated Available Base in Fly Ash and Bottom Ash**

Sample No.	Coal Type	pH of Ash		Sulfur wt %	Calcium		Available Calcium		Available Magnesium		Estimated NP eq/kg	
		Paste (1:1)	Paste (1:20)		wt %	eq/kg	wt %	eq/kg	wt %	eq/kg		
Fly Ash												
101	Bituminous	7.55	9.14	0.279	3.85	1.92	1.34	1.9	1.56	0.58	1.92	
104	Bituminous	6.51	6.03	0.366	0.93	0.46	0.32	0.41	0.34	0.12	0.45	
109	Bituminous	2.81	3.58	2.18	2.7	1.34	0.94	0.91	0.75	0.28	1.22	
115	Subbituminous	11.22	11.73	0.91	15.7	7.81	5.47	2.81	2.31	0.86	6.32	
Bottom Ash												
202	Bituminous	5.4	7.31	0.046	1.4	0.70	0.49	0.53	0.44	0.16	0.65	
205	Bituminous	8.77	7.52	1.532	2.22	1.10	0.77	0.5	0.41	0.15	0.93	
207	Subbituminous	4.28	5.24	0.163	1.43	0.71	0.50	0.76	0.63	0.23	0.73	
208	Subbituminous	11.39	10.63	0.019	9	4.48	3.13	1.75	1.44	0.53	3.67	

All ash samples had enough base to neutralize the median case mill rejects with 0.11 eq/kg of excess acidity. Ash data are from EPRI, 1987.

**Table 4-2  
Chemical Analysis Results for Coal Ash Samples from Two Power Plants for Acid-Base Evaluation**

Parameters	Units	Ash from Plant A (10/92)	Ash from Plant A (10/92)	Ash from Plant A (6/95)	Ash from Plant A (12/97)	Ash from Plant A (9/98)
pH	Std. Unit	9.5	9.6	7.5	10.6	8.0
Sulfate	mg/Kg	890	660	680	408	2,000
Sulfide	mg/Kg	3.9	<1	<1	3.6	<1
Potential Acidity	Tons CaCO <sub>3</sub> /1000 tons	<0.6*	<0.6	<0.6	<0.3	0.31
Neutralization Potential	Tons CaCO <sub>3</sub> /1000 tons	43.1*	48.6	7.5	14.1	13.5
Net Neutralization Potential	Tons CaCO <sub>3</sub> /1000 tons	43*	48	7	13.8	13.2

Parameters	Units	Fly Ash	Bottom Ash	Subgrade Soil
pH	Std. Unit	5.6	5.3	4.7
Total Sulfur	mg/Kg	3900	1100	300
Sulfide-Sulfur	mg/Kg	1600	<200	<200
Neutralization Potential	Tons CaCO <sub>3</sub> /1000 tons	4.7*	5.0	5.4

\*Determined by methods 3.2.4, 3.2.3 and 1.3.1 (EPA-600/2-78-054).

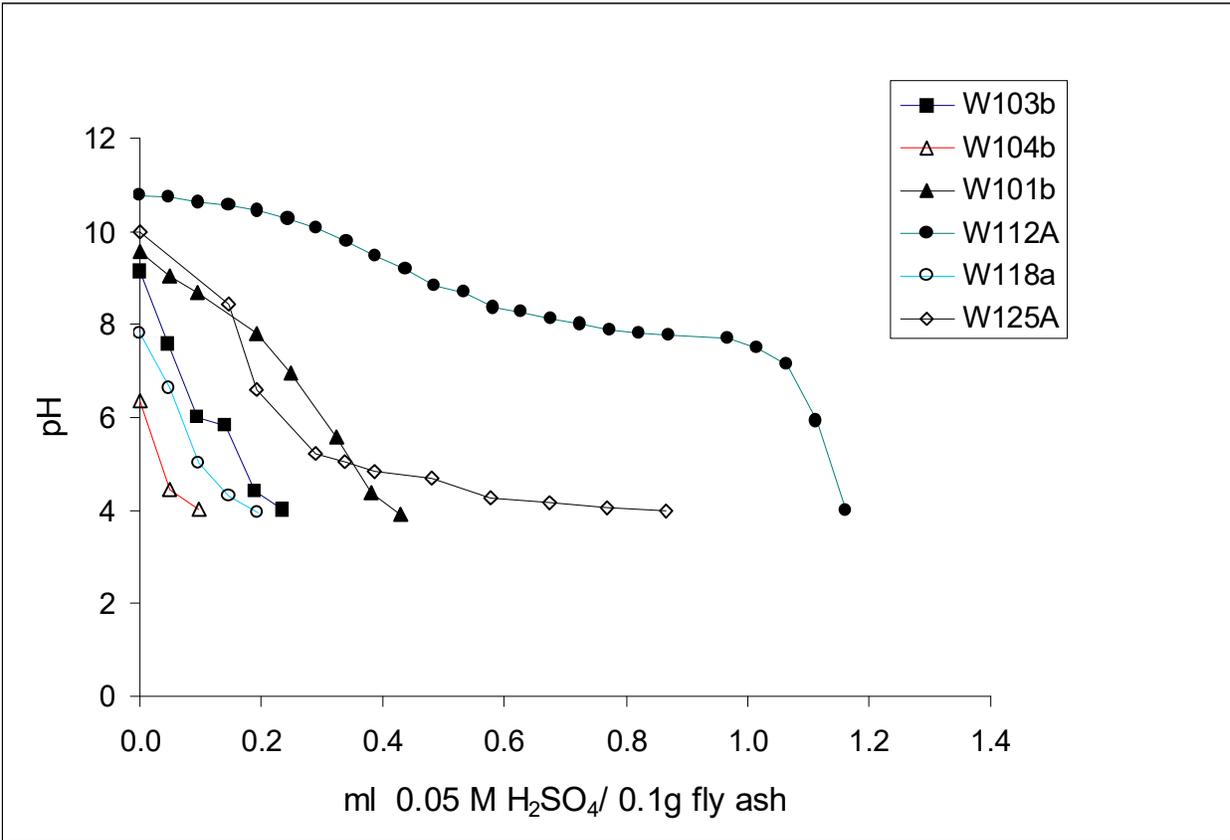


Figure 4-6  
Selected titration curves for fly ash samples

**Table 4-3**  
**Summary of Ash Samples and the Alkalinity Estimates at pH 6 and pH 4**

Sample ID	Ash Type	pH (1:1) (EPRI 1987)	pH (1:10) (This Study)	Alkalinity (mgCaCO <sub>3</sub> /kg) at	
				pH = 6	pH = 4
W118	Fly Ash	3.69	7.06	2,809	7,317
W104	Fly Ash	6.51	6.23	150	2,397
W101	Fly Ash	7.65	9.74	6,693	19,029
W103	Fly Ash	8.14	8.55	5,014	11,748
W112	Fly Ash	9.93	11.79	50,974	58,140
W125	Fly Ash	10.91	10.82	6,558	45,717
W207	Bottom Ash	4.28	–	0	0
W206	Bottom Ash	6.6	–	0	0
W201	Bottom Ash	8.38	–	500	4651
W208	Bottom Ash	11.39		3,500	9,747

– Not measured

# 5

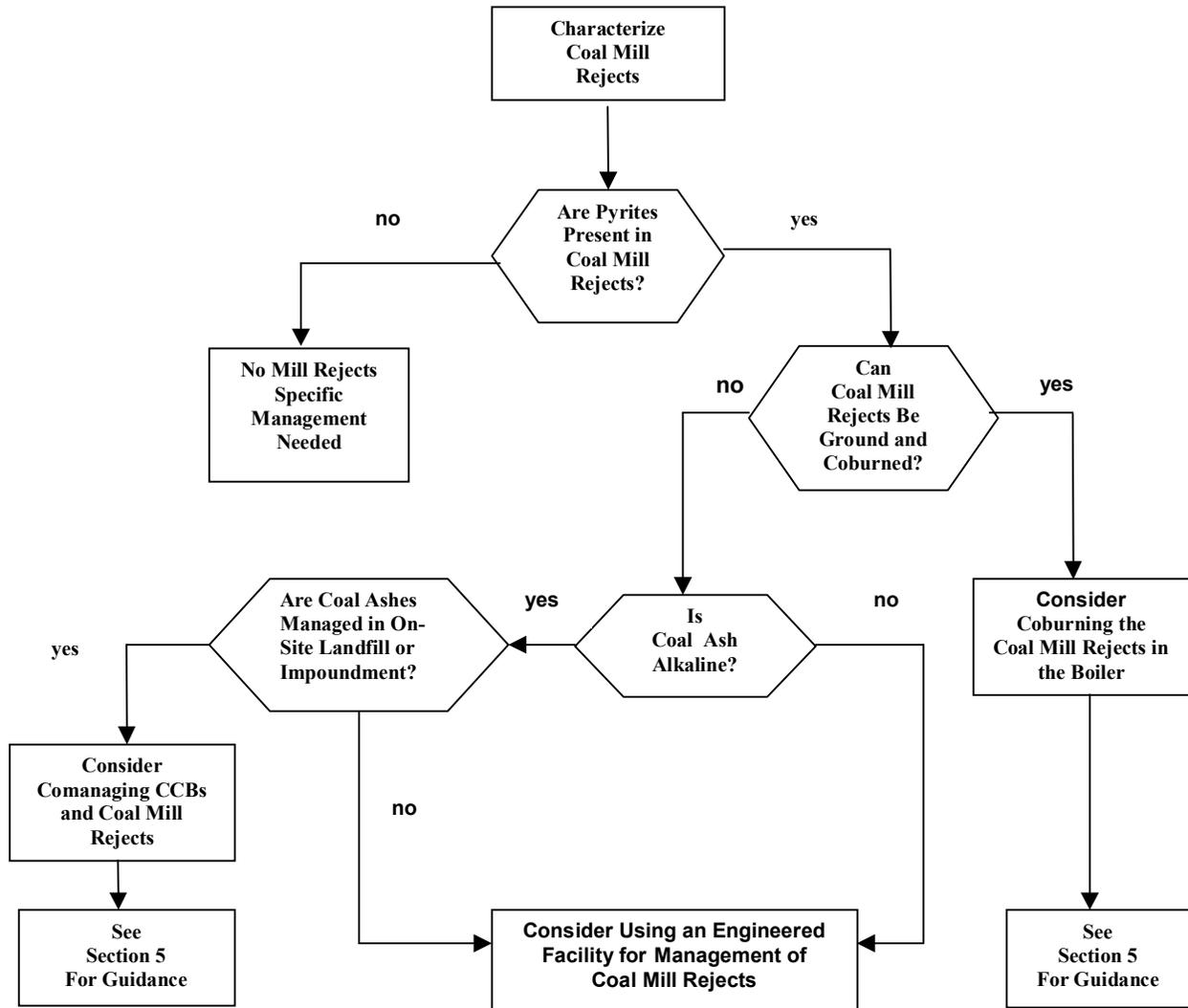
## COAL MILL REJECTS MANAGEMENT ALTERNATIVES

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Since the passage of the Resource Conservation and Recovery Act (RCRA) in 1976, the U.S. Environmental Protection Agency has been developing and promulgating regulations involving the disposal of hazardous and nonhazardous solid wastes in landfills and surface impoundments. The Agency has developed methods to characterize wastes as hazardous or nonhazardous and has established requirements for designing, operating, closing, and postclosure care of disposal facilities. Much of the attention has focused on hazardous wastes, although increasing regulatory attention is being given to nonhazardous solid wastes. Individual states have also developed regulations for landfills and impoundments. Landfills and impoundments that comanage low-volume wastes with coal combustion by products have been exempt from the hazardous waste management regulations under the Bevill amendment to RCRA. However, in 1999 the EPA is completing its Report to Congress, and following the report will make its regulatory determination for the management of the “remaining wastes” from fossil fuel combustion (see Section 1).

In the foregoing sections, technical data and case studies were presented to define the characteristics and current comanagement practices of mill rejects generated at coal-fired power plants. These results indicate that there are large variabilities in mill rejects generation and chemical/mineralogical composition. Iron sulfide (i.e., pyrites) in mill rejects was identified as a source of potential environmental risk because oxidation of pyrites can form acidic leachates containing elevated amounts of iron, sulfate, and some metals such as As, Ni, Zn, and Mn. In some of these case studies, pyrite oxidation had occurred and environmental control technologies were employed by the utilities involved to achieve protection of the nearby ground-and surface-waters. In other case studies, no evidence was found to indicate that pyrite oxidation had occurred. Because mill rejects are most commonly comanaged with coal ash in landfills and impoundments and because the acidic leachate generation potential exists, it is pertinent to offer an industrywide guidance on the comanagement and management issues that captures the existing knowledge on the subject matter. Effective comanagement of mill rejects containing pyrites is based on the premise of minimizing oxidation potential and utilizing the neutralization potential of coal ash, when available. In fact, one can also use the high alkalinity of calcareous soils in the dry climate areas of the U.S. in determining neutralization needs. Figure 5-1 shows a flow diagram which can be followed to select an alternative most suitable for the management of mill rejects on a site-specific basis.

Three alternatives for mill rejects management are discussed below with emphasis on controlling the potential for oxidation of pyrites in the mill rejects in order to protect groundwater and surface water from acidic leachates. The alternatives are: (1) comanagement with ash in an impoundment or a landfill; (2) management of mill rejects separately in an engineered disposal unit; and (3) elimination of the need for mill rejects disposal by regrinding and burning them in plant boilers. Differences in handling of mill rejects are partly a function of whether a dry or wet



**Figure 5-1**  
Flow diagram for evaluation of management alternatives

system is used for collecting fly ash and bottom ash, and whether the mill rejects are collected dry or wet. Figure 5-2 shows three combinations used in handling rejects from pulverizers at actual power plants. The choice of disposal method is also influenced by the quantity of mill rejects produced and the size of the mill reject material.

## **Option 1: Comanagement With Ash in an Impoundment or Landfill**

### ***Impoundment***

Comanagement of mill rejects with coal ash in an impoundment is depicted in Figure 5-3. In this alternative, a mixture of coal ash and mill rejects are sluiced to a lined or unlined pond. Solids are allowed to settle to the bottom and at least one foot of standing water is maintained during the operating life of the impoundment. Flooding the pyritic material minimizes the rate of oxygen diffusion into the solids to less than 1/10,000th that of air and slows the bacterial oxidation process (Kleinman and Crerar, 1979). Thus, this option minimizes the potential for pyrite oxidation.

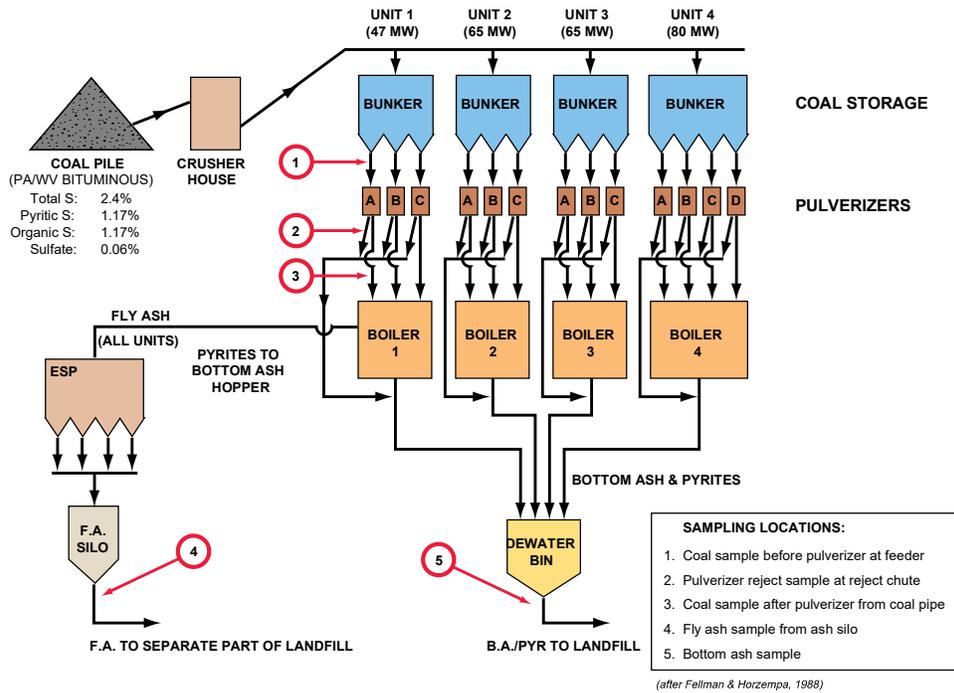
In addition, when the coal ash comanaged with the mill rejects in surface impoundments is alkaline, the coal ash offers neutralization capacity for the acidity in leachate, which might be produced by oxidation of the pyrite. Field data from the MO and BR case studies provide documentation that neutralization occurs because of the considerable amount of calcium and magnesium oxides and carbonates in the coal fly ash, which serves as a source of alkalinity. In surface impoundments where acidic coal ash and mill rejects are comanaged, flooding with water minimizes the potential for oxidation of pyrites and thus provides control on leachate.

Electric utilities have designed and operated surface impoundments at power plants for many decades and are familiar with the topographic, geologic, hydrologic, soil, land-use, and climatic considerations. The comanagement of pyrite-containing mill rejects in the ash impoundments should not alter the primary considerations used by the utility engineers. Therefore, additional discussion on the design of ash ponds for comanagement is not warranted in this report. Several technical resource documents on design, construction, and operation of surface impoundments are readily available from the U.S. EPA, state regulatory agencies, and the engineering community.

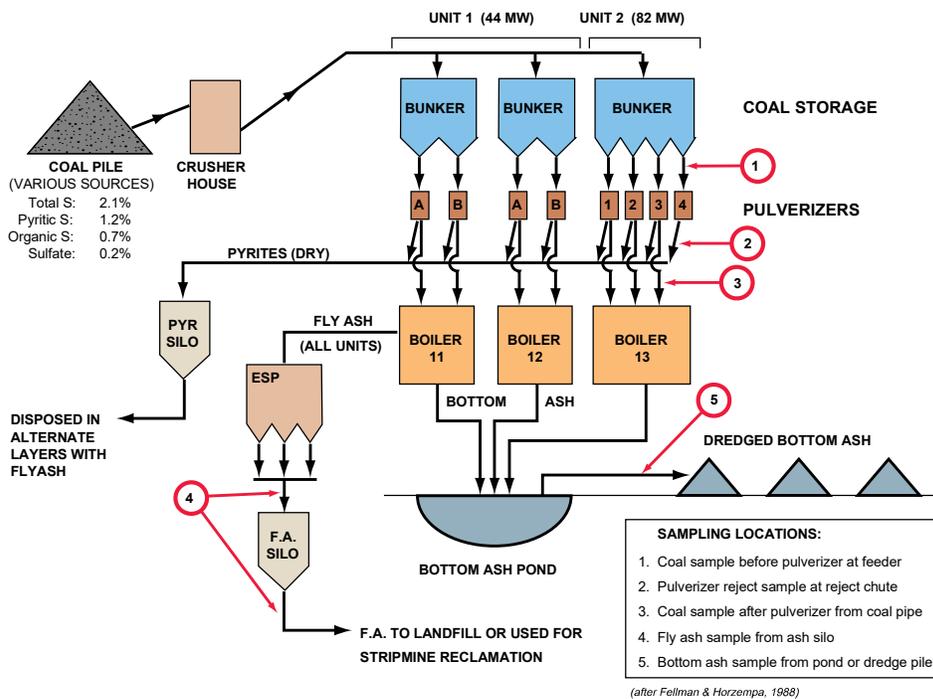
### ***Landfill***

Comanagement of mill rejects with coal ash in a landfill is depicted in Figure 5-4. Under this alternative, a lined or unlined landfill is utilized to place, in lifts, a mixture of coal ash and mill rejects with compacting. Usually these landfills are developed above the groundwater table and have several feet of separation between the saturated zone and the bottom of the coal ash-mill rejects mixture. Oxygen diffusion and rainwater infiltration occur during the operation of these facilities, presenting a potential for pyrite oxidation and generation of acidic leachate. When pyrites are comanaged with alkaline ash the alkalinity in the coal ash neutralizes the acidic

## Plant A: Pyrites Disposed with Bottom Ash



## Plant B: Dry Pyrites Disposed with Fly Ash



**Figure 5-2**  
Examples of mill rejects and ash handling and disposal systems

# Plant C: Wet Pyrites Disposed Separately

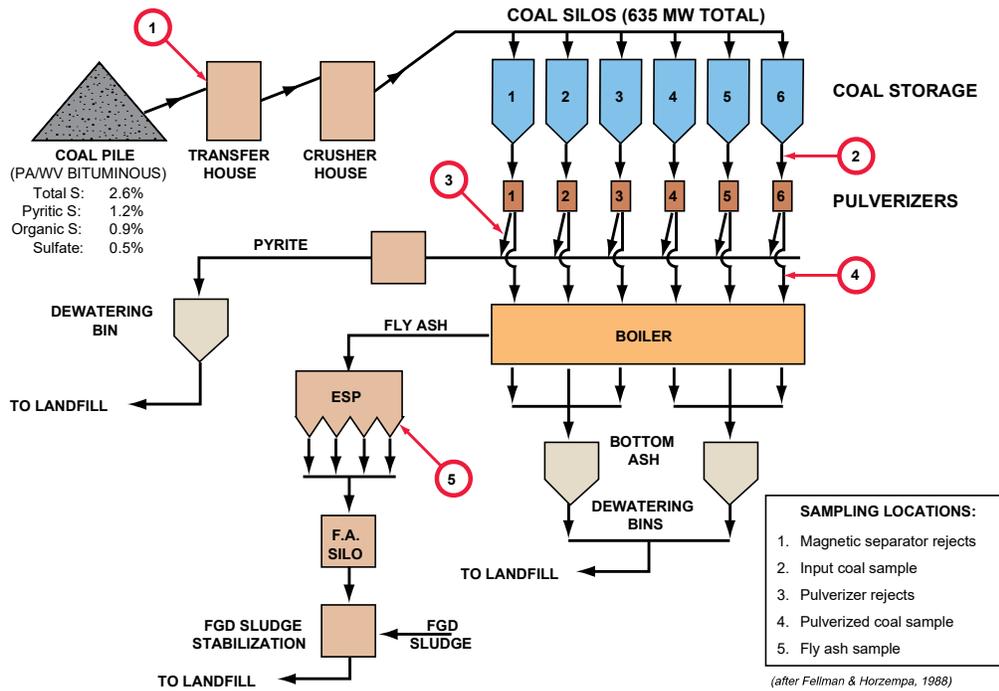


Figure 5-2 (continued)  
 Examples of mill rejects and ash handling and disposal systems

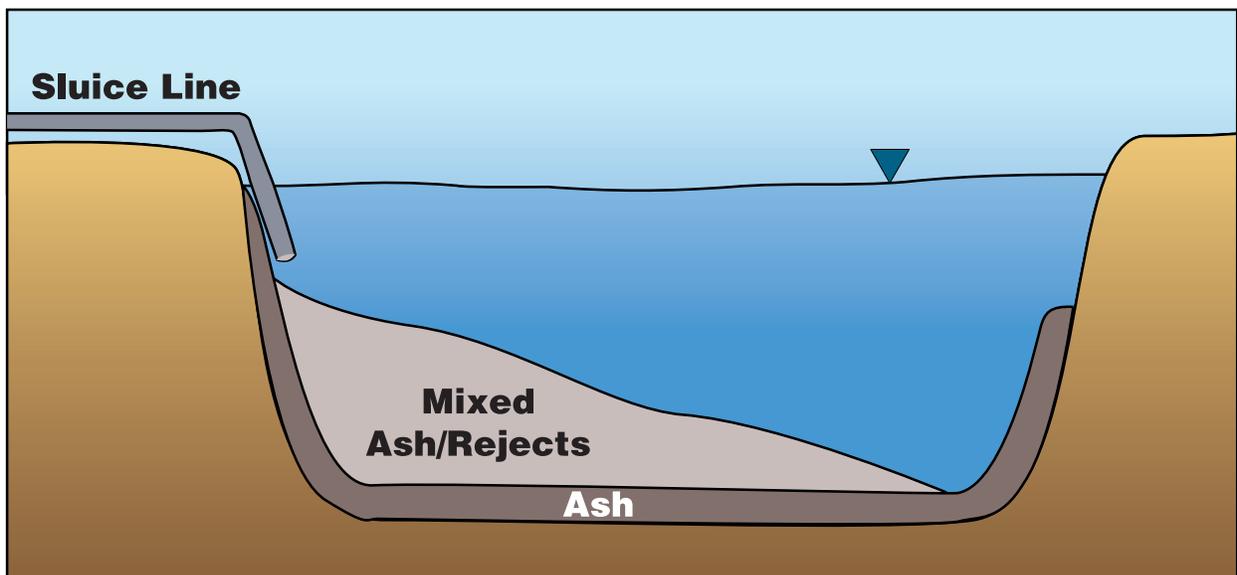
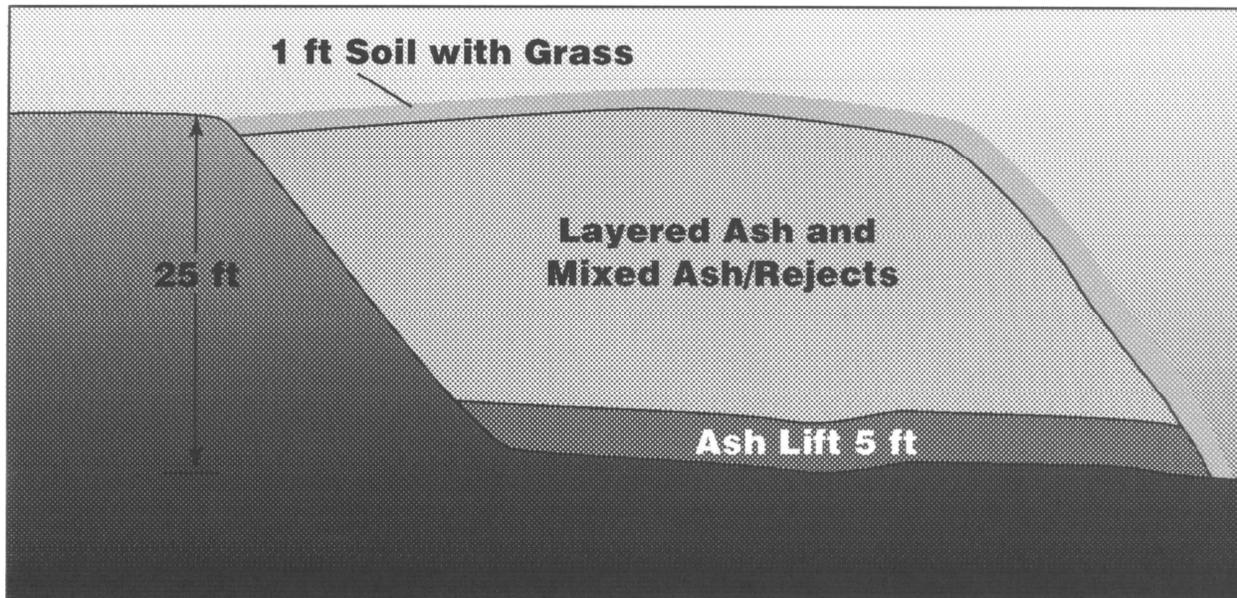


Figure 5-3  
 Schematic of mill reject comanagement in ash impoundment



Note: Drawing not to scale.

**Figure 5-4**  
**Schematic of mill reject comanagement in ash landfill**

leachates generated, thereby minimizing the migration of the acidic leachates to the groundwater and/or discharge to surface creeks or as seeps. However, when the coal ash is acidic and pyrite oxidation occurs, there is a possibility of lateral drainage of acidic leachates if sufficient rainfall and infiltration occur. The FA case study appears to be an illustration of this situation. A low permeability surface cap for infiltration control, a vertical slurry wall as a physical barrier, and an underdrain system to collect leachate were installed at the FA site to control the generation and migration of leachate from the ash and mill rejects containing pyrites. Section 4 contains a discussion and example of methods for estimating the neutralization potential by coal ash. It is possible to add lime to landfills to add a source of alkalinity in addition to infiltration control.

### ***Determining the Need for a Physical Barrier***

The need for a physical barrier beneath a landfill or impoundment depends on the pH of the expected leachate, the quantity of leachate compared to the average flow of groundwater beneath the facility, and the pH of the underlying groundwater. The depth to groundwater beneath the facility and the distance to a surface waterbody or water supply well are also important. For example, if the expected leachate and underlying groundwater are alkaline, a physical barrier may not be needed. If highly permeable formations exist downgradient of the disposal site and the upgradient groundwater pH is acidic, a low permeability barrier may be needed, depending on the alkalinity of the ash and the ratio of mill rejects to ash in the basin.

## **Option 2: Management of Mill Rejects in a Separate Engineered Disposal Unit**

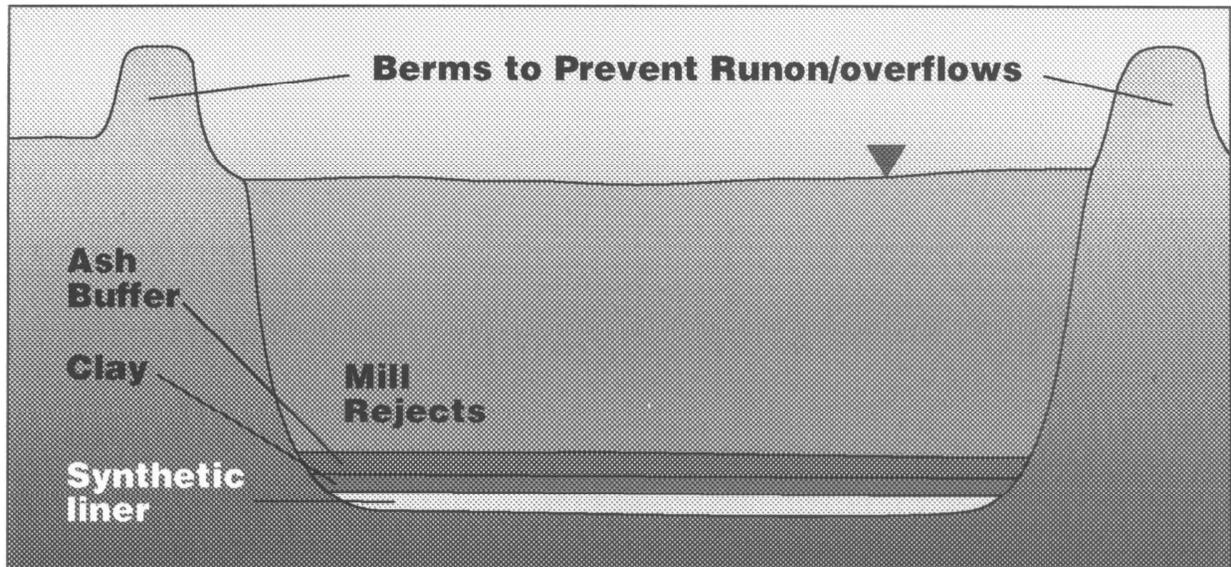
Management of mill rejects in a separate, lined impoundment is depicted in Figure 5-5. This disposal method can be used when most of the ash is sold or trucked to an off-site location. When the mill rejects are kept covered by water, oxidation of pyrites in the mill rejects is negligible, because oxygen diffusion is minimal. The main difference between this type of impoundment and one with ash is that there is no alkalinity from ash available to neutralize the acidity in the leachates should oxidation occur in areas where pyrites are exposed to air. Upon closure, the impoundment is dewatered and capped to minimize infiltration of water and oxygen. A buffer layer of ash and/or lime may be placed below the cap to provide a source of alkalinity in the closed landfill.

Mill rejects can also be managed separately in an engineered landfill. Such a landfill would have a low permeability liner and cap. The cap would be designed to minimize infiltration and prevent erosion. A buffer layer of alkaline fly ash or lime may be placed above the liner and below the cap to provide sources of alkalinity in the landfill.

## **Option 3: Regrinding and Burning to Eliminate Land Disposal**

The Clean Air Act Amendments of 1990 require lower sulfur emissions. Phase I limits to be met by January 1, 1995, are 2.5 lb. SO<sub>2</sub> per million Btu times the fuel rate used in the period from 1985 to 1987. At plants where coal consumption has increased since the base period (1985 to 1987), a further limit on SO<sub>2</sub> emissions is imposed because there is no allowed increase due to higher coal consumption. Coal switching/blending and fuel substitution were the most common options chosen to meet Phase 1 limits. Phase 2 limits, to be met by December 31, 2000, are 1.2 lb SO<sub>2</sub> per million Btu times the 1985-1987 fuel rate. The Phase 2 limits apply to 1,100 generating units. To meet these limits, utilities may need to increase sulfur removal via scrubbers or other methods, switch to lower sulfur coals, blend different types of coal, purchase emissions credits, or switch to noncoal fuels for all or part of the time. Increased sulfur removal in the milling process prior to burning could result in increased volumes of mill rejects.

Burning of reground mill rejects can be an effective method of managing mill rejects. This option was investigated recently by EPRI as an alternative to land-based disposal for mill rejects. Regrinding and burning was evaluated in three ways: calculating the effect of burning pyrites on SO<sub>2</sub> emissions, conducting pilot screening and combustion tests to determine the effect of the material on the equipment and its burning efficiency, and conducting full-scale demonstration tests in actual power plant boilers. Both pilot and full-scale testing have shown that burning up to 4 percent mill rejects with coal can be accomplished in conventional boilers with minimal modifications to air pollution equipment. Air quality standards for SO<sub>x</sub>, NO<sub>x</sub>, and volatile compounds can still be met. A method for estimating the amount of mill rejects that can be burned while still meeting the applicable air quality standards is included below.



**Figure 5-5**  
**Schematic of mill reject comanagement in separate impoundment**

### **Method for Estimating Effect of Coburning on SO<sub>2</sub> Emissions**

The sulfur emissions from coburning of mill rejects and coal can be estimated based on the chemical composition and heating value of the materials. Calculations are made to estimate the pounds of SO<sub>2</sub> per million Btu emitted if a given percentage of mill rejects is burned with coal. Sulfur emissions can be provided for the case with no sulfur controls and with alternative controls. The basic calculations are performed using the following equation:

$$(\text{lb S in coal} - \text{lb S in ash})/\text{lb. coal} \times \text{lb coal}/10^6 \text{ Btu} \times 2 \text{ lb SO}_2/\text{lb S} = \text{lb SO}_2/10^6 \text{ Btu}$$

These values are then multiplied by the fraction of coal burned. All sulfur, except that retained in the ash, is considered to be released to the atmosphere. If the sulfur content in the ash is unknown, an estimate of 10 percent of the sulfur in the pulverized coal can be used. A similar equation is used to estimate the lb SO<sub>2</sub> per 10<sup>6</sup> Btu of mill rejects.

The data needed are the percent of total sulfur in cleaned coal and mill rejects, the sulfur content of the ash, the percent ash, and the heating value of the coal and mill rejects. If heating values are not available, estimates can be made using the following equation (Shannon, 1982):

$$\text{Btu} = 14,600 \text{ C} + 62,000 (\text{H}-\text{O}/8) + 4,000 \text{ S}$$

where C = percent carbon, S = percent sulfur, H = percent hydrogen, and O = percent oxygen and Btu represents the total estimated fuel heating value. The multipliers for each of the elements shown above (carbon, hydrogen, and sulfur) are the approximate heat energy released per pound of fuel from each of the elements. The relative weights of each element from an ultimate analysis are used in this equation.

Example calculations are shown in Table 5-1 for one power plant where most of the necessary data were available (Fellman and Horzempa, 1988). The relative weights of the above elements were provided for the input coals. Percent carbon and sulfur were available for the pulverizer rejects and pulverized coal. The carbon to hydrogen and carbon to oxygen ratios were maintained the same as the input coal. Thus, these ratios were used to estimate hydrogen and oxygen for the rejects and pulverized coal based on the carbon percentage measured in these materials. The resulting sulfur emissions were compared to the Clean Air Act Amendments of 1990 Phase 1 and 2 limits. Plant D could meet Phase 1 SO<sub>2</sub> limits (2.5 lb SO<sub>2</sub> /MBtu) if up to 0.5 percent rejects were burned without SO<sub>2</sub> controls. With at least 50 percent SO<sub>2</sub> removal, this plant could burn 2 percent mill rejects containing 23 to 29 percent pyritic sulfur and 30 to 35 percent total sulfur, while still complying with the Phase 1 limits. Meeting Phase 2 limits (1.2 lb SO<sub>2</sub> /MBtu) would require about 70 percent SO<sub>2</sub> removal if up to 2 percent rejects were burned at this plant. Three other plants tested could also meet the Phase 2 limits with up to 2 percent mill rejects and 70 percent SO<sub>2</sub> control. Obtaining 70 percent removal of sulfur emissions can be accomplished using a range of processes including the wet lime or limestone system, double alkali system, dry scrubber process, and the magnesium slurry process, or a combination of these processes.

The emissions calculations are sensitive to the heating value of the rejects. The higher the heating value of the rejects, the lower the sulfur emissions on a SO<sub>2</sub> per MBtu basis, given the same amount of sulfur. An ultimate analysis of rejects is necessary to obtain the necessary input data to use the above approach. Rejects that contain a high percentage of coal will have higher heating values. Depending on the hardness and density of coal and the type of mill used, rejects can contain over 10 percent coal.

The Phase I limits could be met when coal and up to 4 percent mill rejects were burned with 70 percent removal efficiency for sulfur dioxide, using the median sulfur concentration of 3.4 weight percent in mill rejects from data generated for this project. Meeting the Phase 2 limits for this case would require at least 85 percent removal efficiency. Higher removal efficiencies would be needed for rejects with the maximum sulfur concentration (20.85 weight percent).

Tests on coburning of mill rejects and coal showed that coburning is technically feasible with minimal increases in sulfur emissions depending on the percent of rejects burned. Small modifications to the ESP units may be needed at some power plants. Benefits of coburning mill rejects include improved energy recovery, waste minimization, and elimination of potential environmental concerns related to disposal of mill rejects.

**Table 5-1  
Plant D Estimated Emissions: Coal and Mill Rejects Characteristics**

Parameter	Input Coal	Mill Rejects	Cleaned Coal
Measured Heating Value (Btu/lb)	–	–	–
Carbon as C (%)	75	15	75
Hydrogen as H (%)	4.57	0.91 <sup>a</sup>	4.75 <sup>a</sup>
Oxygen as O (%)	5.38	1.08 <sup>a</sup>	5.38 <sup>a</sup>
Sulfate sulfur (%)	0.71	0.45	0.07
Pyritic sulfur (%)	1.27	22.87	1.09
Organic sulfur (%)	0.69	7.4	1.47
Total sulfur (%)	2.67	30.74	2.63
Moisture content (%)	–	0.8	1.6
Ash content (%)	–	58.36	9.4
Sulfur content in ash (%)	0.83	–	–
Estimated Heating Value (Btu/lb) (Shannon, 1982)	13,473	3900	13,472

**SO<sub>2</sub> Emissions if Varying Quantities of Mill Rejects Burned**

SO <sub>2</sub> Controls	SO <sub>2</sub> Removal Efficiency (%)	With No Rejects	With 1% Rejects	With 2% Rejects
None	0	3.51	5.04 <sup>a</sup>	6.57 <sup>c</sup>
Wet lime and limestone system	95	0.18	0.25	0.33
Double alkali system	90	0.35	0.50	0.66
Dry scrubber system	est. 90	0.35	0.50	0.66
Sodium wet sulfur recovery system	50	1.76	2.52	3.29
Wellman-Lord process	60	1.40	2.02	2.63
Magnesium slurry process	70	1.05	1.51	1.97
Combined efficiency of two or more	80	0.70	1.01	1.31

<sup>a</sup> Estimated based on C:H and C:O ratios in input coal. Measured heating values preferred.

<sup>b</sup> Part from rejects is 1.56 lb SO<sub>2</sub>/M Btu: part from coal 3.48 lb SO<sub>2</sub>/M Btu

<sup>c</sup> Part from rejects is 3.13 lb SO<sub>2</sub>/M Btu: part from coal 3.44 lb SO<sub>2</sub>/M Btu

**Assumptions:**

Sulfur emission calculations based on total sulfur concentrations measured in each coal fraction.

All sulfur is released upon combustion of coal.

If sulfur content of ash is not provided, it is assumed to be 10 percent of the pulverized coal sulfur content.

**Reference:** Fellman and Horzempa, 1988.

### ***Pilot Screening Tests of Coburning***

Pilot tests on cofiring of mill rejects and coal were conducted for EPRI by the Energy and Environmental Research Corporation in 1995 to evaluate the potential for effects on pulverized coal boilers such as decreased efficiency or effects on pollution control equipment such as increased maintenance. The tests were conducted using a widely used coal, Illinois high sulfur coal, with a total sulfur content of 3.1 percent, and mill rejects from a different bituminous coal with 1.5 percent sulfur. The total sulfur content of these mill rejects was 6.1 percent. The heating value of the Illinois coal was calculated to be 11,210 Btu/lb, while the heating value of the mill rejects was 1,931 Btu/lb. Screening tests to determine differences in physical properties that might affect burning were conducted using mixtures of coal with 0, 2, 4, or 10 percent mill rejects. Based on the results of the screening analyses, detailed tests in a combustion test facility were performed with 0 and 4 percent mill rejects.

Composition and properties of the Illinois coal and the mill rejects used in the combustion experiments are shown in Tables 5-2 and 5-3, respectively. The major differences between the original cleaned coal and the mill rejects produced from that coal were that the sulfur content increased from 1.43 percent to 6.1 percent and the ash content increased from 9.4 percent to 80.3 percent in the mill rejects. The heating value of the original coal was 13,206 Btu compared to that of the mill rejects of 1,931 Btu. The comparison between the two fuels combined in the tests, the Illinois coal and the mill rejects, showed similar differences. The mill rejects had a higher sulfur content, 6.1% versus 3.1% in coal, and the sulfur was mostly pyritic sulfur. The ash content was also higher in the rejects, 80.3 percent versus 9.6 percent in the Illinois coal.

Various indices to estimate combustion efficiency and potential effects on maintenance were also calculated for mixtures of the original coal and the mill rejects derived from that coal, using the methods presented in Folsom et al. (1986). The data used in the calculations and the resulting indices are shown in the composition tables (See Tables 5-2 and 5-3). The estimated increase in sulfur emissions was predicted to be 16 percent with 4 percent mill rejects, from 1,250 ppm to 1,450 ppm. Because mill rejects have a lower nitrogen content than coal, it was thought that the NO<sub>x</sub> emissions would be somewhat less. The ash loading was predicted to increase by 38 percent with 4 percent rejects due to the higher ash content in the rejects. The slagging index is based on the temperature at which slag viscosity reaches 250 poise, base-to-acid ratio, iron-calcium ratio, and ash fusion temperature. This index indicated a low slagging tendency even with 10 percent rejects. The fouling index is based on sodium oxide concentration, percent ash, base-to-acid ratio, and sodium plus potassium concentration. This index predicted low fouling tendencies with up to 4 percent rejects. Another potential concern was erosion of equipment due to high ash and silica concentrations. The erosion potential was found to be low with up to 6 percent rejects. The indices for cofiring mill rejects and the Illinois coal were favorable as well.

**Table 5-2  
Composition and Properties of Coal Used in Coburning Tests**

	Proximate Analysis		Ultimate Analysis	
	As Received	Dry Basis	As Received	Dry Basis
% Moisture	6.39	–	% Moisture	6.39
% Ash	8.99	9.60	% Carbon	62.23
% Volatile	38.52	41.15	% Hydrogen	3.86
% Fixed Carbon	<u>46.10</u>	<u>49.25</u>	% Nitrogen	1.22
	100.00	100.00	% Sulfur	2.91
			% Ash	8.99
Btu/lb	10,494	11,210	% Oxygen (diff)	<u>14.40</u>
% Sulfur	2.91	3.11		100.00
MAF Btu		12,400		100.00
Alk. as Sodium Oxide	0.21	0.23		

	Forms of Sulfur			Trace Elements
	As Received	Dry Basis		
% Pyritic	0.09	0.10	Antimony	<1.0
% Sulfate	0.51	0.54	Arsenic	1.0
% Organic (diff)	2.31	2.47	Barium	45.0
% Sulfur	2.91	3.11	Beryllium	0.8
			Cadmium	<0.2
			Chromium	14.0
			Lead	<2.0
			Mercury	0.1
			Silver	<0.2
			Thallium	1.0

	Weight % Ignited Basis	Indices	
		Reducing	Oxidizing
Silicon dioxide	60.54	Silica Value	82.66
Aluminum oxide	18.08	Base : Acid Ratio	0.20
Titanium dioxide	0.87	T <sub>250</sub> Temperature	2819°F
Iron oxide	9.45	Type of Ash	Bituminous
Calcium oxide	2.56	Fouling Index	0.14
Magnesium oxide	0.69	Slagging Index	0.62
Potassium oxide	2.55	Fusion Temperature of Ash (°F)	
Sodium oxide	0.69		
Sulfur trioxide	2.98		
Phosphorus pentoxide	0.26	Initial Deformation (IT)	2193
Strontium oxide	0.03	Softening (ST)	2318
Barium oxide	0.10	Hemispherical (HT)	2430
Manganese oxide	0.03	Fluid (FT)	2621
Undetermined	<u>1.17</u>		2700+
	100.00		

Data are from Maly et al., 1996.

**Table 5-3**  
**Composition and Properties of Mill Rejects Used in Coburning Tests**

Proximate Analysis			Ultimate Analysis		
	As Received	Dry Basis		As Received	Dry Basis
% Moisture	0.38	–	% Moisture	0.38	–
% Ash	79.98	80.29	% Carbon	10.26	10.30
% Volatile	12.29	12.34	% Hydrogen	0.58	0.58
% Fixed Carbon	<u>7.35</u>	<u>7.37</u>	% Nitrogen	0.13	0.13
	100.00	100.00	% Sulfur	6.10	6.12
			% Ash	79.98	80.29
Btu/lb	1924	1931	% Oxygen (diff)	<u>2.57</u>	<u>2.58</u>
% Sulfur	6.10	6.12		100.00	100.00
MAF Btu		9797			
Alk. as Sodium Oxide	1.08	1.08			
<b>Analysis of Ash</b>			<b>Indices</b>		
	<b>Weight % Ignited Basis</b>				
Silicon dioxide	59.29		Silica Value	68.98	
Aluminum oxide	9.90		Base : Acid Ratio	0.41	
Titanium dioxide	0.99		T <sub>250</sub> Temperature	2402°F	
Iron oxide	25.44		Type of Ash	Bituminous	
Calcium oxide	0.65		Fouling Index	0.14	
Magnesium oxide	0.57		Slagging Index	2.51	
Potassium oxide	1.52				
Sodium oxide	0.35		<b>Trace Elements</b>	<b>ppm</b>	
Sulfur trioxide	0.86		Antimony	4.0	
Phosphorus pentoxide	0.15		Arsenic	210.0	
Strontium oxide	0.01		Barium	210.0	
Barium oxide	0.06		Beryllium	<2.0	
Manganese oxide	0.21		Cadmium	<2.0	
Undetermined	<u>0.00</u>		Chromium	20.0	
	100.00		Lead	<17.0	
			Mercury	0.7	
			Silver	<2.0	
			Thallium	15.0	
<b>Fusion Temperature of Ash (°F)</b>			<b>Ash Analysis (Source Coal)</b>		
	<b>Reducing</b>	<b>Oxidizing</b>	<b>% Dry Basis</b>		
Initial Deformation (IT)	2047	2631	SiO <sub>2</sub>	47.41	
Softening (ST)	2121	2692	Al <sub>2</sub> O <sub>3</sub>	30.75	
Hemispherical (HT)	2216	2700+	TiO <sub>2</sub>	1.59	
Fluid (FT)	2590	2700+	Fe <sub>2</sub> O <sub>3</sub>	15.64	
			CaO	1.28	
			MgO	0.70	
			K <sub>2</sub> O	2.25	
			Na <sub>2</sub> O	0.37	
			SO <sub>3</sub>	0.00	
			P <sub>2</sub> O <sub>5</sub>	0.00	
			Mn <sub>3</sub> O <sub>4</sub>	0.00	
			SrO	0.00	
			BaO	<u>0.00</u>	
			Total	99.99	
<b>Fuel Analysis (Source Coal)</b>					
	<b>As Received</b>				
% Moisture	6.08				
% Ash	9.42				
% Sulfur	1.43				
Heating Value	13,206 Btu/lb				

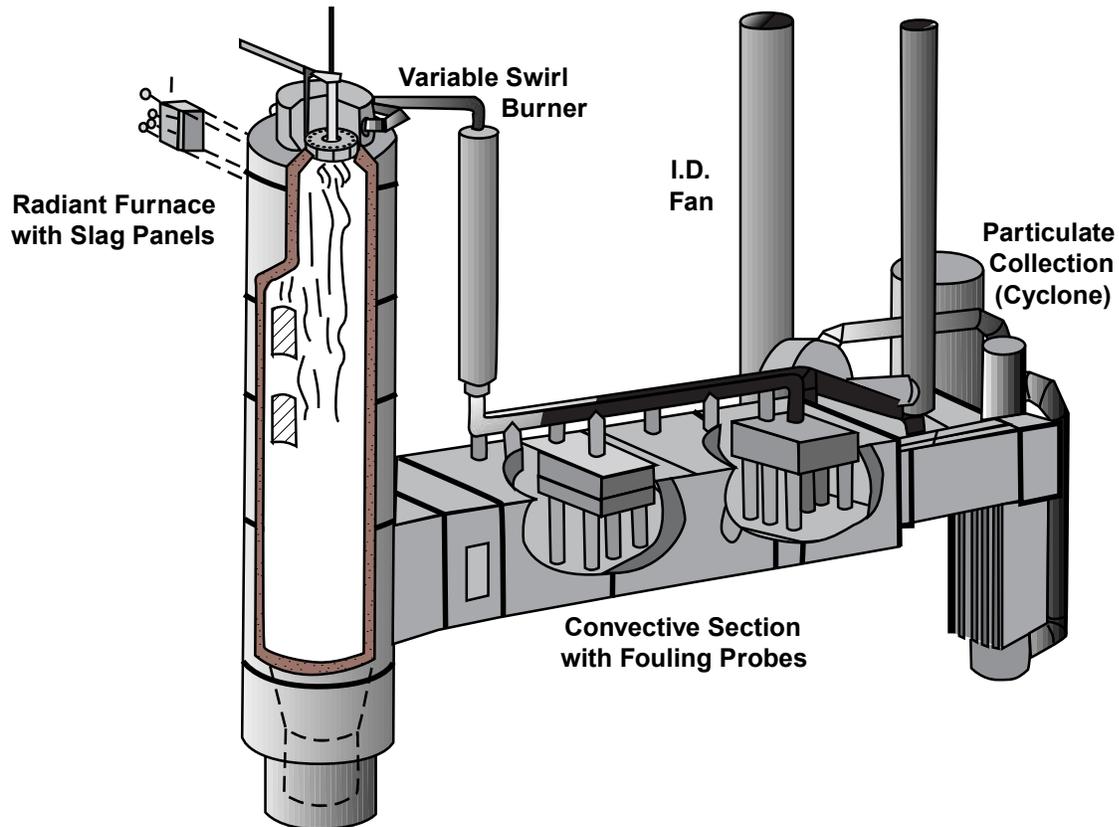
Data are from Maly et al., 1996.

### ***Pilot-Scale Combustion Tests***

Screening combustion tests on sulfur, nitrogen, and carbon monoxide emissions were conducted in a 600,000 lb/hr Fuel Evaluation Facility, depicted in Figure 5-6, using mixtures of Illinois coal and 0, 2, 4, or 10 percent mill rejects. The tests showed that SO<sub>2</sub> emissions increased by 16 percent from 3,100 to 3,600 ppm when 10 percent mill rejects were burned and by 8 percent when 4 percent rejects were burned. As shown in Figure 5-7a, the increase in sulfur emissions was less than predicted based on fuel composition, indicating that more sulfur was retained by the ash particulates than predicted. Nitrogen emission tests showed that the minimum NO<sub>x</sub> emissions were achieved at the same swirl setting, 25 percent, even when 10 percent mill rejects were burned. The emissions were slightly less than when only coal was burned, particularly at higher swirl settings (Figure 5-7b). The difference in emissions may be partly due to the lower nitrogen and volatiles content of the rejects. The carbon monoxide emissions monitoring showed that CO emissions were less than 50 ppm for all mixtures tested and the differences between mixtures were small (Figure 5-7c). When oxygen levels were above 1.5 percent, carbon monoxide levels remained the same. Typical boiler operating conditions are 3 percent excess oxygen. The conclusion of these emission tests was that burning mill rejects would not be likely to cause problems in the boilers, and that 4 percent mill rejects seemed to be the optimum upper limit for these specific mixtures.

Detailed combustion tests were conducted in the same facility as the screening tests to evaluate differences in boiler performance and maintenance issues when no rejects and 4 percent rejects were burned. Furnace-related tests evaluated flame stability, furnace temperatures, slagging potential, and fouling potential. The flame stability and temperature profiles were similar with or without rejects. Slagging potential was determined by inserting panels into the furnace at different heights to determine the nature and thickness of deposits built up on the panels. The difference in heat transfer from the boiler to the water walls was also calculated. In the near burner region (top panel), the heat absorption and scale deposition for the two mixtures were about the same. The deposits were easily removed. The middle panel below the burner showed similar heat transfer trends with slightly lower transfer toward the end of the 11-hour test. The deposits for the reject mixtures were somewhat thicker, but could be removed by sootblowing. The bottom panel had 10 percent less heat transfer by the end of the test, but similar trends overall. Slagging potential was slightly higher for the reject mixture than the coal, but deposits were easier to remove than those on the middle panel. Overall, these tests showed that some additional sootblowing might be needed. The fouling tests were conducted using probes placed in the connective section of the test furnace, which corresponds to the superheater region of a full-scale boiler. Parameters needed to calculate heat absorption and fouling factors were measured. Tests on fouling potential showed similar heat absorption and fouling factors for the two mixtures and that low or high temperature superheater problems were not likely to occur. The deposits formed on the probes could be removed by sootblowers.

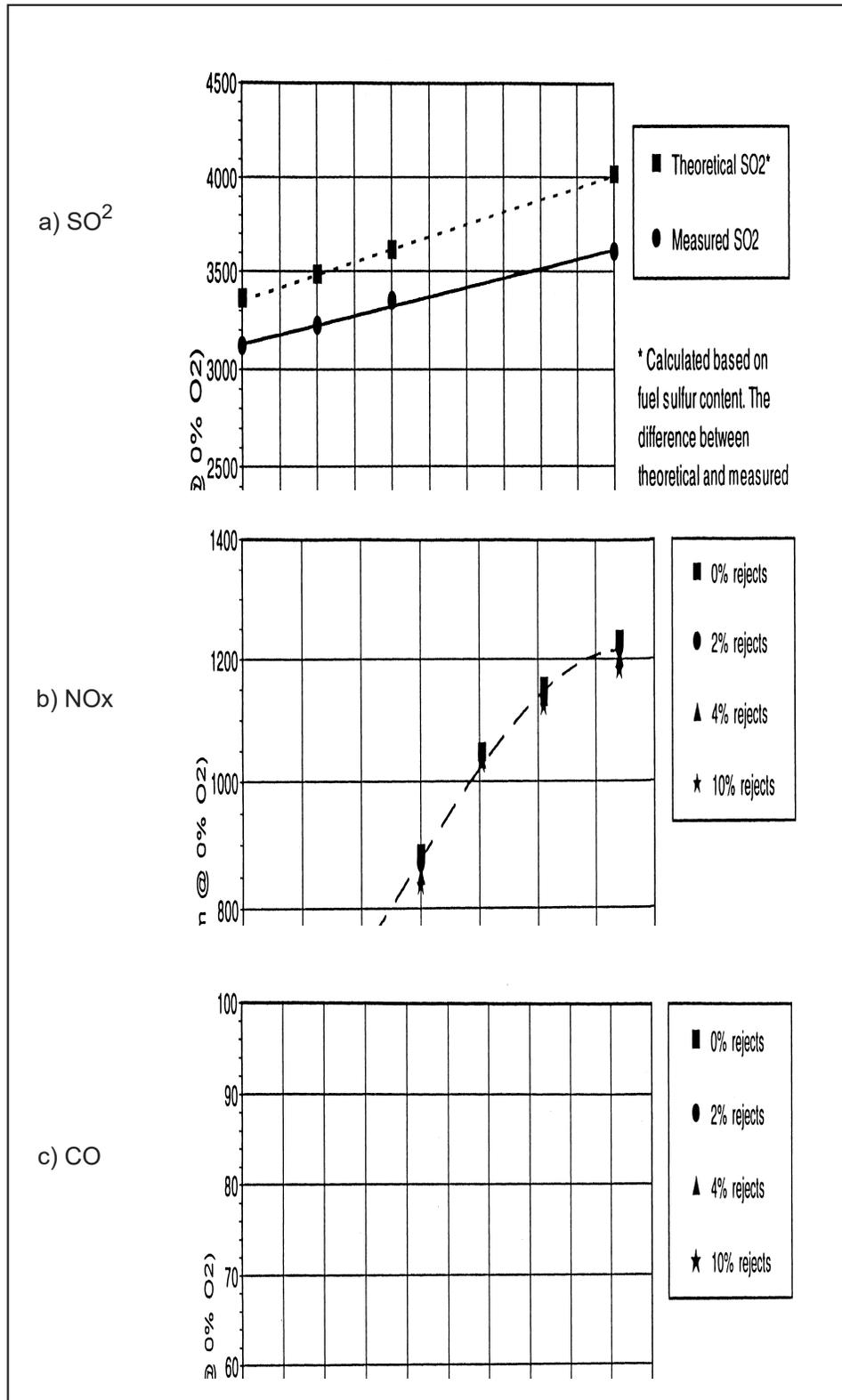
### Fuel evaluation facility



### Fuel preparation

- Coal: ground in deep bowl mill
- Rejects: ground in hammer mill
- Both ground so 70 percent less than 200 mesh
- Could not mix in roller with baffles due to varying densities
- Mixed fuels in pneumatic transport line to burner

**Figure 5-6**  
Schematic of combustion facility used in coburning test  
(after Maly et al., 1996).



**Figure 5-7**  
**Emissions from pilot coburning test**

Additional tests were conducted to determine the effect of mill rejects on particulate control equipment. The particle size distributions for the two mixtures were similar, with the same mean diameter, 8 microns (Figure 5-8). Carbon burnout values were essentially the same, 99.9 percent, and implied that nearly all the carbon was consumed for both coal and coal-reject mixtures. Resistivity was measured in ash from both combustion tests. It was higher for the mill rejects mixture than for coal only,  $7 \times 10^{11}$  ohm-cm versus  $1 \times 10^{11}$  ohm-cm at 300 to 350°F, which is a typical operating temperature for cold-side electrostatic precipitators. When resistivity exceeds  $1 \times 10^{12}$  ohm-cm, collection efficiency of the ESP unit can decrease. The combination of increased fly ash quantity and higher resistivity could require some modifications of ESP units, depending on the specific coal-reject properties and equipment being used.

The overall conclusion of these tests was that regrinding and coburning of mill rejects is technically feasible. Benefits of burning could include improved energy recovery, waste minimization, and elimination of potential environmental concerns with reject storage/disposal. However, regrinding and coburning of mill rejects could result in small increases in sulfur emissions, depending on the percent of mill rejects burned. Some ESP units may need to be modified.

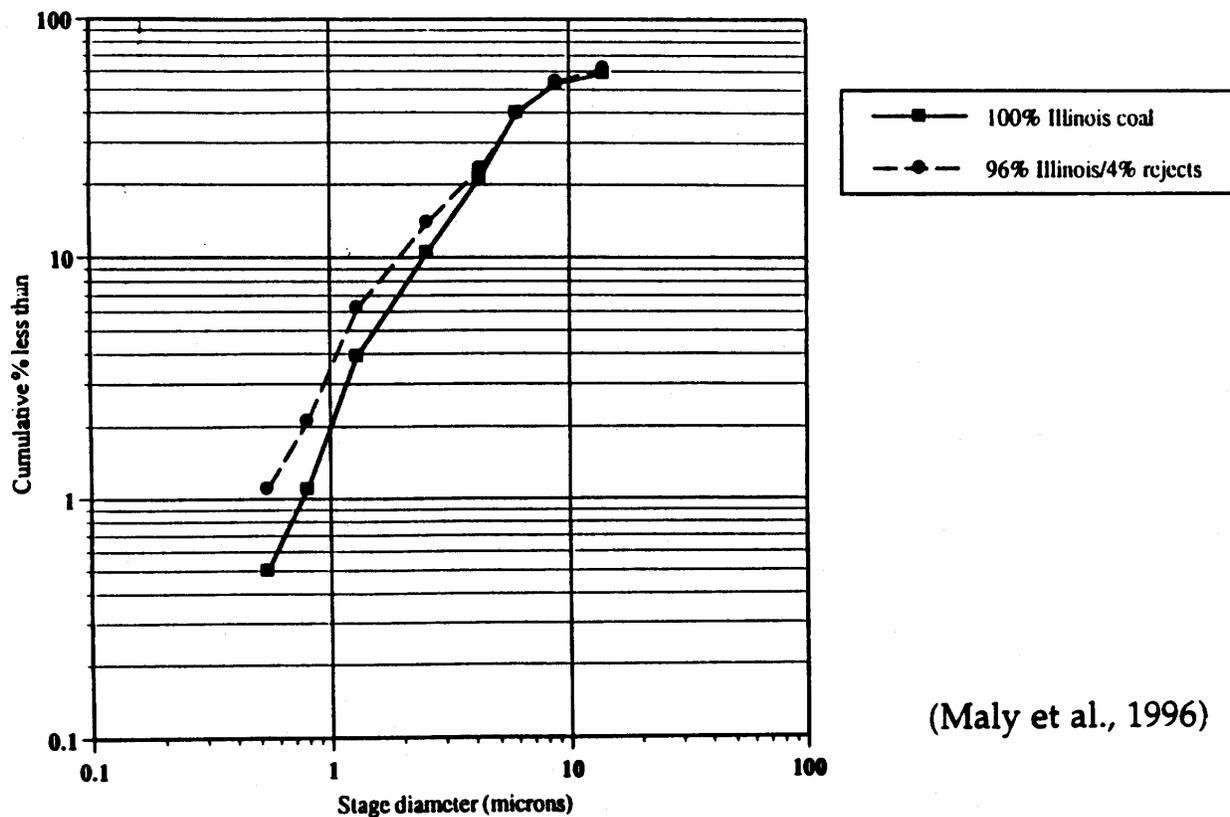


Figure 5-8  
Fly ash particle size distributions for coal only and coal/mill rejects mixture



# 6

## PERFORMING CLOSURE AND POSTCLOSURE OPERATIONS

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### Background and Considerations for Closure

The foregoing sections addressed the environmental management alternatives for mill rejects produced at the coal fired power plants. Case studies on the comanagement of mill rejects with CCBs were also summarized. The technical data and case studies indicate that there are large variabilities in both the generation and the chemical/mineralogical composition of mill rejects. These results also indicate that pyrites are not always present in mill rejects, and when they are, they generally comprise a small percentage (<5%) of the total quantity.

When present, pyrites (i.e., iron sulfide) in mill rejects were identified as a source of potential environmental risk. When pyrites are allowed to undergo oxidation, the resulting acidity and other constituents in the leachate have the potential for impacting land and water resources. In some of the case studies discussed earlier, pyrite oxidation had occurred and environmental control technologies were employed by the utilities involved to achieve protection of the nearby ground- and surface-waters. In the remaining case studies, either no evidence was found to indicate that pyrite oxidation had occurred, or the comanaged mill rejects did not contain much pyritic material.

This section provides some general guidelines for the closure of waste management units containing pyrites. As discussed, effective comanagement of mill rejects containing pyrites is based on the premise of minimizing oxidation potential and utilizing neutralization capacity of coal ash and the high alkalinity of calcareous soils. This same premise is also applicable to comanagement units containing CCBs and mill rejects with pyrites in an impoundment or a landfill. After the useful life of the comanagement units, closure and postclosure operations commence. This section, adapted from EPA Draft Industrial D Guidance Chapter 11, focuses on recommended closure and postclosure operations for the two principal comanagement units: landfills and impoundments. Site-specific conditions may justify alternative approaches that are consistent with Federal, State, and local regulations.

As a preliminary issue, it should be emphasized that comanagement units containing CCBs and mill rejects without pyrites would not need to use capping materials for the purpose of minimizing oxygen diffusion. Similarly, if the acid-base accounting and/or testing of wastes in the comanagement unit indicates very low or negligible potential for the generation of acidic leachates, then the closure plans should specify a corresponding level of closure and postclosure care requirements.

The proper closure of comanagement units with pyrites entails addressing unacceptable environmental and human health risks in a manner that minimizes the need for further maintenance or future corrective action at the site. For in-place closure, the unit should be closed in a manner that also avoids future disruptions of necessary protective measures. The closure plan for a facility serves as the mechanism for the owner or the operator to describe the appropriate methods to complete all the activities necessary to close the facility. Most states regulate the closure of landfills and impoundments and require postclosure monitoring on a site-specific basis.

For postclosure care of comanagement units containing mill rejects and CCBs, the overall goals are to minimize the oxidation of pyrites, thus minimizing the potential for generation of acidic leachates, and to provide maintenance of the final cover until such time as it is determined that care is no longer necessary. In general, this can be accomplished by capping a management unit with an intermediate layer of alkaline ash with or without lime and a surface layer of 6 to 12 inches of soil consistent with relevant State regulations. The soil cap provides a partial oxygen barrier to slow the rate of oxygen diffusion, and the intermediate layer of alkaline ash with or without lime provides a neutralization buffer as well as helps minimize diffusion of oxygen into the mill rejects. In addition, the unit surface and surrounding surfaces should be graded to increase surface runoff and minimize infiltration. Also, during the postclosure period, monitoring of the unit is generally necessary to ensure that unacceptable releases and impacts are not occurring.

A number of technical resources that are available from EPA and the State agencies can assist electric utility industry engineers design closure plans on a site-specific basis. (Please see the list of references in Table 6-3 at the end of this section).

## **Closure Plans**

A closure plan is the primary resource for implementation of a proper closure. A well-designed plan is comprehensive, takes into account all aspects of the closure scenario, and is clearly articulated so as to be understandable to staff who will implement its specific activities. The plan also needs to be sufficiently detailed to enable calculation of the costs of closure and postclosure care, so that sufficient funding can be set aside for those activities.

A facility owner can take into account the following factors in developing a closure plan:

- Overall goals and objectives of closure;
- Future land use;
- Type of comanagement unit;
- Types, amount, and physical state of the comanaged materials in the unit;
- Constituents associated with the comanaged solids;
- Schedule (overall and interim);
- Costs to implement closure;

- Steps to monitor progress of closure actions, including inspections, maintenance activities, and necessary monitoring (e.g., ground water and leachate monitoring) where appropriate;
- Revisions to health and safety plan, as necessary;
- Contingency plans;
- Final cover information (if applicable);
- Parameters to assess performance of the unit throughout the postclosure period.

The plan should address the types of waste that have been or are expected to be deposited in the management unit and the constituents that can reasonably be associated with those wastes. Besides taking into account all of the above considerations, a closure plan for a comanagement unit containing mill rejects needs to be tailored to account for the unique characteristics of the mill rejects. Information about the amount and distribution of pyrites in the comanagement unit could facilitate design of the final cover and determination of the types of activities to be undertaken during the postclosure care period.

The closure plan typically contains detailed information regarding the closure strategy. For example, where a final cover is planned, the closure plan should take into consideration seasonal precipitation that could influence the performance of the cover as well as the monitoring system. Information concerning freeze cycles and the depth of frost permeation will provide supporting information with which to assess the adequacy of the cover design. For a comanagement unit containing a significant amount of pyrites in the mill rejects, a closure plan may also address considerations of a physical barrier, such as a slurry wall, to control lateral migration of leachates. The MO, BR and FA sites discussion above provide examples where such design considerations were warranted.

The closure plan should outline a closure schedule, including the dates the waste was initially placed in the unit, the date when closure will begin, and the date when closure is expected to be completed. Generally, closure should commence when the unit has reached capacity or has received the last expected waste for disposal. For units containing inorganic wastes, closure as soon as possible after the last expected waste has been received is particularly important. A period of 180 days is a good general guide for completing closure, but the actual time frame will be dictated by site-specific conditions. Similarly, other site-specific conditions, such as precipitation or winter weather, may also cause delay in completing closure. The closure should be scheduled in consultation with State and local regulatory authorities.

Even within a waste management unit, some areas will be closed on different schedules, with certain areas in partial closure, while other areas continue to operate. The schedules and partial closure activities (such as intermediate cover) should be considered in the closure plan. Although the processes for closing such areas may not be different than those for closing the unit as a whole, it is still more efficient to integrate partial closure activities into the closure plan.

For a strategy that involves engineering controls, such as physical barriers and final covers, the plan should provide detailed specifications, including descriptions of the cover materials in each layer and their permeability as well as any drainage control measures included in the operation of

the final cover. Also measures should be identified to verify the continued integrity of the final cover and the proper operation of the drainage control strategies.

The closure plan should also provide a detailed description of the monitoring that will be conducted to assess the performance of the comanagement unit throughout the postclosure period. These measurements include monitoring leachate volume and characteristics, if applicable, to ensure that a cover is minimizing infiltration and oxidation of pyrites in the comanagement unit. It is important to include appropriate groundwater quality standards with which to compare groundwater monitoring data. The performance measures section of the plan should establish, prior to completing closure, the parameters that will be used to monitor successful closure of the unit. If limits on these parameters are exceeded, it will provide an early warning that the final cover system is not functioning as designed and that measures should be undertaken to identify and correct problems.

## **Closure by Use of Final Cover Systems**

A comanagement unit may be closed by means of a final cover system. This approach is common for landfill units and some surface impoundment units where solids are left in place. The choice of final cover materials and design should be the result of a careful review and consideration of all site-specific conditions that will affect the performance of the cover system. Environmental professionals and State and local environmental protection agencies can provide information on the engineering properties of cover materials necessary to design and install a final cover system.

This section addresses some of the technical issues that should generally be considered when selecting cover materials and designing a cover system. It discusses the various potential components of final cover systems, including the types of materials that can be used, and advantages and disadvantages of each, and interaction between the various components.

### ***Purpose and Goal of Final Cover Systems***

The principal goals of final cover systems are to:

- Protect human health and the environment by reducing or eliminating potential for leachate generation and contaminant release;
- Minimize infiltration of precipitation into the waste management unit to minimize generation of leachates within the unit by promoting surface drainage and maximizing run-off;
- Minimize risk by providing physical separation between waste and humans, plants, and animals; and
- Minimize long-term maintenance needs.

For optimal performance, the final cover system should be designed to minimize permeability, surface ponding, and the erosion of cover material. To avoid the accumulation of leachate within a unit, the cover system should be no more permeable than the liner system. For example, if a

unit's bottom liner system is composed of a low-permeability material, such as compacted clay or a geomembrane, then the cover should also be composed of a low-permeability material.

In order to ensure that the final cover performs as desired, quality assurance and quality control must be given priority during construction and installation of the final cover. For general information on quality assurance for construction of final covers, see U.S. EPA reports: EPA 625-R-94-008 (1994a), EPA625-4-91-025 (1991), and EPA530-Solid Waste-89-047 (1989b).

### ***Technical Considerations for Selecting Cover Materials***

Several environmental and engineering factors can affect cover materials and should be considered in the choice of those materials.

#### **How can climate affect a final cover?**

Effects from the freeze and thaw cycles can lead to the development of microfractures in low permeability soil layers. These effects also can cause the realignment of interstitial fines (silts and clays), thereby increasing the hydraulic conductivity of the final cover. As a result, it is important to determine the maximum depth of frost penetration at a site and design covers accordingly (in other words, ensure barrier layers are below the maximum frost penetration depth). Information regarding the maximum frost penetration depth for a particular area can be obtained from the Natural Resource Conservation Service with the U.S. Department of Agriculture, or from local utilities, construction companies, universities, or State agencies.

#### **How can settlement and subsidence affect a final cover?**

When waste consolidates, settlement and subsidence can result. Excessive settlement and subsidence can significantly impair the integrity of the final cover system by causing ponding of water on the surface, fracturing of low permeability infiltration layers, and failure of geomembranes. The degree and rate of waste settlement are difficult to estimate.

#### **How can erosion affect the performance of a final cover?**

Erosion can adversely affect the performance of the final cover of a unit by causing rills that require maintenance and repair. Extreme erosion may lead to the exposure of the infiltration layer, initiate or contribute to sliding failures, or expose the waste. Anticipated erosion due to surface-water run-off for a given design criteria may be approximated using the USDA Universal Soil Loss Equation (U.S. EPA 1989a). Careful evaluation of potential erosion loss, and optimization of the final cover design through selection of the best available soil materials, can result in reduced maintenance needs of the final cover. An important consideration is the establishment of a vegetative cover, which will not only improve the appearance of a unit, but will also control erosion of the final cover. The vegetation components of the erosion layer should have the following characteristics:

- Locally adapted perennial plants that are resistant to various climatic changes reasonably expected to occur at the site;

- Roots that will not disrupt the low-permeability layer;
- The ability to thrive in low-nutrient soil with minimum nutrient addition; and
- The ability to survive and function with little or no maintenance.

Why are interfacial and internal friction properties for cover components important?

Adequate friction between cover components, such as geomembrane barrier layers and soil drainage layers, as well as between any geosynthetic components, is required to prevent extensive slippage or interfacial shear. Water and ice may affect the potential for cover components to slip. Sudden sliding can tear geomembranes or cause sloughing of earthen materials. Internal shear may also be a concern for composite or geosynthetic clay liner materials. Measures to improve stability include using flatter slopes or textured geosynthetic membranes, geogrids designed to resist slipping forces, or otherwise reinforcing the cover soil.

Can dry soil materials affect a final cover?

Desiccation, the natural drying of soil materials, may have an adverse affect on the soil layers, compromising the final cover. Although this process is most commonly associated with layers of low permeability soil, such as clay, it can cause problems with other soil types as well. Desiccation causes cracks in the soil surface extending downward. Cover layers are generally not very thick, and therefore these cracks can extend through an entire layer, radically changing its hydraulic conductivity or permeability. Care should be taken to detect desiccation cracks at an early stage in time to mitigate its damage.

Can plants and animals have an effect on a final cover?

When selecting the plant species to include in the vegetative cover of mill rejects comanagement units, consideration should be given to the potential for root systems to grow through surface cover layers and penetrate underlying barrier layers. Such root penetration will form preferential pathways for water infiltration and compromise the integrity of the final cover system. Similarly, the presence of burrowing animals should be foreseen when designing the final cover system. Such animals may burrow in the surface layers and can potentially breach the underlying barrier layer. Strategies for mitigating the effects described here are discussed below in the context of protection layers composed of gravel or cobbles.

### ***Components of a Final Cover***

Cover systems can be designed in a variety of ways to accomplish closure goals. This flexibility allows a final cover design system to integrate site-specific technical considerations that may affect performance. This section discusses the potential components or layers of a final cover system, their functions, and appropriate materials for each layer. Table 6-1 presents the types of layers and typical materials that may exist in a final cover. The minimum appropriate thicknesses of each of the five types of layers depends upon many factors including site drainage, erosion potential, slopes, types of vegetative cover, type of soil, and climate.

**Table 6-1**  
**Types of Layers in Final Cover Systems**

Layer	Type of Layer	Typical Materials
1	Surface (Erosion, Vegetative Cover) Layer	Topsoil, Geosynthetic Erosion Control Layer, Cobbles
2	Protection Layer	Soil, Recycled or Reused Waste Materials, Cobbles
3	Drainage Layer	Sand and Gravel; Geonet or Geocomposite; Chipped or Shredded Tires; Bottom Ash
4	Barrier (Infiltration) Layer	Compacted Clay, Geomembrane, Geosynthetic Clay Liner
5	Foundation Layer	Sand or Gravel, Soil, Geonet or Geotextile, Recycled or Reused Waste Material

Source: Jesionek *et al.*, 1995.

### What function does the surface layer serve?

The role of the surface layer in the final cover system is to promote the growth of native, nonwoody plant species, minimize erosion, restore the aesthetics of the site, and protect the barrier layer. The surface layer should be thick enough so that the root systems of the plants do not penetrate the underlying barrier layer. The vegetation on the surface layer should be resistant to drought and temperature extremes, able to survive and function with little maintenance, and also be able to maximize evapotranspiration, which will limit water infiltration to the barrier layer. Consult with agriculture or soil conservation experts concerning appropriate cover vegetation. Finally, the surface layer should be thick enough to withstand long-term erosion and to prevent desiccation and freeze/thaw effects of the barrier layer. The U.S. EPA recommends a thickness at least 12 inches for the surface layer. Consult with the State agency to determine the appropriate minimum thickness in cold climates to protect against freeze-thaw effects.

### What types of materials can be used in the surface layer?

**Topsoil** has been by far the most commonly used material for surface layers. The principal advantages of using topsoil in the surface layer include its general availability and its suitability for sustaining vegetation. When topsoil is used as a surface layer, the roots of plants will reinforce the soil, reduce the rate of erosion, decrease run-off, and control infiltration by removing water from the soil through evapotranspiration. If topsoil is to be used in the surface layer, the soil should have sufficient water-holding capacity to sustain plant growth. There are some concerns with regard to using topsoil. For example, topsoil requires ongoing maintenance, especially during periods of drought or heavy rainfall. Prolonged drought can lead to cracking in the soil, creating preferential pathways for water infiltration. Heavy rainfall can lead to erosion causing rills or gullies, especially on newly-seeded or steeply sloping covers. If the topsoil does not have sufficient water holding capacity, it may not adequately support surface plant growth, and evapotranspiration may excessively dry the soils. In this case, irrigation may be required to restore the water balance within the soil structure. Topsoil is also vulnerable to penetration by burrowing animals.

**Geosynthetic erosion control material** can be used as a cover above the topsoil to limit erosion prior to the establishment of a mature vegetative cover. The geosynthetic material can include embedded seeds to promote plant growth, while minimizing soil run-off. It can be anchored or reinforced to add stability on steeply sloped covers. Geosynthetic material, however, does not enhance the water-holding capacity of the soil. In arid or semi-arid areas, therefore, the soil may still be prone to wind and water erosion if its water-holding capacity is insufficient.

**Cobbles** may be a suitable material for the surface layer in arid areas or on steep slopes which might hinder the establishment of vegetation. If they are large enough they will provide protection from wind and water erosion. Cobbles can also protect the underlying barrier layer from intrusion by burrowing animals, but cobbles may not be available locally, and their use does not protect the underlying barrier layer from water infiltration. Because cobbles create a porous surface through which water can percolate, they do not ordinarily support vegetation. Wind-blown soil material can fill voids between cobbles, and plants may establish themselves in these materials. This plant material should be removed, as its roots are likely to extend into the underlying barrier layer in search of water.

What function does the protection or biotic barrier layer serve?

A protection or biotic barrier layer may be added below the surface layer, but above the drainage layer, to protect the latter from intrusion by plant roots or burrowing animals. This layer adds depth to the surface layer, increasing its water storage capacity and protecting underlying layers from freezing and erosion. In many cases, the protection layer and the surface layer are combined to form a single cover layer.

What types of materials can be used in the protection layer?

**Soil** will generally be the most suitable material for this layer, except in cases where special design requirements exist for the protection layer. The advantages and disadvantages of using soil in the protection layer are the same as those stated above in the discussion of the surface layer topsoil. Factors impacting the thickness and type of soil to use as a protection layer include freeze and thaw properties and the interaction between the soil and drainage layers. Other types of materials that may be used in the protection layer include cobbles with a geotextile filter, gravel and rock, and recycled or reused waste.

**Cobbles with a geotextile filter** can form a good barrier against penetration by plant roots and burrowing animals in arid sites. The primary disadvantage is that cobbles have no water storage capacity and allow water percolation into underlying layers.

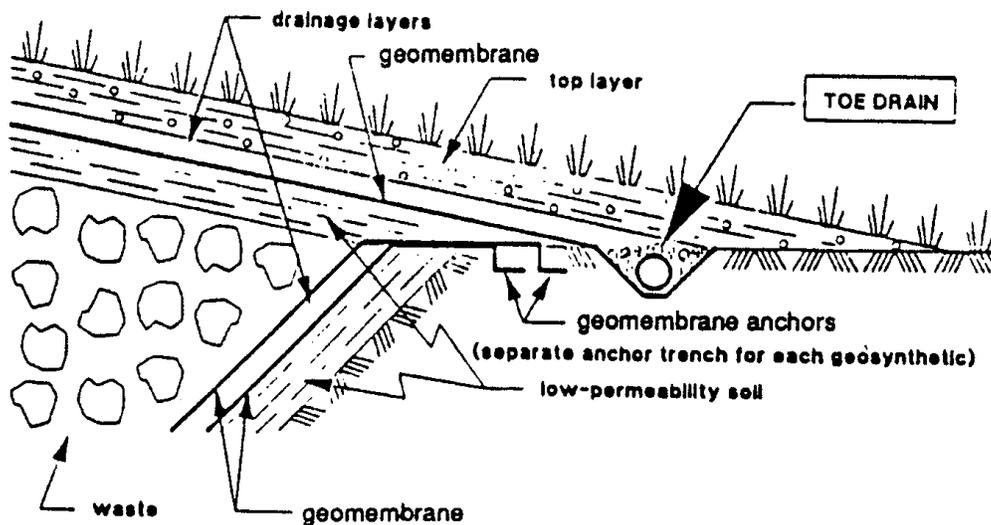
**Gravel and rock** are similar to cobbles since they can form a good barrier against penetration by plant roots and burrowing animals. Again, this use is usually only considered for arid sites, because gravel and rocks have no water storage capacity and allow water percolation into underlying layers.

**Coal combustion products** such as fly ash and bottom ash may be used in the protection layer, where allowable under State law. The advantages of using these materials in the protection layer

are that they store water that has infiltrated past the surface layer, which can then be returned to the surface through evapotranspiration, and that they offer protection against burrowing animals and penetration by roots. If planning to use CCBs in the protection layer, consider its impact on surface run-off at the unit's perimeter. Design controls to ensure run-off does not contribute to surface-water contamination.

### What function does the drainage layer serve?

A drainage layer may be placed below the surface layer, but above the barrier layer, to direct infiltrating water to drainage systems at the toe of the cover (see Figure 6-1). For drainage layers, the thickness will depend on the level of performance being designed and the properties of available materials. For example, some geonet composites, with a minimal thickness of less than 1 inch, may have a transmissivity equal to a much thicker layer of aggregate or sand. The U.S. EPA recommends thickness of the low permeability soil drainage layer to be 12 inches with at least a 3 percent slope at the bottom of the layer. Based on standard practice, the drainage layer should have a hydraulic conductivity in the range of  $10^{-2}$  to  $10^{-3}$  cm/sec. Water infiltration control through a drainage layer improves slope stability by reducing the duration of surface and protection layer saturation. In this role, the drainage layer works with vegetation to remove infiltrating water from the cover and protect the underlying barrier layer. If this layer drains the overlying soils too well, it could lead to the need for irrigation of the surface layer to avoid the development of desiccation cracks. Another consideration for design of drainage layers is that the water should discharge freely from the layer at the base of the cover. If outlets at the base become plugged or are not of adequate capacity, the toe of the slope may become saturated and potentially unstable. In addition, when designing the drainage layer, consider using flexible corrugated piping in conjunction with either the sand and gravel or the gravel with geotextile filter material to facilitate the movement of water to the unit perimeter.



Source: U.S. EPA, 1991. *Design and construction of RCRA/CERCLA final covers.*

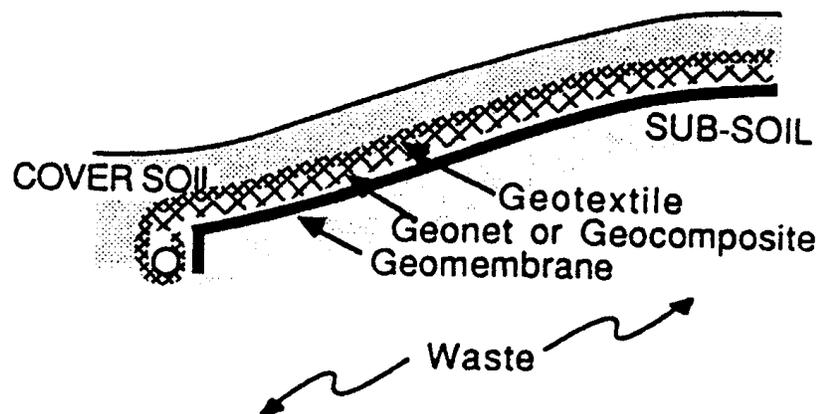
**Figure 6-1**  
**Drainage Layer Configuration**

What materials can be used in the drainage layer?

**Bottom ash, sand and gravel** are a common set of materials used in the drainage layer. The principal consideration in their use is the conductivity required by the overall design. There may be cases in which the design requires the drainage of a large amount of water from the surface layer, and the hydraulic properties of the sand and gravel layer may be insufficient to meet these requirements. The advantages of using bottom ash, sand and gravel in the drainage layer include the ability to protect the underlying barrier layer from intrusion, puncture, and temperature extremes. The principal disadvantage to these materials is that they are subject to intrusion from the overlying protective layer that may alter their hydraulic conductivity. Similarly, fines in the sand and gravel can migrate downslope, undermining the stability of the cover slope. A graded filter or a geotextile filter can be used to separate and protect the sand and gravel from intrusion by the overlying protection layer.

**Gravel with a geotextile filter** is also a widely-used design, whose applicability may be limited by the local availability of materials. The gravel promotes drainage of water from the overlying layers, while the geotextile filter prevents the clogging of granular drainage layers. Again, be aware of the possibility that a gravel drainage layer may drain overlying soils so well that irrigation of the surface layer may become necessary. The principal advantage to a gravel/geotextile drainage layer is the engineering community's considerable body of knowledge regarding their use as drainage materials. Other advantages include their ability to protect underlying layers from intrusion, puncture, temperature extremes, and their common availability. The geotextile filter provides a cushion layer between the gravel and the overlying protection layer.

**Geonet with geotextile filter** materials can be used to form an effective drainage layer directly above a compacted clay or geomembrane liner (see Figure 6-2). They may be a suitable alternative in cases where other materials, such as sand and gravel, are not locally available. The principal advantage is that lightweight equipment can be used during installation, reducing the risk of damaging the underlying barrier layer.



Source: U.S. EPA, 1991. *Design and construction of RCRA/CERCLA final covers.*

**Figure 6-2**  
**Geonet With Geotextile Filter Design For Drainage Layer.**

The disadvantages associated with these materials are that they provide little protection for the barrier layer against extreme temperature changes, and there can be slippage between the geocomposite interfaces with geomembranes, geotextiles, or low permeability soil barrier materials. Furthermore, problems can arise in the horizontal seaming of the geotextile drainage layer on long slopes.

**Chipped or shredded tires** are an additional option for drainage layer materials. These have been used for bottom drainage layers in the past and may be suitable for cover drainage layers as well. Consult with the State agency to determine whether this option is an acceptable practice.

What function does the barrier layer serve?

The barrier layer is the most critical component of the cover system because it prevents water infiltration into the waste. It also indirectly promotes the storage and drainage of water from the overlying protection and surface layers. This layer will be the least permeable component of the final cover system. Typically, the hydraulic conductivity of a barrier layer is between  $10^{-9}$  and  $10^{-7}$  cm/sec.

What types of materials can be used in the barrier layer?

**Single compacted clay liners (CCLs)** are the most common material used as barrier layers in final cover systems. CCL popularity arises largely because of the local availability of materials and the engineering community's extensive experience with their use. Drying and subsidence are the primary difficulties posed by CCLs. When the clay dries, cracks appear and provide preferential pathways along which water may enter the waste, promoting leachate formation. Dry waste materials within the unit contribute to drying from below, while a range of climatological conditions, including drought, can affect CCLs from above. Even with extremely thick surface protection layers, CCLs may still undergo some desiccation.

Clay liners are also vulnerable to subsidence within the waste unit. This problem can first manifest itself during liner construction. As the clay is compacted with machinery, the waste may not provide a stable, even foundation for the compaction process. This will make it difficult to create the evenly measured lifts comprising the liner. As waste settles over time, depressions can form along the top of the CCL. These depressions put differential stresses on the liner, causing cracks which compromise its integrity. For instance, a depression of only 5 to 11 inches across a 6-foot area may be sufficient to crack the liner materials.

**Single geomembrane liners** are sheets of a plastic polymer combined with other ingredients to form an effective barrier to water infiltration. Such liners are simple and straightforward to install, but they are relatively fragile and can be easily punctured during installation or by movement in surface layer materials. The principal advantage of a geomembrane is that it provides a relatively impermeable barrier with materials that are generally available. It is not damaged by temperature extremes and therefore does not require a thick surface layer. The geomembrane is more flexible than clay and not as vulnerable to cracking caused by subsidence within the unit. The principal disadvantage is that it provides a point of potential slippage at the interface with the cover soils. Such slippage can tear the geomembrane, even if it is anchored.

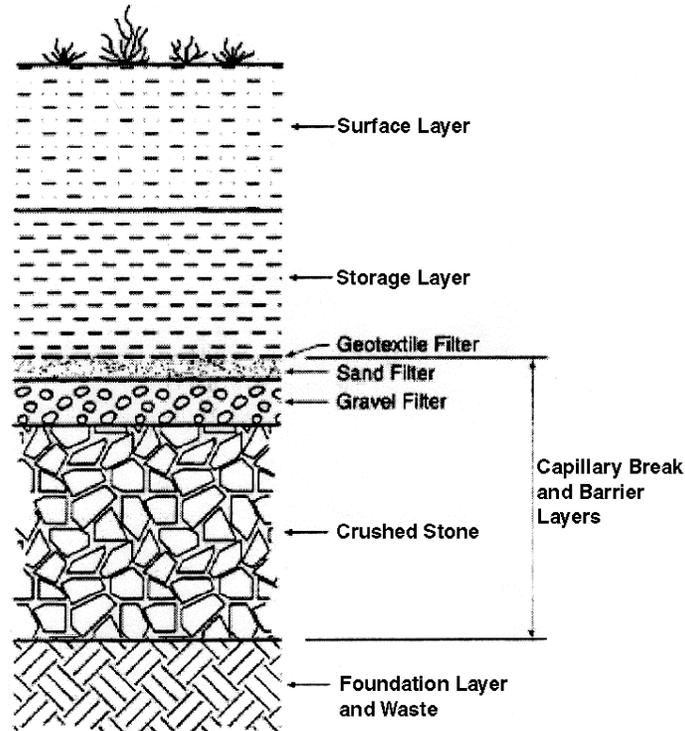
**Single geosynthetic clay liners (GCLs)** are composed of bentonite clay supported by geotextiles or geomembranes held together with stitching or adhesives. These liners are relatively easy to install and have some self-healing capacity for minor punctures. They are easily repaired by patching. The main disadvantages include low shear strength, low bearing capacity, vulnerability to puncture due to relative thinness, and potential for slippage at interfaces with under- and over-lying soil materials.

**Geomembrane with compacted clay liners (GCCLs)** can be used to mitigate the shortcomings of each material when used alone. In this composite liner, the geomembrane acts to protect the clay from desiccation, while providing increased tolerance to differential settlement within the waste. The clay acts to protect the geomembrane from punctures and tearing. Both act as an effective barrier to water infiltration. The principal disadvantage is slippage between the geomembrane and surface layer materials.

**Geomembrane with geosynthetic clay liners (GGCLs)** can also be used as a barrier layer. As with geomembrane and CCL combinations, each component serves to mitigate the weakness of the other. The geosynthetic material is less vulnerable than its clay counterpart to cracking and has a moderate capacity to self-heal. The geomembrane combined with the GCL is a more flexible cover and is less vulnerable to differential stresses from waste settlement. Neither component is readily affected by extreme temperature changes, and both work together to form an effective barrier layer. The potential disadvantage is slippage between the upper and lower surfaces of the geomembrane and some types of GCL and other surface layer materials. The geomembrane is still vulnerable to puncture, so placement of cover soils is important to minimize such damage.

### ***Capillary-Break Final Covers***

The capillary-break (CB) approach is an alternative design for a final cover system (see Figure 6-3). This system relies on the fact that for adjacent layers of fine- and coarse-textured soil to be in water-potential equilibrium, the coarse-grained soil (such as crushed stone) will tend to have a much lower water content than the fine-grained soil (such as sand). Furthermore, the conductivity of water through a soil decreases exponentially with its water content, or stated another way, as a soil becomes more dry, its tendency to stay dry increases. Therefore, as long as the strata in a capillary break remain unsaturated (remain above the water table), the overlying fine-textured soil will retain nearly all the water and the coarse soil will behave as a barrier to water percolation due to its dryness. Since this phenomenon breaks down if the coarse layer becomes saturated, this alternative cover system is most appropriate for semiarid and desert environments.



Adapted from [www.hanford.gov/eis/hraeis/eisdoc/graphics/fige-1.gif](http://www.hanford.gov/eis/hraeis/eisdoc/graphics/fige-1.gif)

**Figure 6-3**  
**Example of a Capillary-Break Final Cover System.**

What types of materials are used in capillary-break covers?

The CB cover system typically consists of five layers: surface, storage, capillary-break, barrier, and foundation. The surface, barrier, and foundation layers play the same role in the cover system as described above. The storage layer consists of fine material, such as silty sand. The capillary-break, or coarse, layer consists of granular materials, such as gravel and/or coarse sand. A fabric filter is often placed between the coarse and fine layers.

### ***The Hydrologic Evaluation of Landfill Performance (HELP) Model***

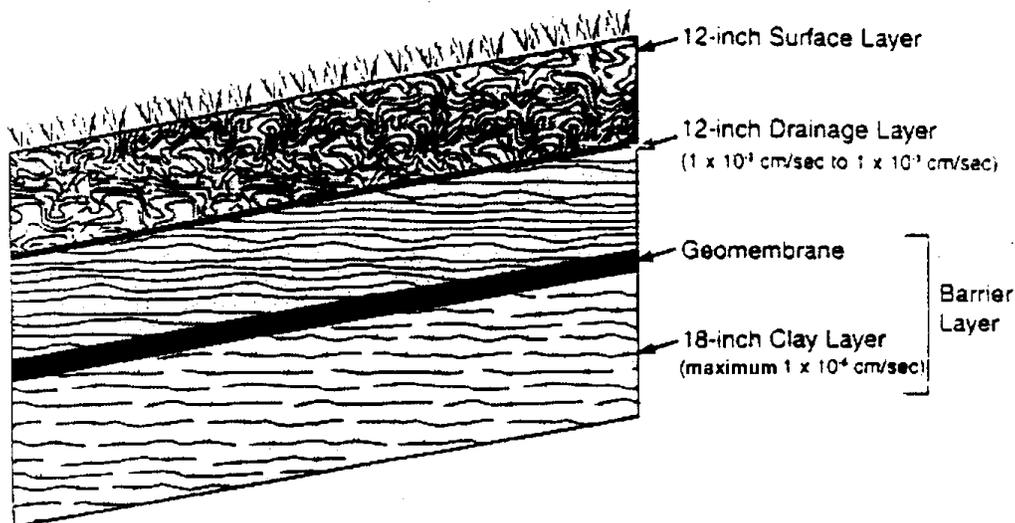
The relative performance of various cover designs can be evaluated with the Hydrologic Evaluation of Landfill Performance (HELP) model, developed by the U.S. Army Corps of Engineers Waterway Experiment Station for EPA (U.S. EPA 1988) and enhanced in 1994. The HELP model was designed specifically to support permit writers and engineers in evaluating alternative cover and liner configurations.

The HELP model integrates run-off, percolation, and subsurface-water flow actions into one model. The HELP model can be used to estimate the flow of water across and through a final cover. To achieve this, the HELP model uses precipitation and other climatological information to partition rainfall and snowmelt into surface runoff, evaporation, and downward infiltration

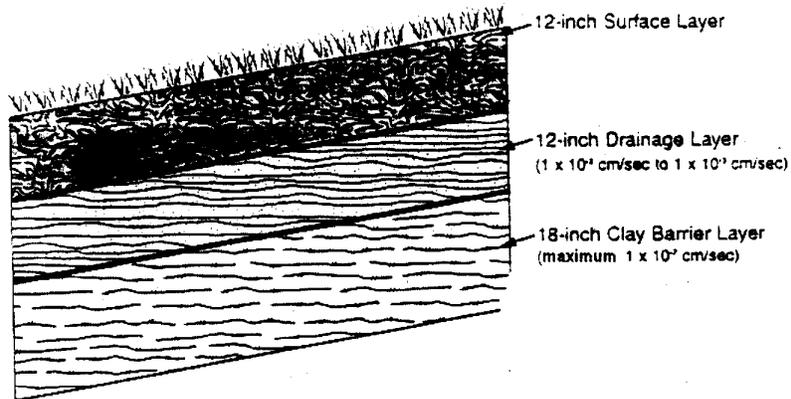
through the barrier layer to the waste. The HELP model essentially divides a waste management unit into layers, each defined in terms of soil type, which is related to the hydraulic conductivity of each. Users supply specific information on the layers and climate, and this information is input to the model. In performing its calculations, the model takes into account the reported engineering properties of each layer, such as slope, hydraulic conductivity, and rates of evapotranspiration, to estimate the amount of precipitation that may enter the waste unit through the final cover. To use the HELP model properly, refer to the HELP Model User's Guide and documentation (U.S. EPA. 1994b, U.S. EPA. 1994c). The HELP model, User's Guide, and supporting documentation may be obtained by calling the National Technical Information Service (NTIS) at 800 553-6847.

### Recommended Cover Systems

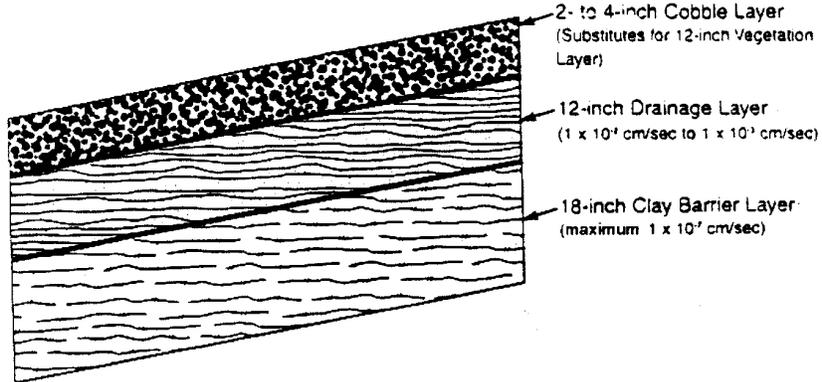
Figures 6-4 through 6-8 present U.S. EPA recommended minimum final cover systems. The recommended final cover systems correspond to a waste management unit's bottom liner system. A unit with a single geomembrane bottom liner system, for example, should include, at a minimum, a single geomembrane in its final cover system unless an evaluation of site-specific conditions shows an equivalent reduction in infiltration. Table 6-2 below summarizes the recommended final cover systems based on the unit's bottom liner system. While the recommended minimum final cover systems include closure layer component thicknesses and hydraulic conductivity, the cover systems can be modified to address site-specific conditions.



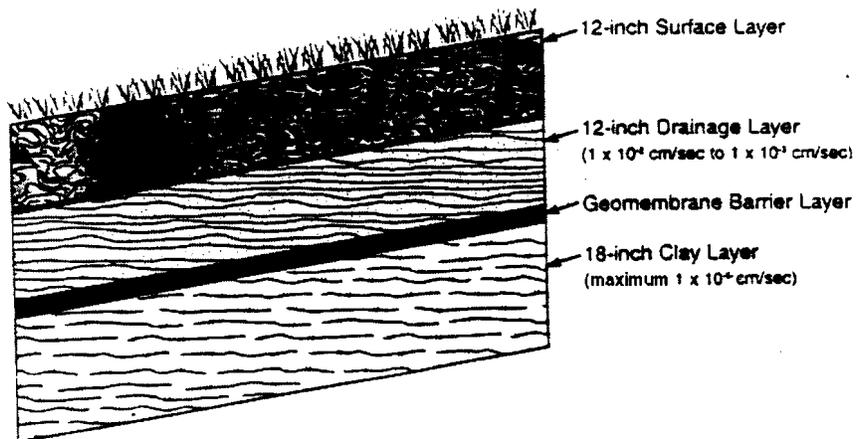
**Figure 6-4**  
**Final Cover System For A Unit With A Double Or Composite Liner.**



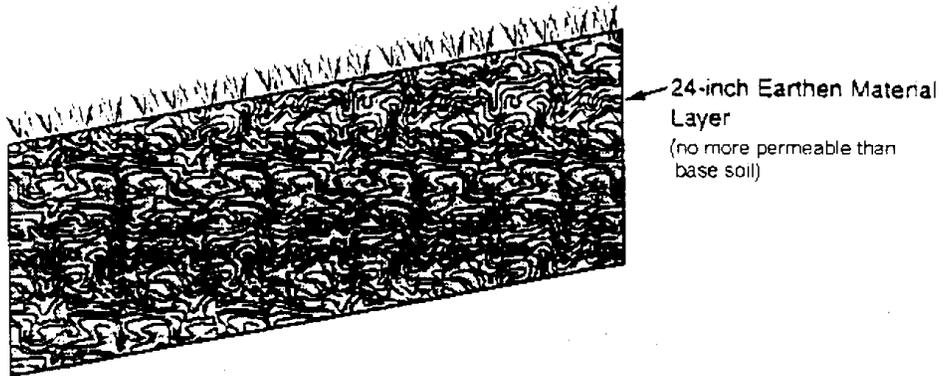
**Figure 6-5**  
Final Cover System For A Unit With A Single Clay Liner.



**Figure 6-6**  
Final Cover System For A Unit With A Single Clay Liner In An Arid Area.



**Figure 6-7**  
Final Cover System For A Unit With A Single Synthetic Liner.



**Figure 6-8**  
**Final Cover System For A Unit With A Natural Soil Liner.**

**Table 6-2  
Types Of Recommended Final Cover Systems**

Type of Bottom Liner	Recommended Cover System Layers (From top layer down)	Thickness (In inches)	Hydraulic Conductivity (In cm/sec)
Double Liner	Surface Layer	12	not applicable
	Drainage Layer	12 <sup>a</sup>	1x10 <sup>-2</sup> to 1x10 <sup>-3</sup>
	Geomembrane	30mil(PVC) 60mil (HDPE)	-
	Clay Layer	18	less than 1x10 <sup>-5</sup>
Composite Liner	Surface Layer	12	not applicable
	Drainage Layer	12 <sup>a</sup>	1x10 <sup>-2</sup> to 1x10 <sup>-3</sup>
	Geomembrane	30 mil (PVC) 60 mil (HDPE)	-
	Clay Layer	18	less than 1x10 <sup>-5</sup>
Single Clay Liner	Surface Layer	12	not applicable
	Drainage Layer	12 <sup>a</sup>	1x10 <sup>-2</sup> to 1x10 <sup>-3</sup>
	Clay Layer	18	less than 1x10 <sup>-7</sup>
Single Clay Liner in an Arid Area	Cobble Layer	2-4	not applicable
	Drainage Layer	12 <sup>a</sup>	1x10 <sup>-2</sup> to 1x10 <sup>-3</sup>
	Clay Layer	18	less than 1x10 <sup>-7</sup>
Single Synthetic Liner	Surface Layer	12	not applicable
	Drainage Layer	12 <sup>a</sup>	1x10 <sup>-2</sup> to 1x10 <sup>-3</sup>
	Geomembrane	30 mil (PVC) 60 mil (HDPE)	-
	Clay Layer	18	less than 1x10 <sup>-5</sup>
Natural Soil Liner	Earthen Material	24 <sup>b</sup>	No more permeable than base soil

<sup>a</sup> This recommended thickness is for low permeability soil material with at least a 3 percent slope at the bottom of the layer. Some geonet composites, with a minimal thickness of less than 1 inch, may have a transmissivity equal to a much thicker layer of aggregate or sand.

<sup>b</sup> Thickness may need to be increased to address freeze/thaw conditions.

## Closure When Future Ash Mining is Planned

In its draft guidance document for management of industrial solid waste, EPA uses the term “closure by waste removal” to describe the removal and decontamination of all waste, waste residues, contaminated ground water, soils, and containment devices. This approach is common for waste piles and some surface impoundments. In the coal ash management context, the term may be used to describe closure achieved by the removal or “mining” of ash from a disposal unit for reuse.

Removal and decontamination are complete when the constituent concentrations throughout the unit and any areas affected by releases from the unit do not exceed numeric cleanup levels. Check with the State agency to see if it has established any numeric cleanup levels or methods for establishing site-specific levels. In the absence of State cleanup levels, metals and organics should be removed to either statistically equivalent background levels or to maximum contaminant levels (MCLs) or health-based numbers (HBNs)<sup>1</sup>. Metals and organics may have different cleanup levels, but they both need to be based on either local background levels or on health-based guidelines. Future land use considerations may also be important in determining the appropriate level of cleanup. One tool that can be used to help evaluate whether waste removal is appropriate at the site is the risk-based corrective action (RBCA) process. The RBCA process provides guidance on integrating ecological and human health risk-based decision-making into the traditional corrective action process.

### ***Establishing Baseline Conditions***

As a good management practice, establish the baseline conditions for a waste management unit. Baseline conditions are the background constituent concentrations at a site prior to waste placement operations. Identifying the types of contaminants that may be present, provides an indication of the potential contamination resulting from the operation of a unit and the level of effort and resources that may be required to reach closure. Naturally-occurring elevated background levels that are higher than targeted closure levels may be encountered. In such cases, consult with the State agency to determine whether these elevated background levels are a more appropriate targeted cleanup level. The identification of potential contaminants will also provide a guideline for selecting sampling parameters. In the event that constituents other than those initially identified are discovered through subsequent soil and water sampling, this may indicate that contaminants are migrating from another source.

In some cases, waste contaminants may have been present at the site before a waste management unit was constructed or migrated to the site from another unrelated source. In these situations, closure may still proceed, provided that any contamination originating from the closing unit is removed to appropriate cleanup levels. Determine whether additional remediation is required under other federal or State laws, such as the Resource Conservation and Recovery Act (RCRA) or the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or State cleanup laws.

#### **How should baseline conditions be established?**

Initial soil and ground water sampling around, within, and below a comanagement unit will serve to identify baseline conditions. Sampling can detect contaminant levels that exceed background levels or federal, State, or local health-based benchmarks. Contact local environmental protection officials for guidance on the number and type of samples that should be taken. If the initial round of sampling does not reveal any contaminant levels that exceed benchmarks,

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<sup>1</sup>Access the Integrated Risk Information System (IRIS), a database of human health effects that may result from exposure to environmental contaminants, to learn about the regulatory and technical basis for MCLs at <[www.epa.gov/ngispgm3/iris/Regulatory.html](http://www.epa.gov/ngispgm3/iris/Regulatory.html)>. Call the EPA Risk Information Hotline at 513 569-7254 for more information.

proceed with the removal of waste and the restoration of the unit. If the sampling does reveal contamination that exceeds the benchmarks, consider ways to remediate the site in compliance with federal, State, or local requirements.

### ***Removal Procedures***

Proper removal procedures are vital to the long-term, postclosure care of a unit and surrounding land. Properly removing waste, can minimize the need for further maintenance, thereby saving time and money and facilitating reuse of the land. Perform closure by waste removal in a manner that prevents the escape of waste constituents to the soil, surface water, ground water, and atmosphere. After removing the waste, remove all equipment, bases, liners, soils, and any other materials containing waste or waste residues. Finally, the land should be returned to the appearance and condition of surrounding land areas to the extent possible consistent with the closure and postclosure plans.

Should there be a plan for waste removal procedures?

The waste removal process should be fully described in a closure plan. The removal process description should address estimates of the volumes and types of waste and contaminated equipment or structures to be removed during closure. It should also include the types of equipment to be used, the removal pattern, and the management of loading areas. The closure plan should also detail actions to be taken to minimize and/or prevent emissions of waste during closure activities. For example, if activities during closure include loading and transporting waste in trucks, the closure plan should describe the steps that will be taken to minimize air emissions from windblown dust. Proper quality assurance and quality control during the waste removal process will help ensure that the removal proceeds in accordance with the waste removal plan. A key component of the waste removal procedure is the consideration of proper disposal of any wastes or contaminated materials.

### ***Disposal or Reuse of Removed Wastes***

When a unit is closed by removing waste, waste residues, contaminated ground water, soils, and containment devices, ensure that disposal or reuse of these materials is in compliance with applicable Federal and State laws. If the composition of the waste can not be determined using process knowledge, then it should be tested using applicable test procedures for characterizing waste. Then consult with the State agency to determine what requirements apply to waste of that kind.

### ***Final Sampling and Analysis***

The purpose of final sampling and analysis is to ensure that target cleanup levels have been achieved. While initial sampling is intended to establish baseline levels of contaminants, final sampling is used more as a safeguard to make sure levels have not changed. It is important to conduct a final sampling, in addition to the initial sampling, because removal actions can

increase the contaminant levels at the site, and sometimes contamination is overlooked in the initial baseline sampling event.

Is it necessary to develop a sampling and analysis plan?

Because of the importance of accurate sampling, develop a sampling and analysis plan to ensure correct sampling procedures. This plan should include information on selection of sampling locations, sampling protocols, methods, quality assurance and quality control procedures, and procedures for analysis of samples and reporting of results. The plan should also address the selection of analytical constituents, based on current and historic operations at the facility and closing unit, and the initial review of the wastes present in the unit. Consult with qualified professionals and the State agency to develop the plan and conduct and analyze sampling activities.

Guidance for sample collection, preservation, preparation, and analysis can be found in the following standard testing methods:

- Test Methods for Evaluating Solid Waste, Physical Chemical Methods, Third Edition, U.S. EPA, SOLID WASTE-846;
- Methods for Chemical Analysis of Water and Wastes, U.S. EPA, EPA600-4-79-020;
- Standard Methods for the Examination of Water and Wastewater, American Society for Testing Materials (ASTM), American Public Health Association, American Water Works Association, and Water Pollution Control Federation; and
- The ASTM Standard Test Methods for Analysis of Water and Wastes.

How should the sampling data be used?

The results of this sampling event should be compared to the results of the baseline event, and any discrepancies should be noted. The results can be compared to performance measures established at the beginning of the closure process with State or local regulators. Closure plans incorporating waste removal should include a sampling and analysis plan for the initial and final sampling and analysis efforts. The plan should specify procedures to ensure that sample collection, handling, and analysis will result in data of sufficient quality to plan and evaluate closure activities. The sampling and analysis plan should be designed to define the nature and extent of contamination at/or released from the closing unit. The level of detail in the sampling and analysis plan should be commensurate with the complexity of conditions at the closing unit.

## **Postclosure Care Considerations When Final Cover is Used**

Units that will close with a final cover, should consider the following factors:

- Routine maintenance of the unit's systems, including the final cover, leachate collection and removal systems, surface-water controls, and ground water monitoring systems where appropriate;

- The names and telephone numbers of facility personnel for emergencies;
- Mechanisms to ensure the integrity of the final cover system, such as posted signs or notifications on deeds;
- The anticipated uses of the property during the postclosure period;
- The length of the postclosure care period;
- Costs to implement postclosure care; and
- Conditions that will cause postclosure care to be extended or shortened.

The closure plan should also include the names and telephone numbers of facility personnel who can be contacted in case of emergency.

### ***Maintenance***

After the final cover is installed, some maintenance and repair will be necessary to keep the cover in good working condition. Maintenance may include mowing the vegetative cover periodically and reseeding, if necessary. Repair the cover when erosion or subsidence occurs. Maintaining healthy vegetation will ensure the stability of slopes, reduce surface erosion, and reduce leachate production by increasing evapotranspiration. A regular schedule for site inspections of maintenance activities during the postclosure period, as well as prompt repair of any problems found at inspection, may help ensure the proper performance of the cover system. Maintenance of the proper thickness of surface and drainage layers will ensure long-term minimization of liquids and protection of geomembranes, if present.

What maintenance and repair activities should be conducted after the final cover has been installed?

In the case of damage to the final cover, determine the cause of damage, so that proper repair measures may be taken to prevent recurrence. For example, if the damage is due to erosion, potential causes may include the length and steepness of slopes, insufficient vegetation growth due to poor planting, or uneven settlement of the waste. Sedimentation basins and drainage swales should be inspected after major storms and repaired or cleaned, as necessary.

Components of the leachate collection and removal system, such as leachate collection pipes, manholes, tanks, and pumps should also receive regular inspection and maintenance. If possible, flush and pressure-clean the collection systems on a regular basis to reduce sediment accumulation and to prevent clogging caused by biological growth. The manholes, tanks, and pumps should be visually inspected at least annually, and valves and manual controls should be exercised even more frequently, because leachate can corrode metallic parts. Repairs will help prevent future problems, such as leachate overflow from a tank due to pump failure.

Inspect and repair ground water monitoring wells during the postclosure period. Proper operation of monitoring wells is essential to determine whether releases from a closed waste management unit are occurring. For example, ground water monitoring wells should be inspected to ensure that they have not been damaged by vehicular traffic or vandalism. Physical

scraping or swabbing may be necessary to remove biological clogging or encrustation from calcium carbonate deposits from well screens.

### ***Monitoring During Postclosure Care***

Postclosure care monitoring should include the leachate collection system, surface-water controls, and the ground water monitoring system where appropriate. Postclosure monitoring will serve as the main source of information about the integrity of the final cover and liners.

What should be considered when monitoring postclosure leachate and groundwater?

The quantity of leachate generated should be monitored, as this is a good indicator of the performance of the closure system. If the closure system is effective, the amount of leachate generated should decrease over time. In addition, the concentration of contaminants in leachate should, in time, reach an equilibrium. An abrupt decline in the contaminant concentration could mean that the cover has failed, and surface water has entered the waste and diluted the leachate. Ground water monitoring should be conducted to ensure leachate has not contaminated ground water supplies.

An appropriate level of groundwater monitoring will vary depending on facility-specific considerations and State requirements. Most states require groundwater monitoring based on the review of the facility permit application. The states then establish frequencies, procedures, and parameters for the site-specific monitoring programs. Some states require that corrective action measures be initiated within a defined time period following the detection of groundwater contamination. Groundwater monitoring programs at a facility generally incorporate a conceptual model of site hydrogeology into the design of effective monitoring system consisting of both downgradient monitoring wells and upgradient/background monitoring wells. The upgradient/background wells are to provide representative samples of background water quality. The downgradient wells can detect changes in groundwater quality before the groundwater reaches any downgradient receptors such as surface waters or water supply wells. A sufficient number of groundwater wells are utilized in a site-specific manner to collect and analyze groundwater samples from the background and downgradient wells at the frequency specified for the facility. Evaluation and refinement of the groundwater monitoring program may be accomplished on an as-needed basis. Appropriate Quality Assurance and Quality Control procedures should be included in the groundwater monitoring program. Both the U.S. EPA and State regulators have a number of technical guidance documents available for designing and implementing groundwater monitoring programs. These reports offer valuable resources to the owners and operators of landfills and surface impoundments.

### ***Recommended Length of the Postclosure Care Period***

The overall goal of postclosure care is to provide care until wastes no longer present a threat to the environment. Threats to the environment during the postclosure care period can be evaluated using leachate and ground water monitoring data to determine whether there is a potential for migration of waste constituents at levels that might threaten human health and the environment.

Ground water monitoring data can be compared to drinking water standards or health-based criteria to determine whether a threat exists.

Leachate volumes and constituent concentrations may also be used to show that the unit does not pose a threat to human health and the environment. The threats posed by constituent concentrations in leachate should be evaluated based on potential release of leachate to ground water and surface waters. The length of individual postclosure care periods will depend on the type of waste being managed, the type of waste management unit, and a variety of site-specific characteristics. Contact the State agency to determine what postclosure period the State agency recommends. In the absence of any State guidance on the appropriate length of the postclosure period, consider a minimum of 30 years.

### ***Closure and Postclosure Cost Considerations***

The facility manager of a closed industrial unit, is responsible for that unit. To ensure long-term protection of the environment, account for the costs of closure and postclosure care when making initial plans. There are guidance documents available to help plan for the costs associated with closing a unit. For example, estimating guides by the R.S. Means Co. provide up-to-date costs for most construction-related work, such as moving soil, cost of material and labor for installing piping. Also consider establishing financial assurance mechanisms so that the necessary funds will be available to complete closure and postclosure care activities, if necessary. Financial assurance fosters long-range financial planning and encourages internalization of the future costs associated with waste management units. It also promotes proper design and operating practices, because the costs for closure and postclosure care are often less for units operated in an environmentally protective manner. Check with the State agency to determine whether financial assurance is required and what types of financial assurance mechanisms may be acceptable.

The amount of necessary financial assurance is based on site-specific estimates of the costs of closure and postclosure care. The estimates should reflect the costs that a third party would incur in conducting closure and postclosure activities. This ensures adequate funds will be available to hire a third party to carry out necessary activities. Consider updating the cost estimates annually to account for inflation and whenever changes are made to the closure and postclosure plans. For financial assurance purposes, if a State does not have a regulation or guidance regarding the length of the postclosure care period, 30 years should be used as a planning tool for developing closure and postclosure cost estimates.

By ensuring future availability of funds, financial assurance mechanisms can offer an alternative to providing full funding for closure and postclosure care at the time of closure. For example, trust funds may be built up gradually during the operating life of a waste management unit. By having an extended “pay-in” period for trust funds, the burden of funding the closure and postclosure care will be spread out over the economic life of the unit. Alternatively, a corporate financial test or third-party alternatives, such as surety bonds, letters of credit, insurance, or guarantees can be used.

## What costs can be expected to be associated with the closure of a unit?

The cost of constructing a final cover or achieving closure by waste removal will depend on site-specific activities. Consider developing written cost estimates before closure procedures begin. For closure by means of a final cover, the cost of constructing the final cover will depend on the complexity of the cover profile, final slope contours of the cover, whether the entire unit will be closed (or partial closure) and other site-specific factors. For example, the components of the final cover system, such as a biotic layer, will affect costs. In addition, closure cost estimates would also include final cover vegetation, run-on and run-off control systems, leachate collection and removal systems, groundwater monitoring wells, and access controls, such as fences or signs. Closure costs may also include costs for construction quality assurance, engineering fees, accounting and banking fees, insurance, permit fees, legal fees, and, where appropriate, contingencies for cost overruns, reworks, emergencies, and unforeseen expenses.

For closure by means of waste removal, closure costs would include the costs of removal procedures, decontamination procedures, and sampling and analysis. Closure costs should also consider the costs for equipment to remove all waste, transport it to another waste management unit, and properly dispose of it or to reuse it. In addition, fugitive dust emission controls, such as dust suppression practices, may need to be included as a closure cost.

## What costs can be expected to be associated with postclosure care?

After a waste management unit is closed, monitoring and maintenance are needed to ensure that the closed unit remains secure and stable. Consider the costs to conduct postclosure care and monitoring for at least 30 years (in the absence of State regulation or guidance). Postclosure care costs should include both annual costs, such as monitoring, and periodic costs, such as cap or monitoring well replacement.

For units closed by means of a final cover, consider the costs for a maintenance program for the final cover and associated vegetation. This program may include repair of damaged or stressed vegetation, and maintenance of side slopes. Costs to maintain the runoff and runoff control systems, leachate collection and removal systems, and groundwater monitoring wells should also be expected. In addition, sampling and analysis costs may need to be factored into the postclosure cost estimates.

Postclosure costs should be updated annually as a record of actual unit costs is developed. Some costs, such as erosion control and groundwater sampling, may be reduced over time as the vegetation on the cover matures and a meaningful amount of monitoring data is accumulated. Due to site-specific conditions, a shorter or longer postclosure period may be determined to be appropriate.

## How can long-term financial assurance for a unit be obtained?

Some of the different forms of financial assurance mechanisms include prepayment, surety, insurance, guarantee, corporate guarantees, and financial tests. Prepayment is a method whereby cash, liquid assets, certificates of deposit, or government securities are deposited into a fund

controlled by a trustee, escrow agent, or State agency. The prepayment amount should be such that the principal plus accumulated earnings over the projected life of the waste management unit would be sufficient to pay closure and postclosure care costs. Surety, insurance, and guarantee are methods to arrange for a third party to guarantee payment for closure and postclosure activities, if necessary. Passing a financial test such as accounting ratio, net worth, bond rating, or combination of these standards, establishes the existence of the necessary financial strength to pay for closure and postclosure costs. This guidance, however, does not recommend specific acceptable financial assurance mechanisms.

## **Action Items for Performing Closure and Postclosure**

Consider the following while developing closure and postclosure care activities for comanagement units.

- Develop a closure and postclosure plan, specifying the activities, unit type, waste type, and schedule of the closure.
- If using a final cover to accomplish closure:
  - a. Include the specifications for the final cover in the closure plan;
  - b. Address site-specific factors that may affect cover performance;
  - c. Select the appropriate materials to use for each layer of the final cover;
  - d. Evaluate the effectiveness of the final cover design using an appropriate methodology or modeling program;
  - e. Establish a maintenance plan for the cover system;
  - f. Establish a program for monitoring leachate collection, and ground water quality, during the postclosure period; and
  - g. Ensure proper quality assurance and quality control during final cover installation and postclosure monitoring.
- If accomplishing closure when future ash mining is planned:
  - a. Establish baseline conditions and check to see if the state requires numeric cleanup levels;
  - b. Develop removal procedures;
  - c. Develop a sampling and analysis plan; and
  - d. Ensure proper quality assurance and quality control during sampling and removal activities.
  - e. Determine what postclosure activities will be appropriate at the site.
  - f. Estimate the costs of closure and postclosure care activities and consider financial assurance mechanisms to help plan for these future costs.

**Table 6-3**  
**Resources For Developing Closure Plans**

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- Texas Natural Resource Conservation Commission. Industrial & Hazardous Waste Division. 1993. Closure Guidance Documents (Draft). September.
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- U.S. EPA. 1994c. The Hydrologic Evaluation of Landfill Performance (HELP) Model: Engineering Documentation for Version 3. EPA600-R-94-168b.
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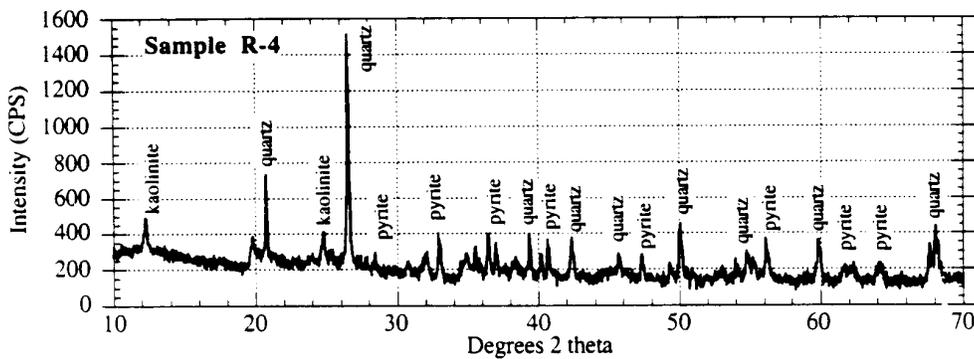
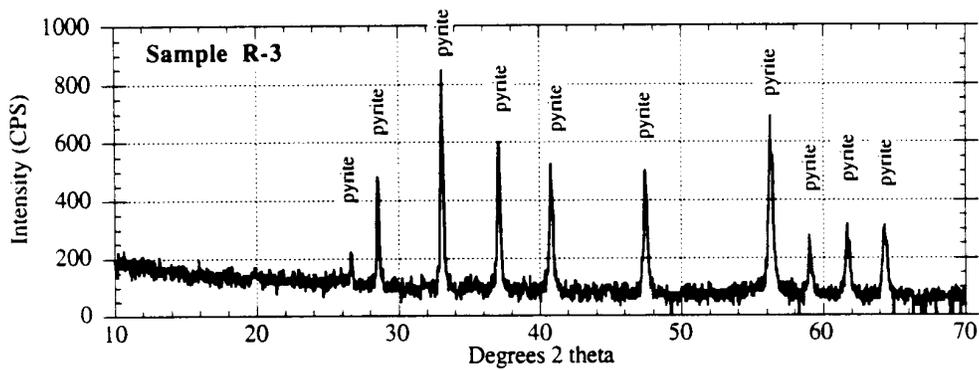
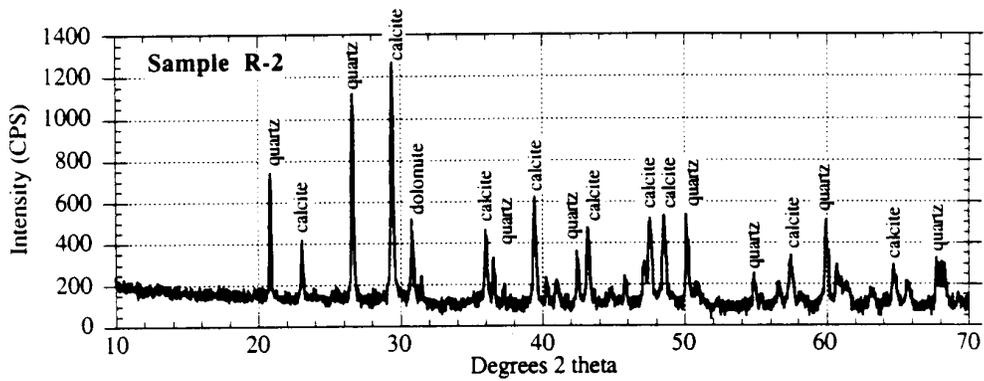
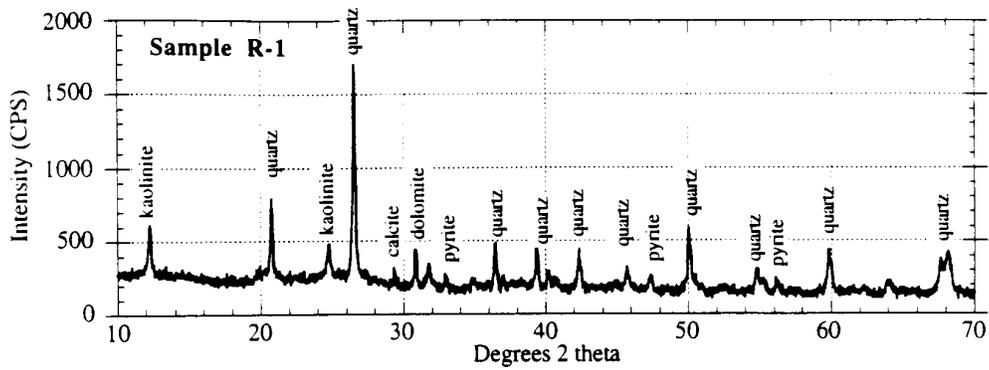
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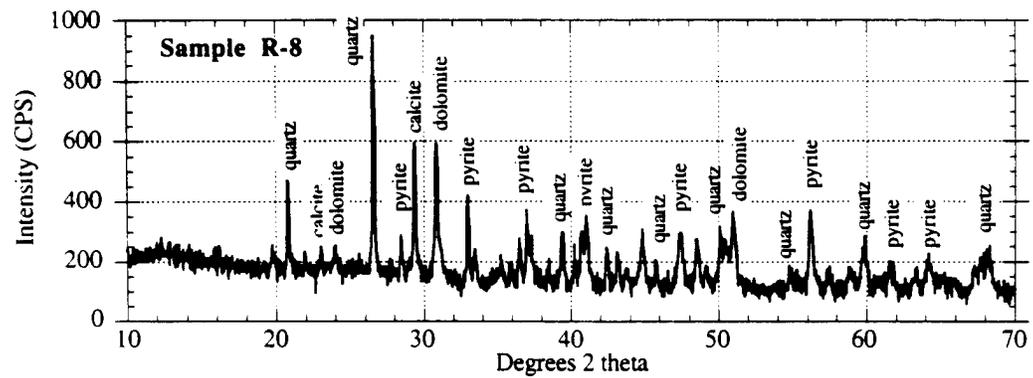
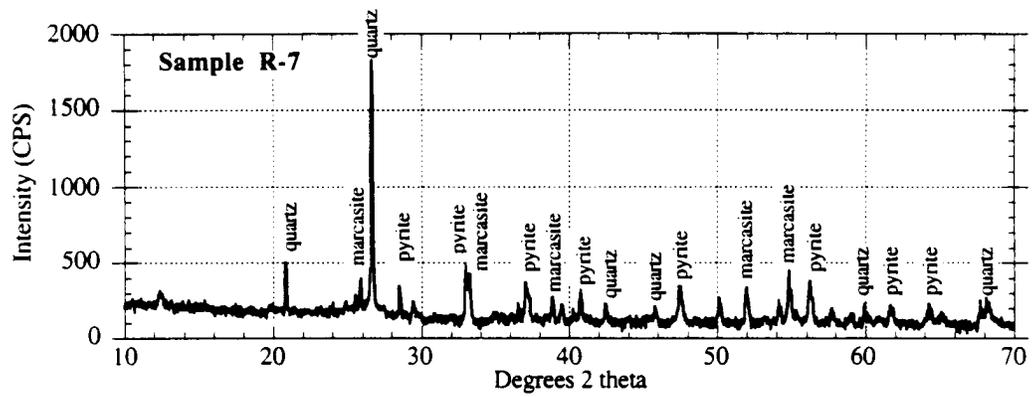
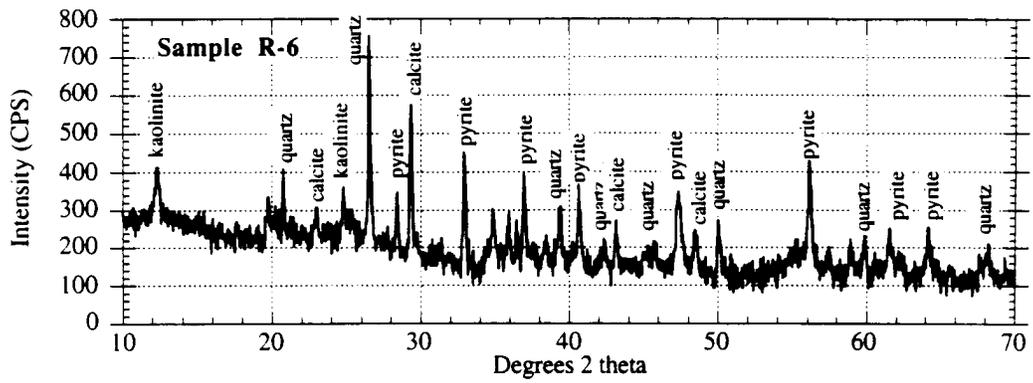
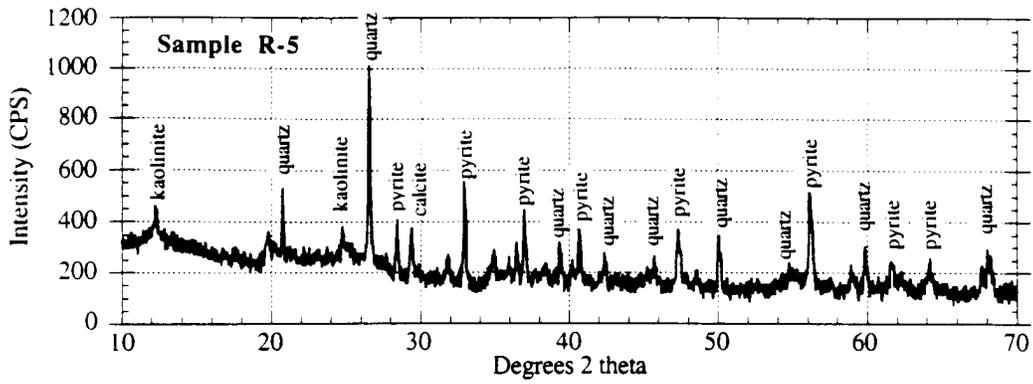
## X-RAY DIFFRACTOGRAMS

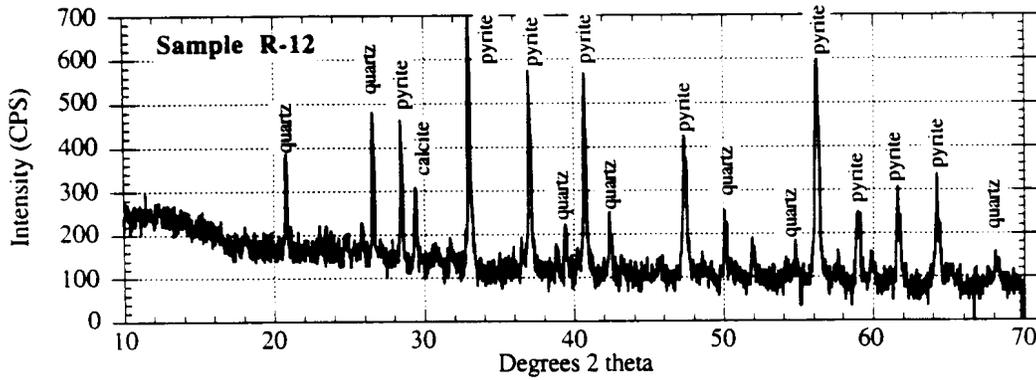
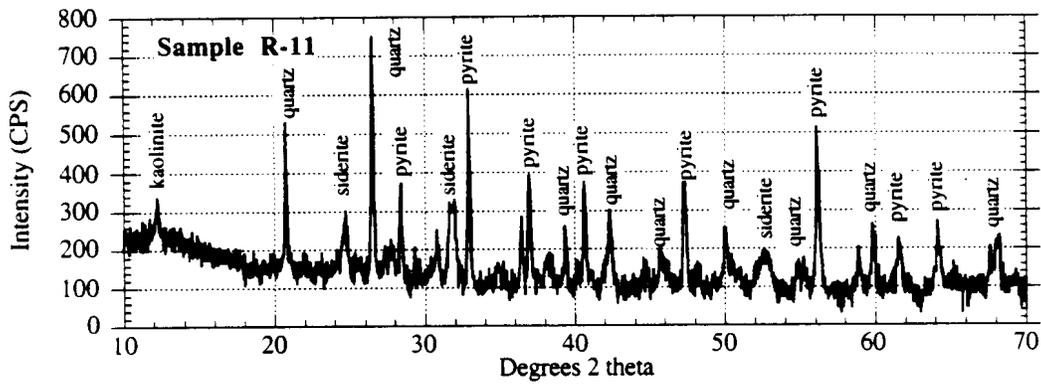
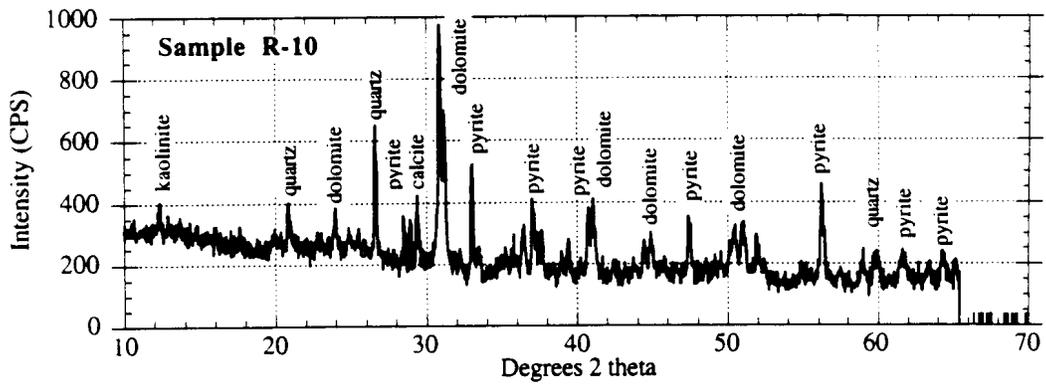
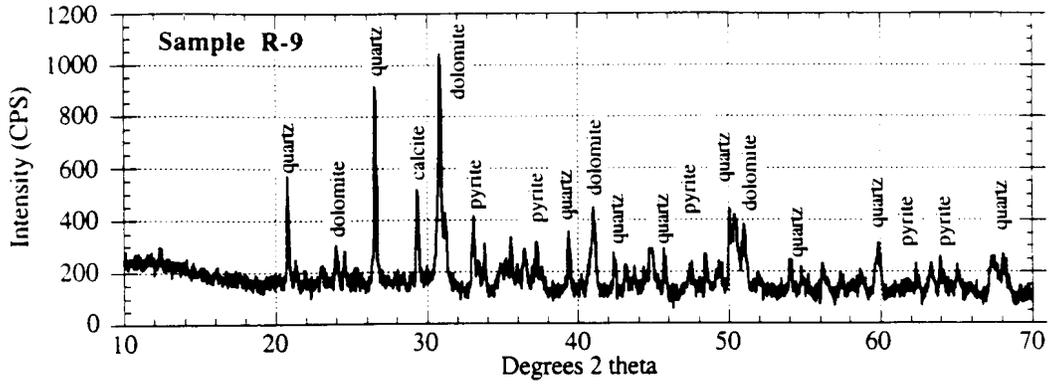
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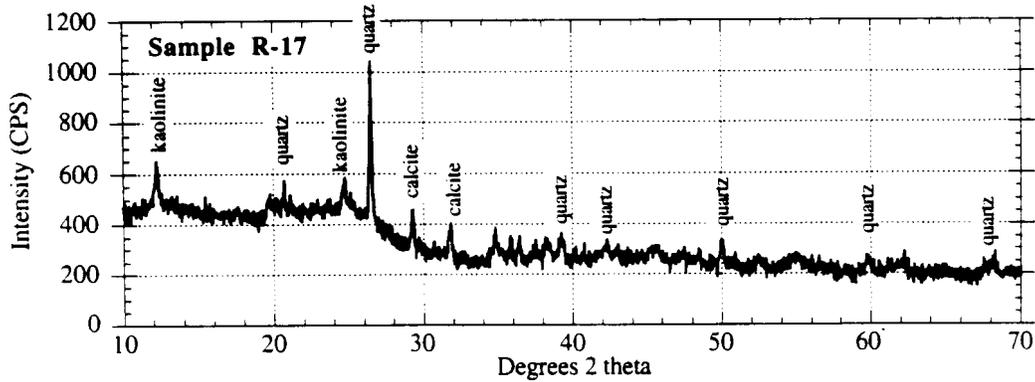
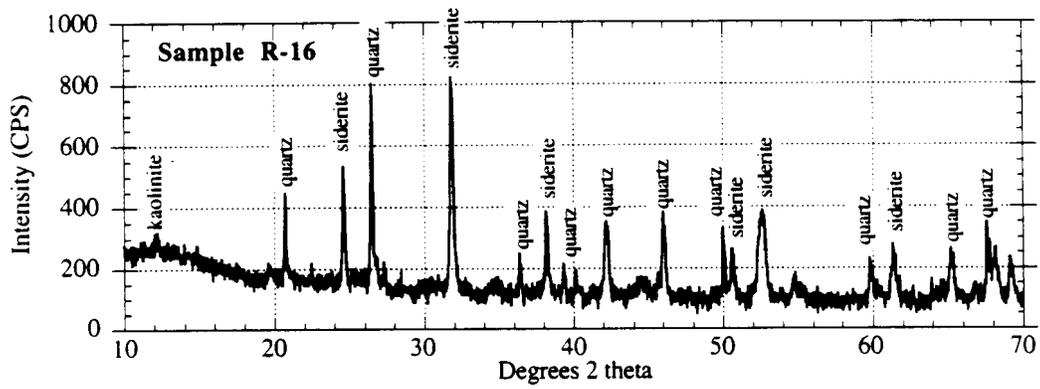
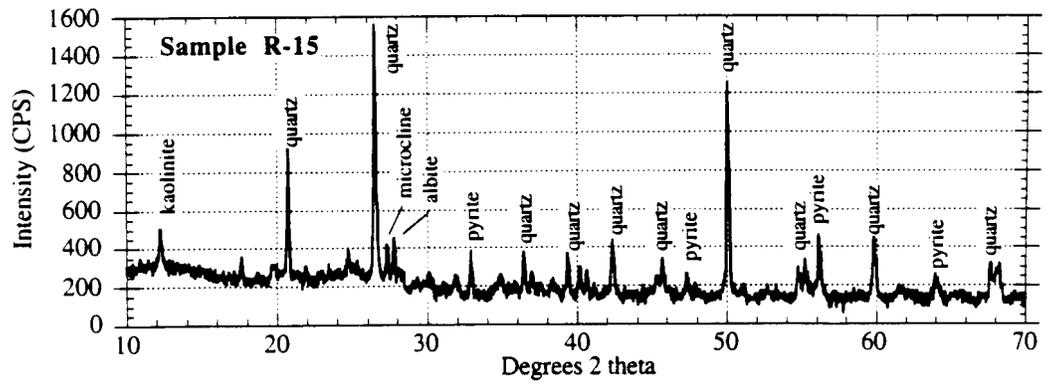
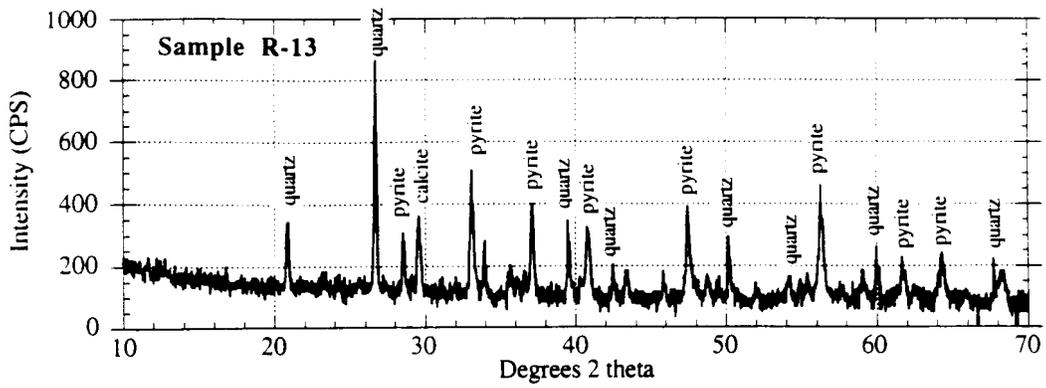
The x-ray diffraction patterns in this appendix are for the 19 mill rejects samples analyzed for this project. The mill reject samples were first crushed in an Iler Rock Crusher. A 2 g subsample was then ground with an agate mortar and pestle to less than 62  $\mu\text{m}$ . The finely-ground material was then placed in a Plexiglass sample holder for X-ray analysis. The major minerals were determined using a Scintag XDS-2000 X-ray diffraction system. Samples were scanned using  $\text{CuK}_{\alpha}$  radiation at 45 KV and 40 MA from  $10^{\circ}$  to  $70^{\circ} 2\phi$ , at a scan rate of  $1^{\circ}$  per minute. The spectra were then analyzed using Scintag software on a Digital Microvax 3100 to determine the relative abundance of minerals present in the samples based on relative peak intensity. A qualitative estimate of the amount of a given mineral was made using the following classification: abundant - distinct, high intensity peaks relative to other minerals; present - distinct peaks of moderate intensity; and minor - identifiable peaks of low intensity. The samples with more mineral matter had higher intensities on the diffractograms. The major minerals found by X-ray diffraction were quartz, pyrite, calcite, dolomite, kaolinite, siderite, marcasite, and the feldspars albite and microcline. The crystalline component of the mill rejects was dominated by silicate minerals, followed by carbonate minerals and then sulfide minerals. The minerals found in these samples are consistent with those expected from published literature (Berkowitz, 1994).

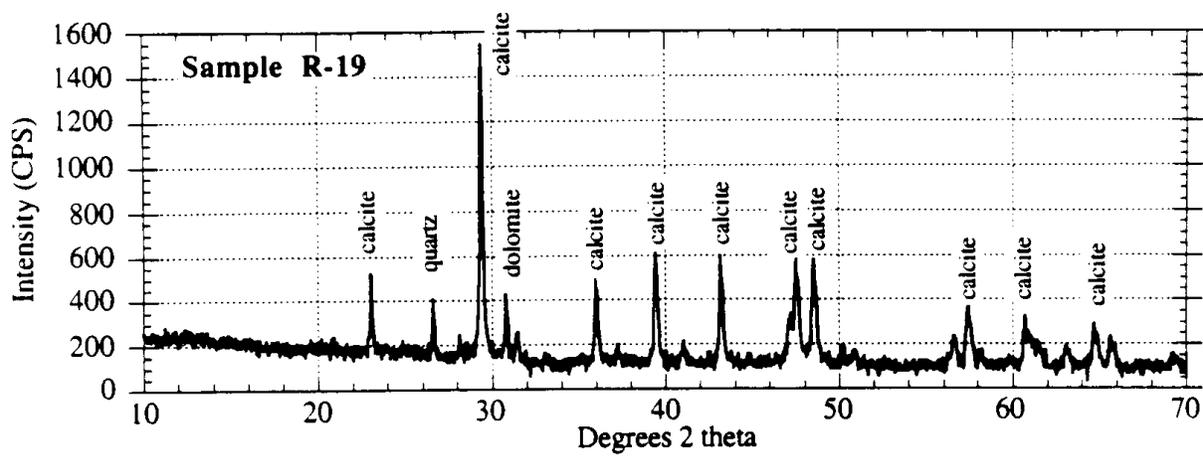
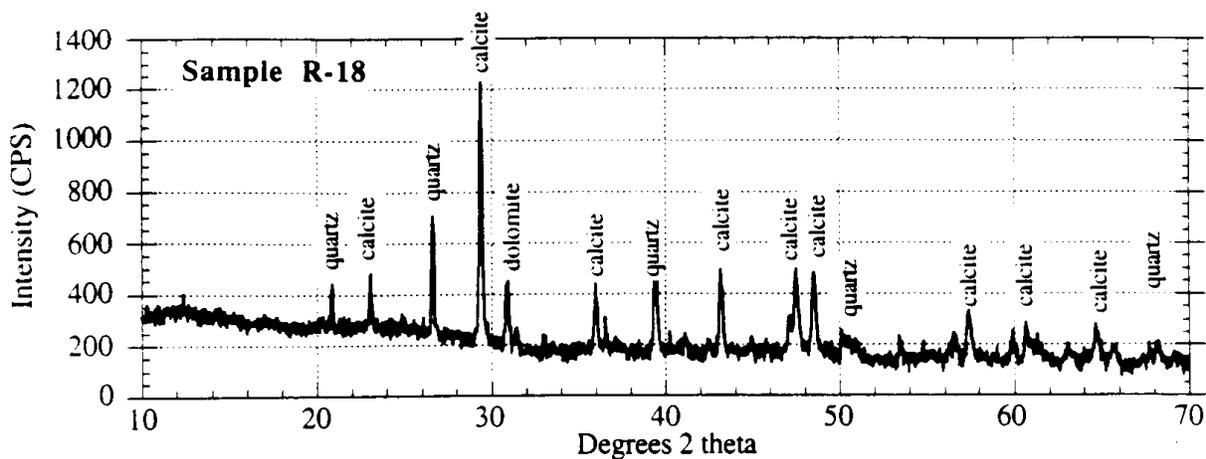
X-RAY DIFFRACTOGRAMS











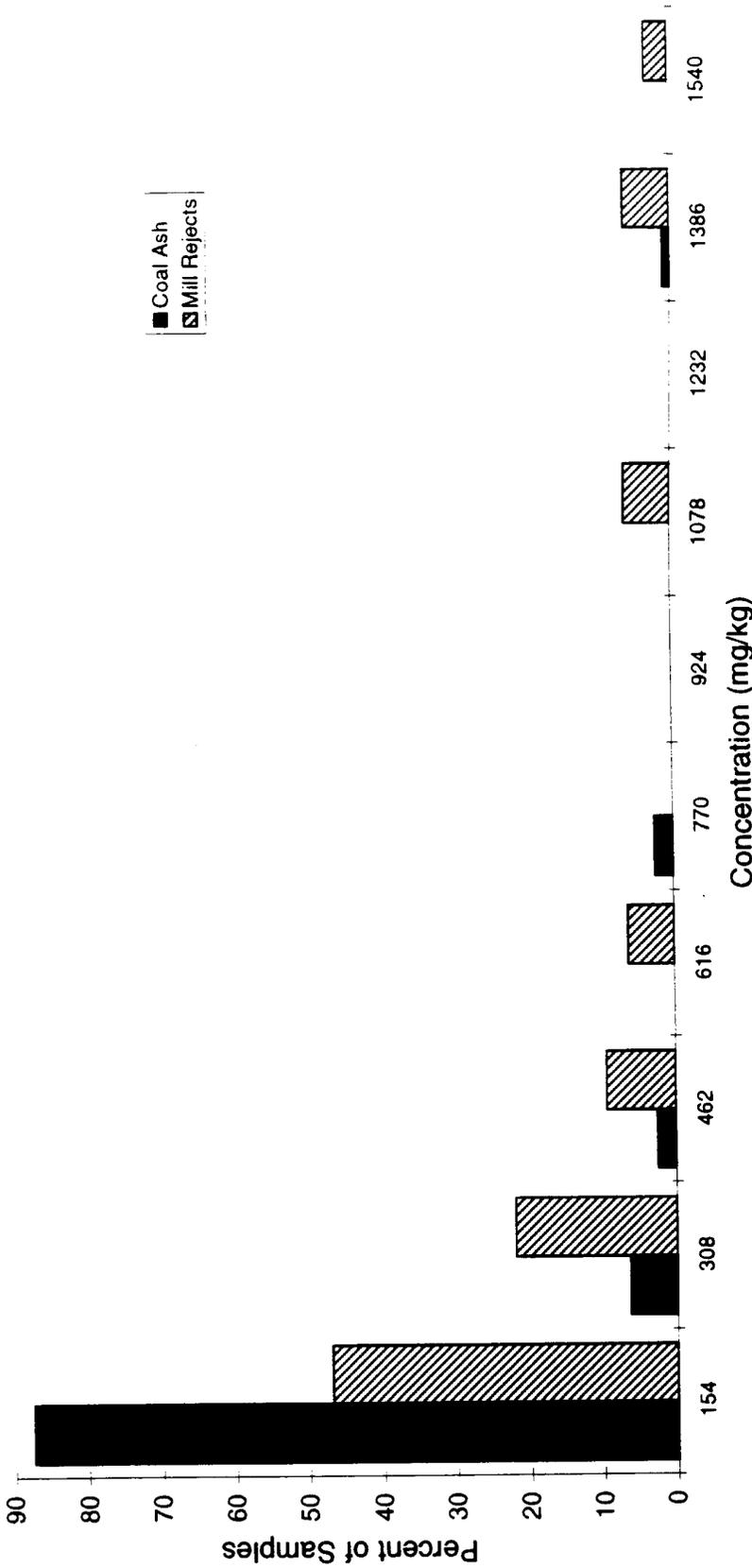
# ***B***

## **DISTRIBUTIONS OF COAL ASH AND MILL REJECTS**

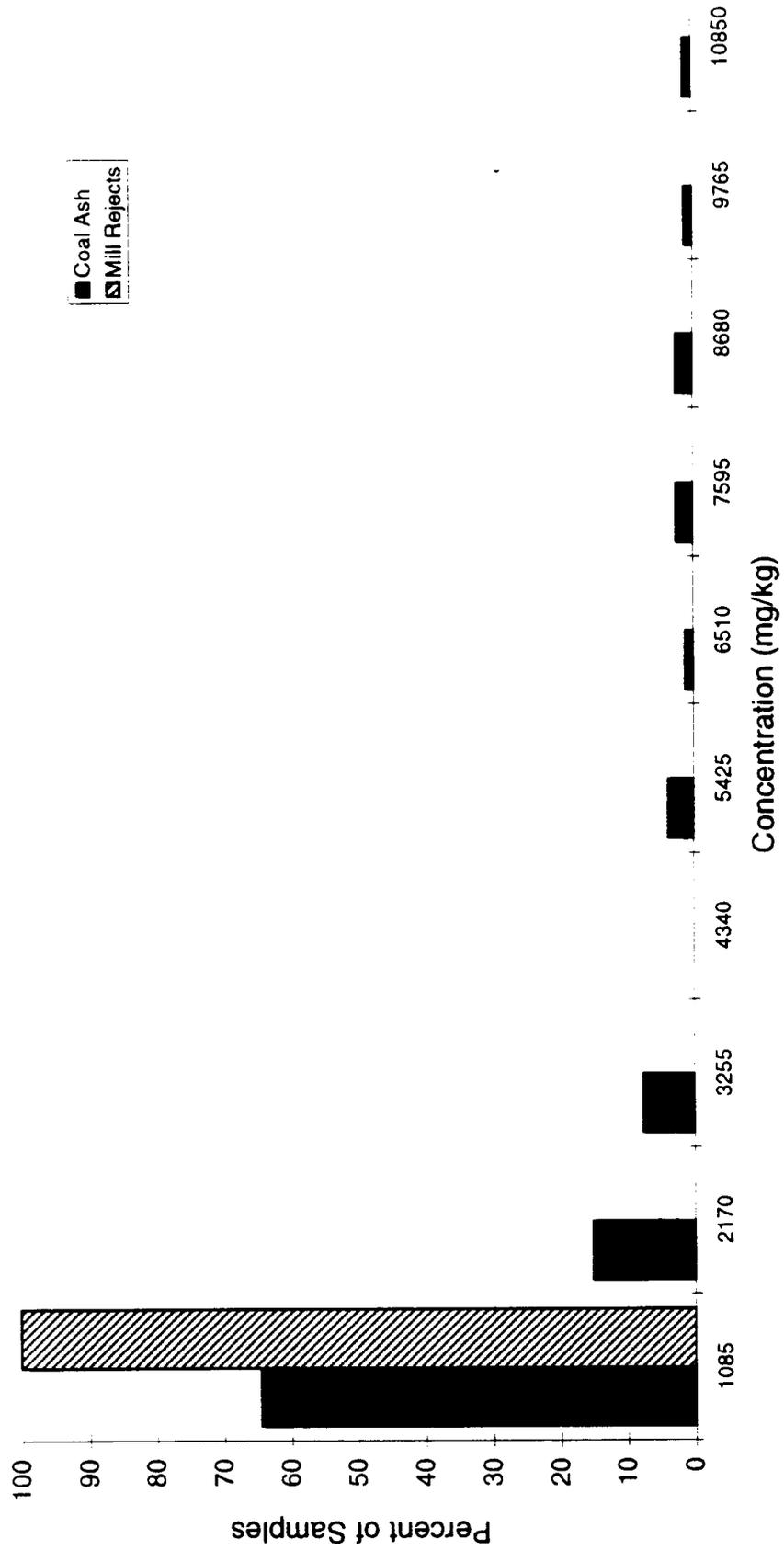
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The chemical composition distribution plots in this appendix were generated using data for 31 mill reject samples, 39 fly ash samples, and 40 bottom ash samples. The mill rejects data used are from the 19 samples analyzed for this project; four samples from EPRI, 1987; and eight samples from Fellman and Horzempa, 1988.

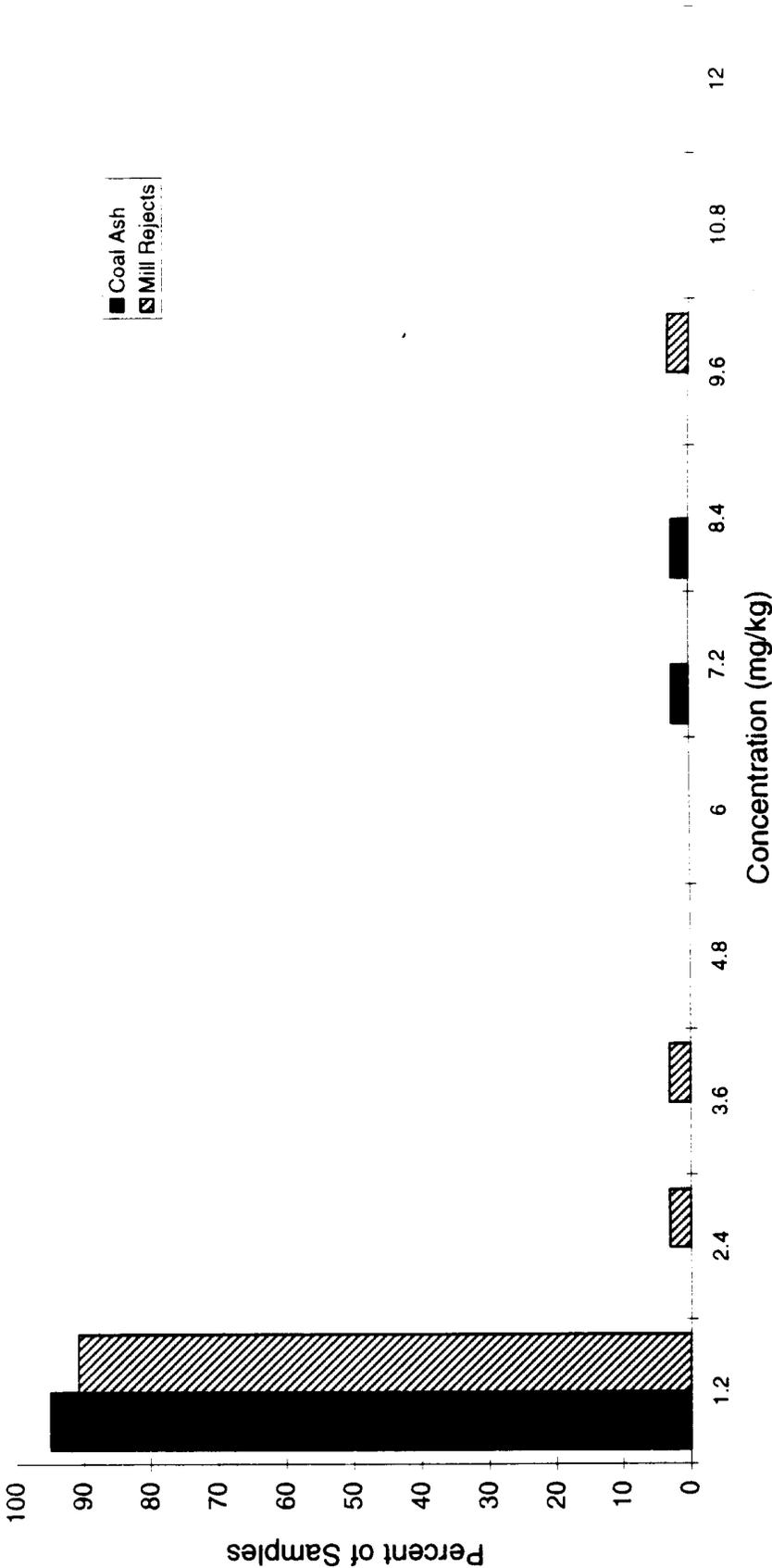
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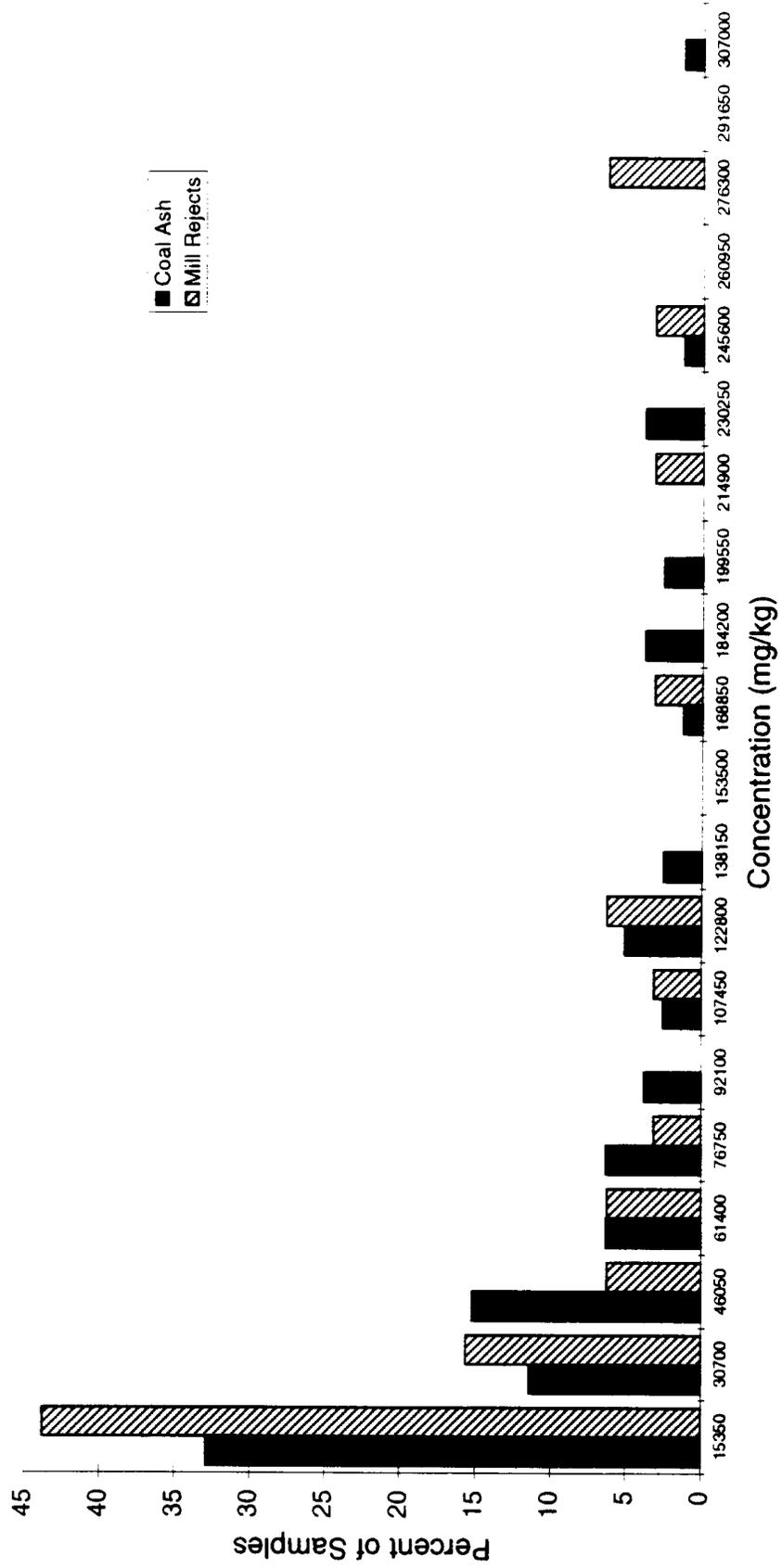
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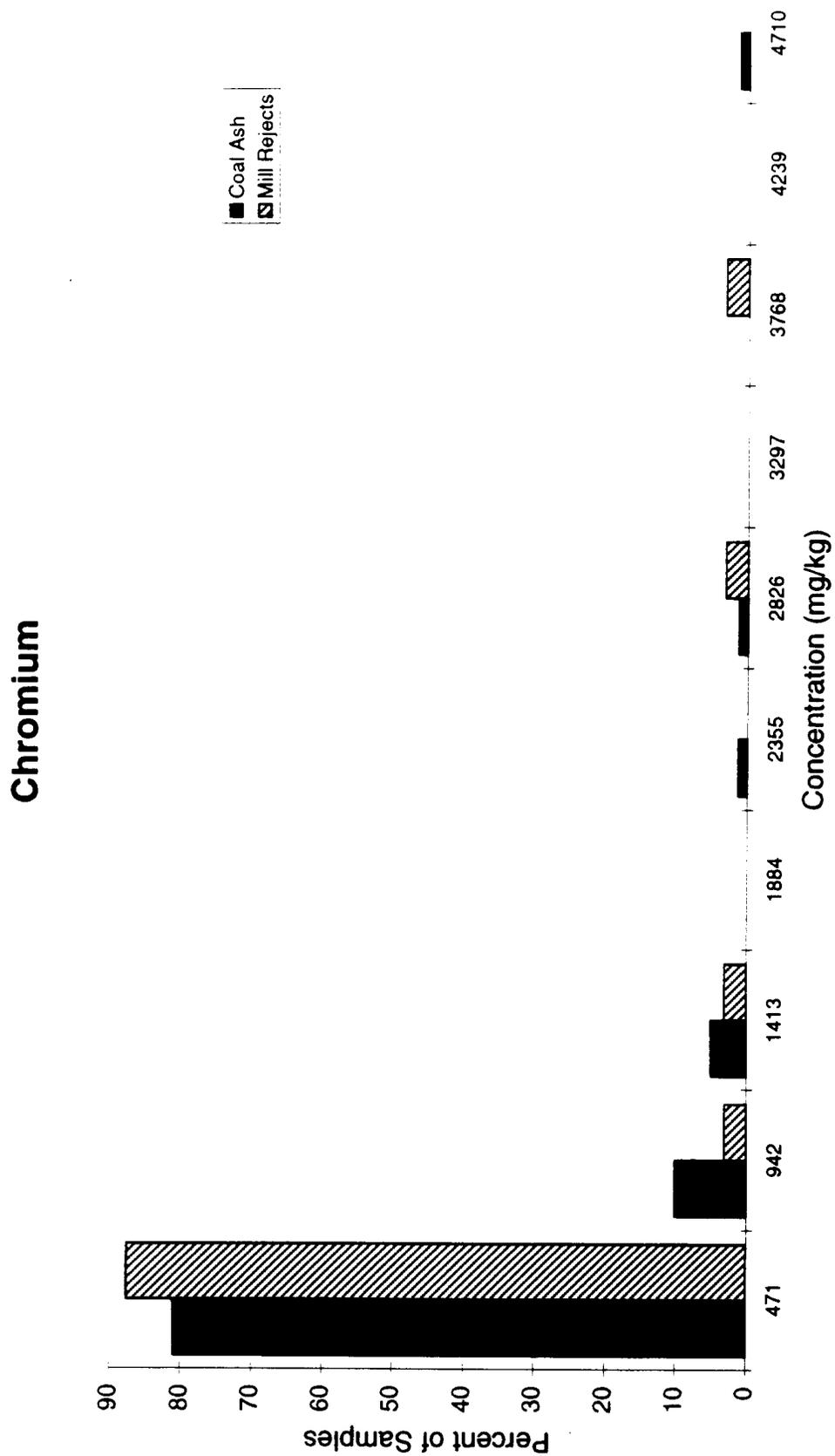


Cadmium - (Outlier of 16.9 mg/kg for coal ash not included.)

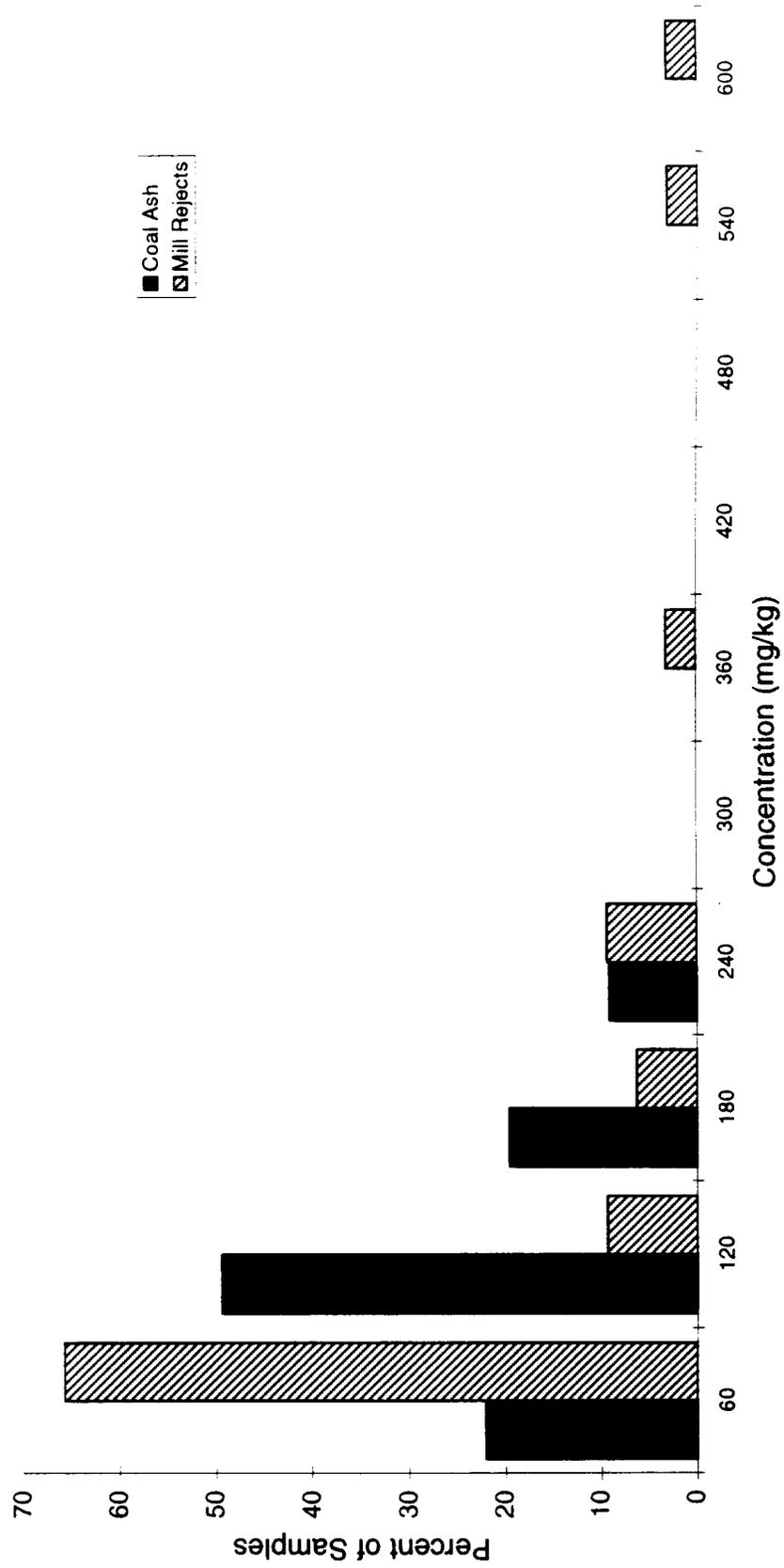


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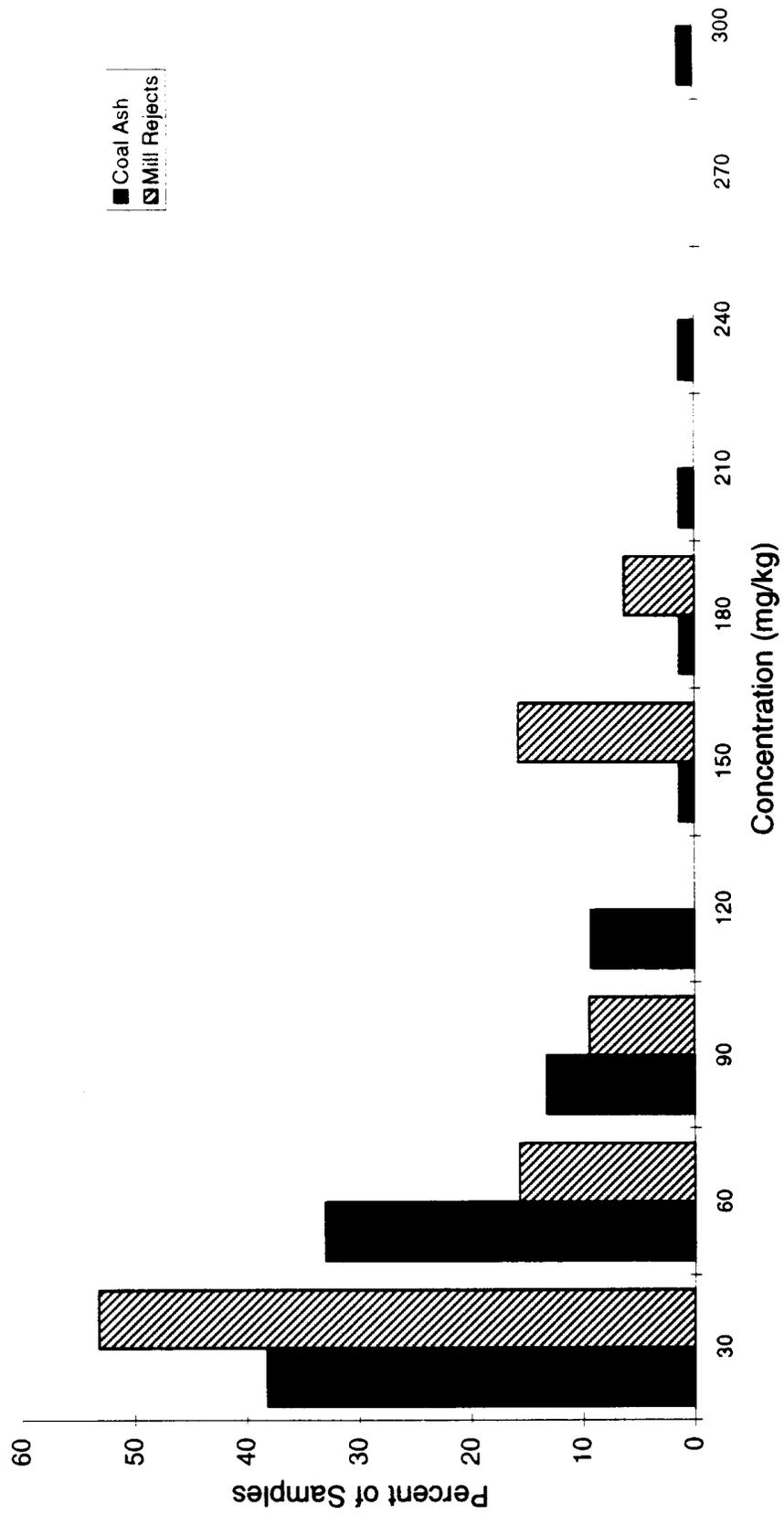




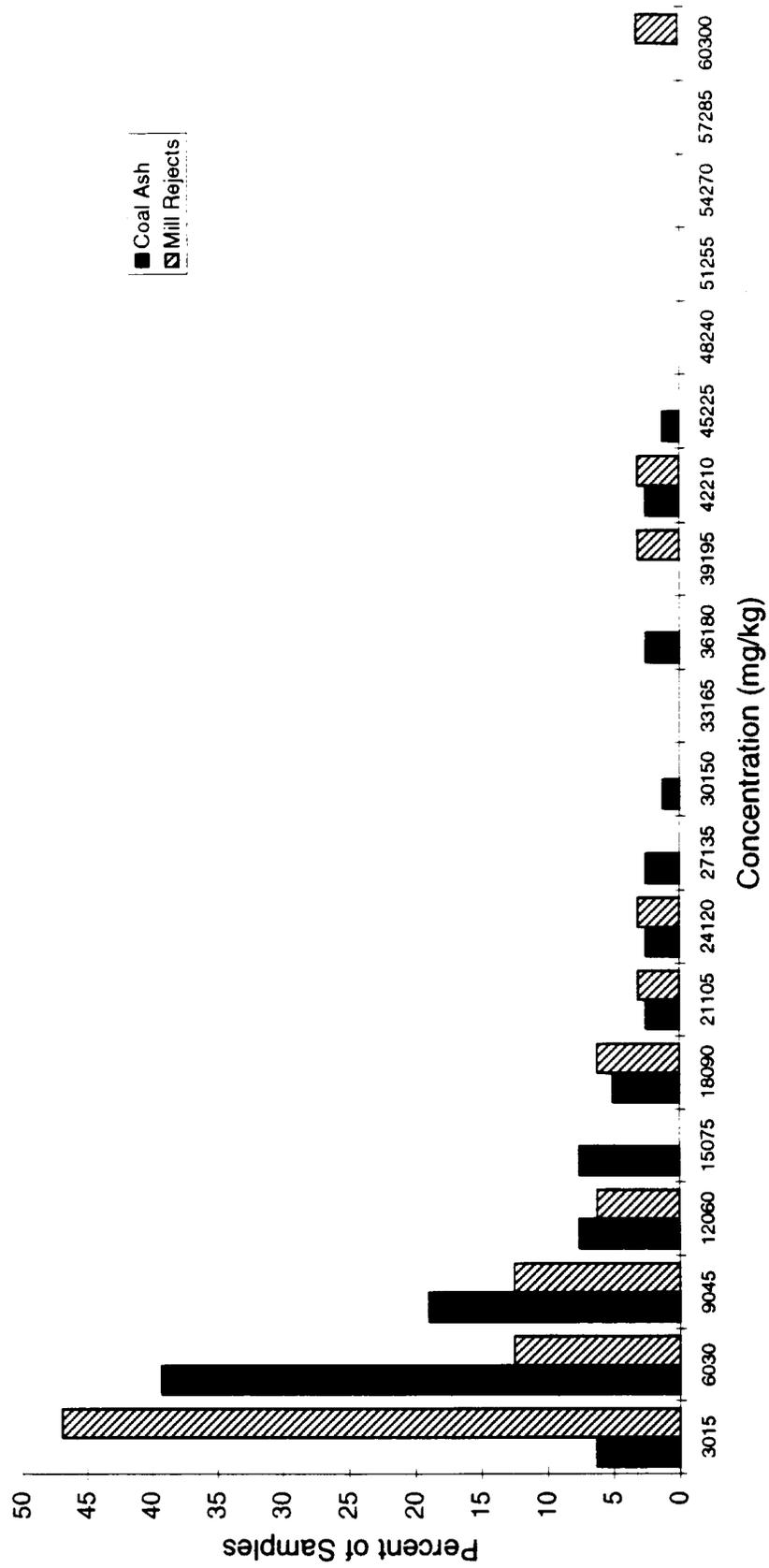
Copper - (Outliers of 1047 and 1452 mg/kg for coal ash not included.)



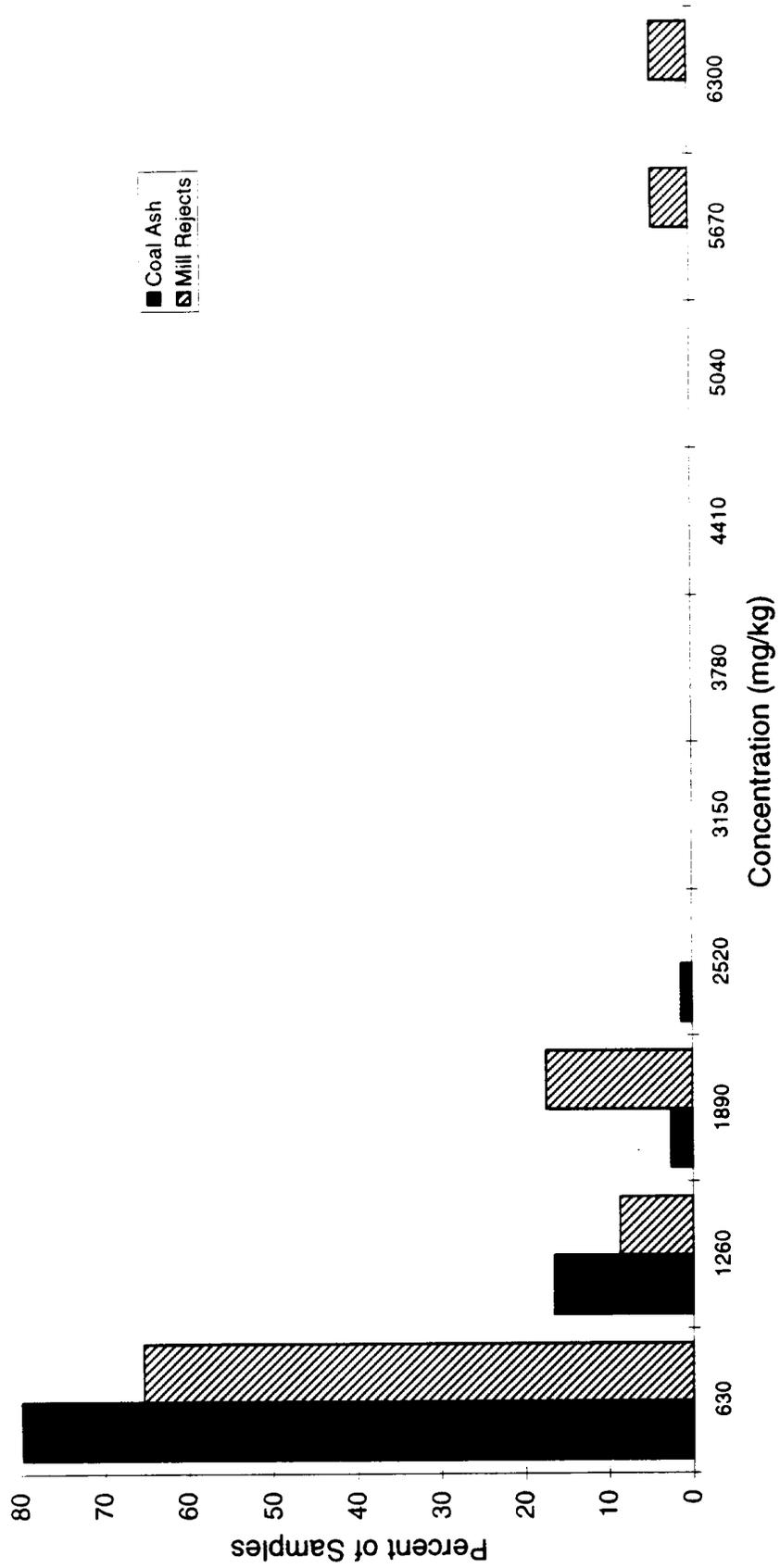
Lead - (Outliers of 843, 1340, and 2120 mg/kg for coal ash not included.)



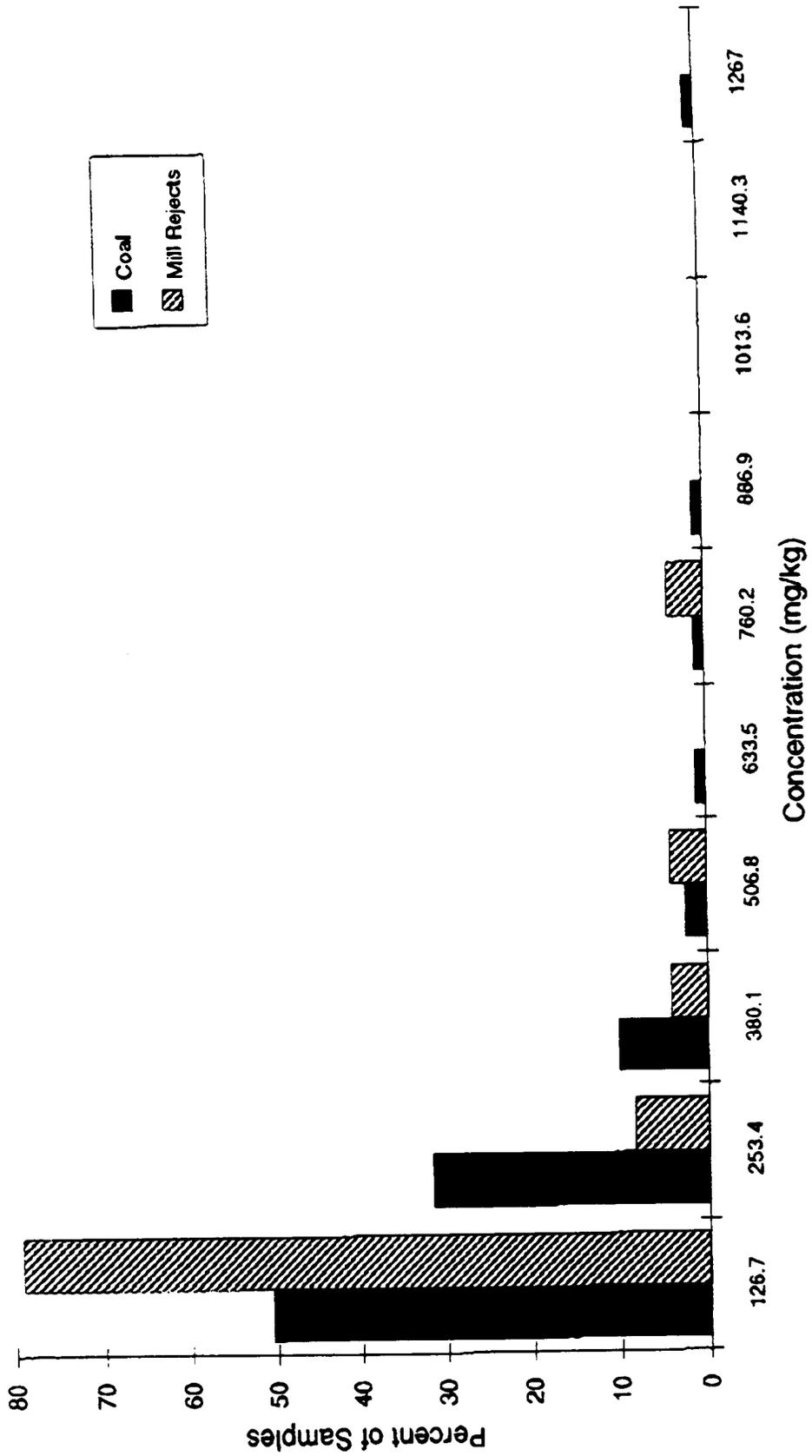
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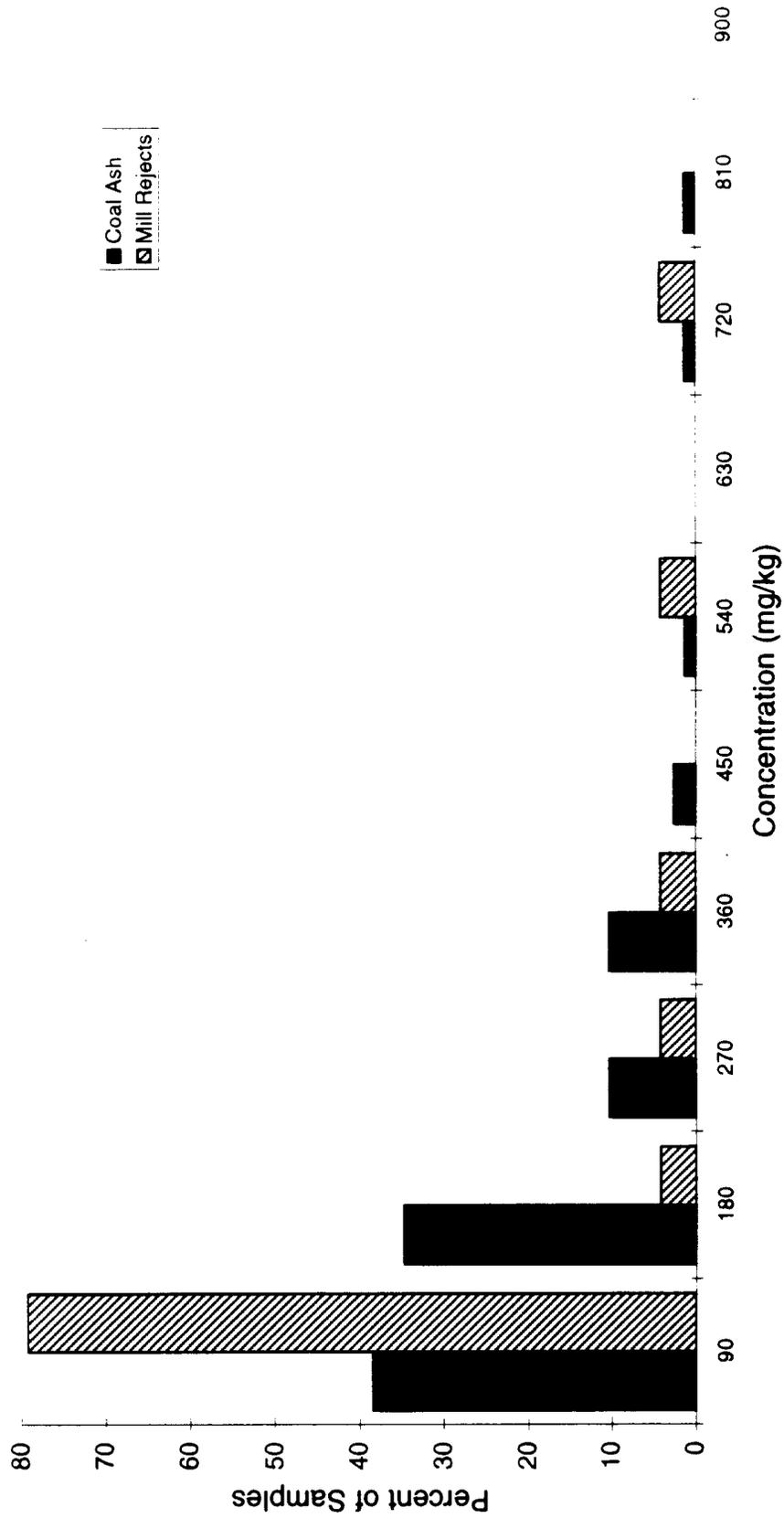
**Manganese - (Outlier of 146100 mg/kg for mill rejects not included.)**



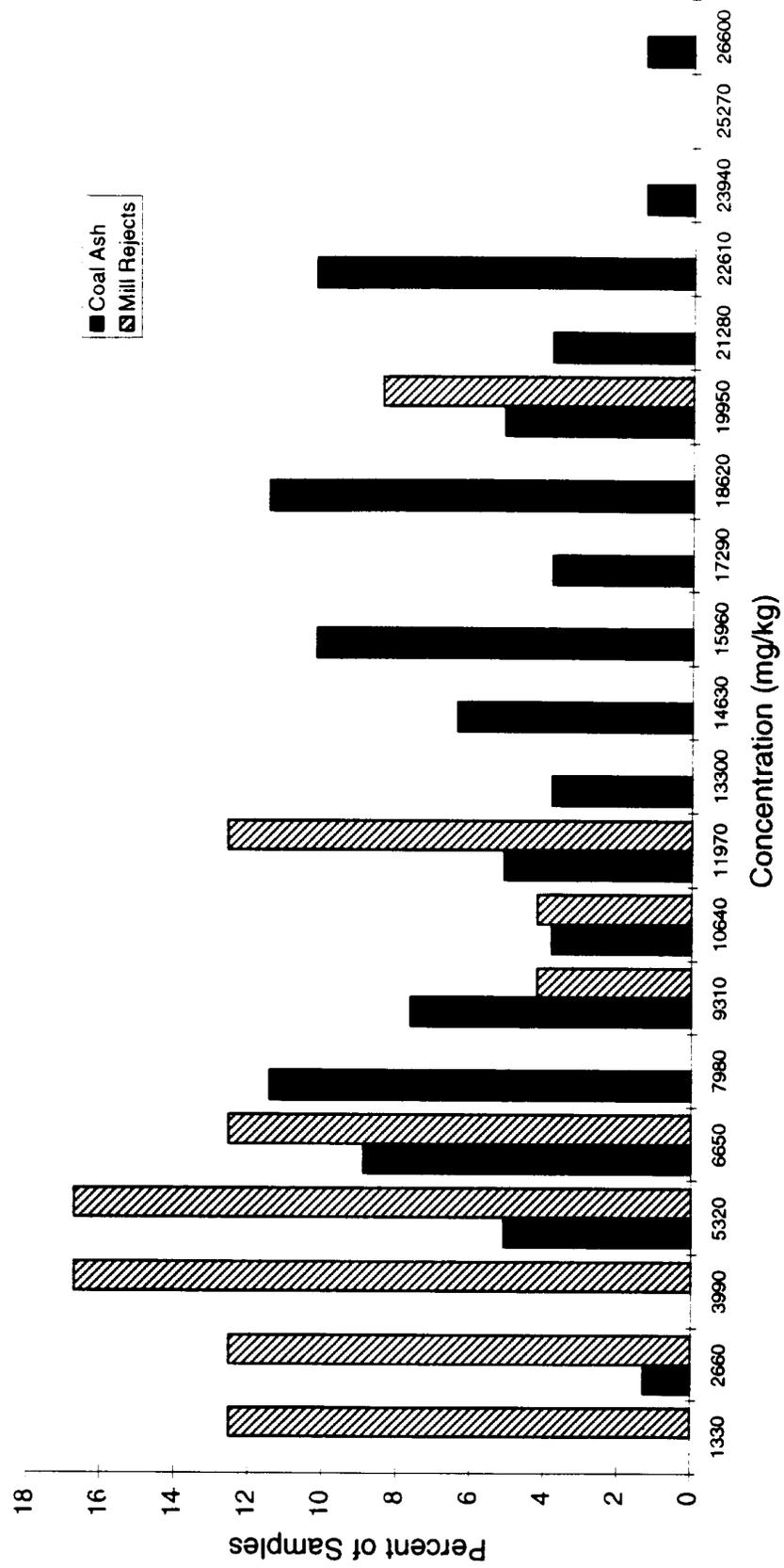
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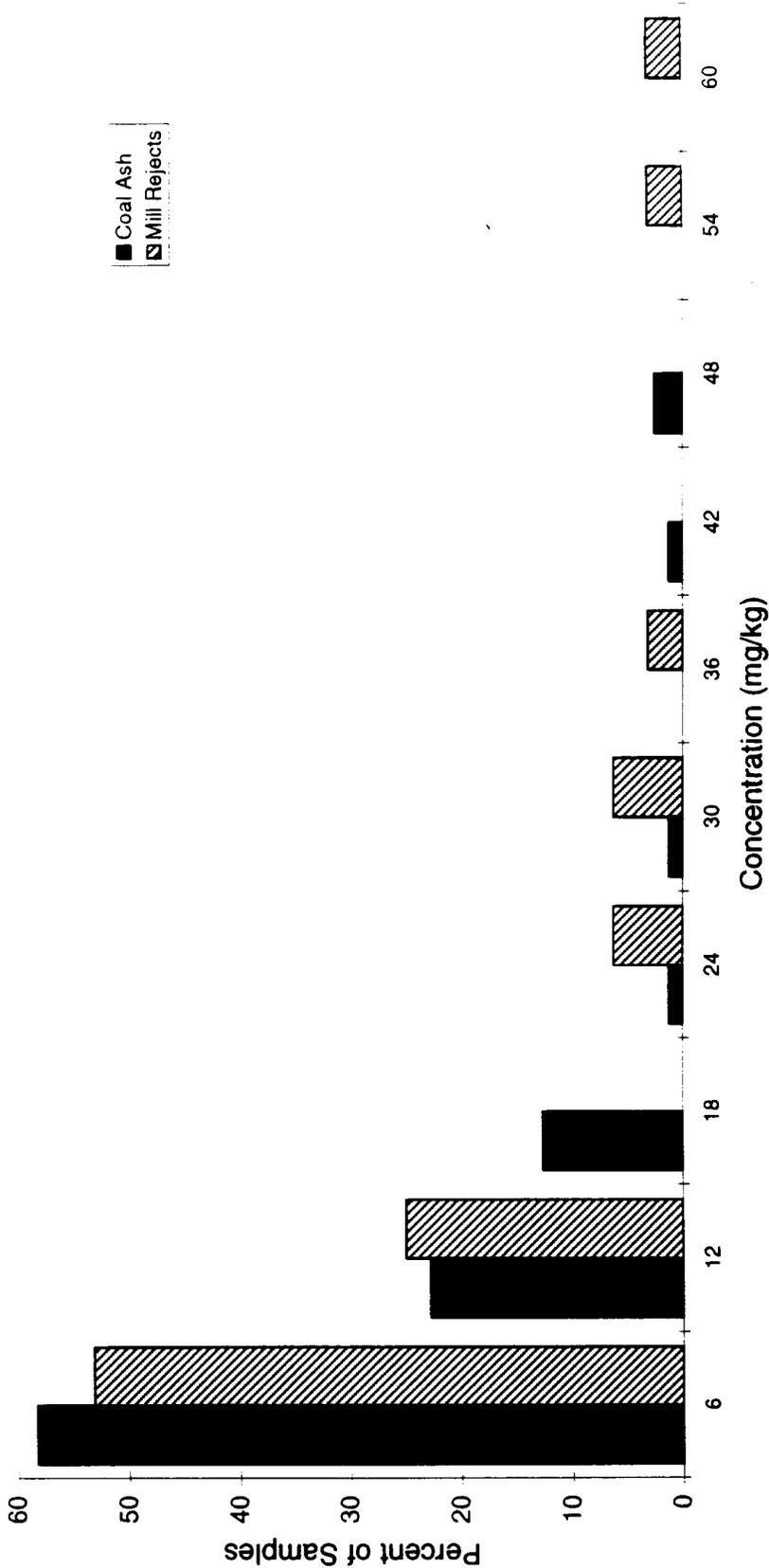
Nickel - (Outlier of 1267 mg/kg for coal ash not included.)



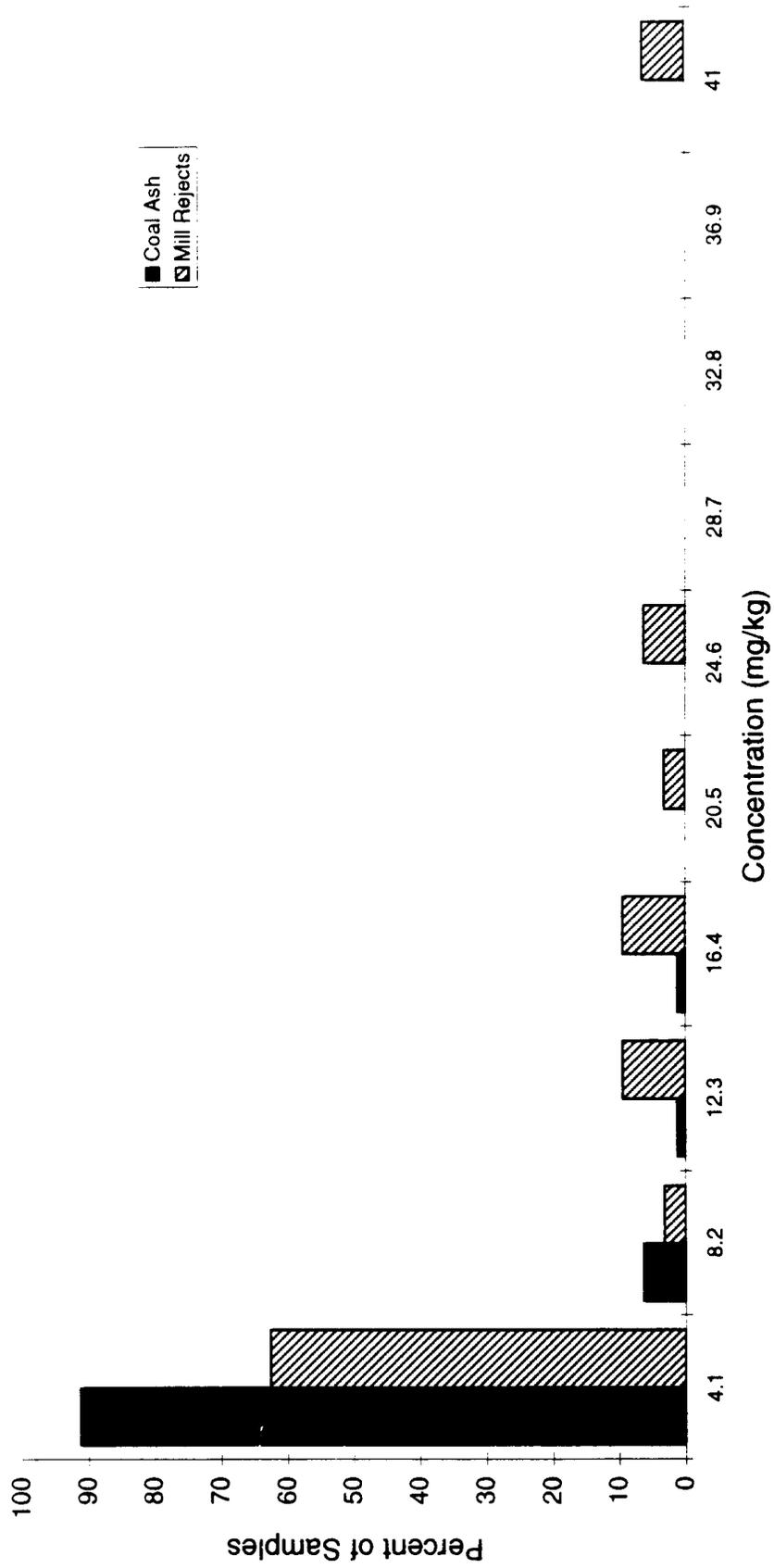
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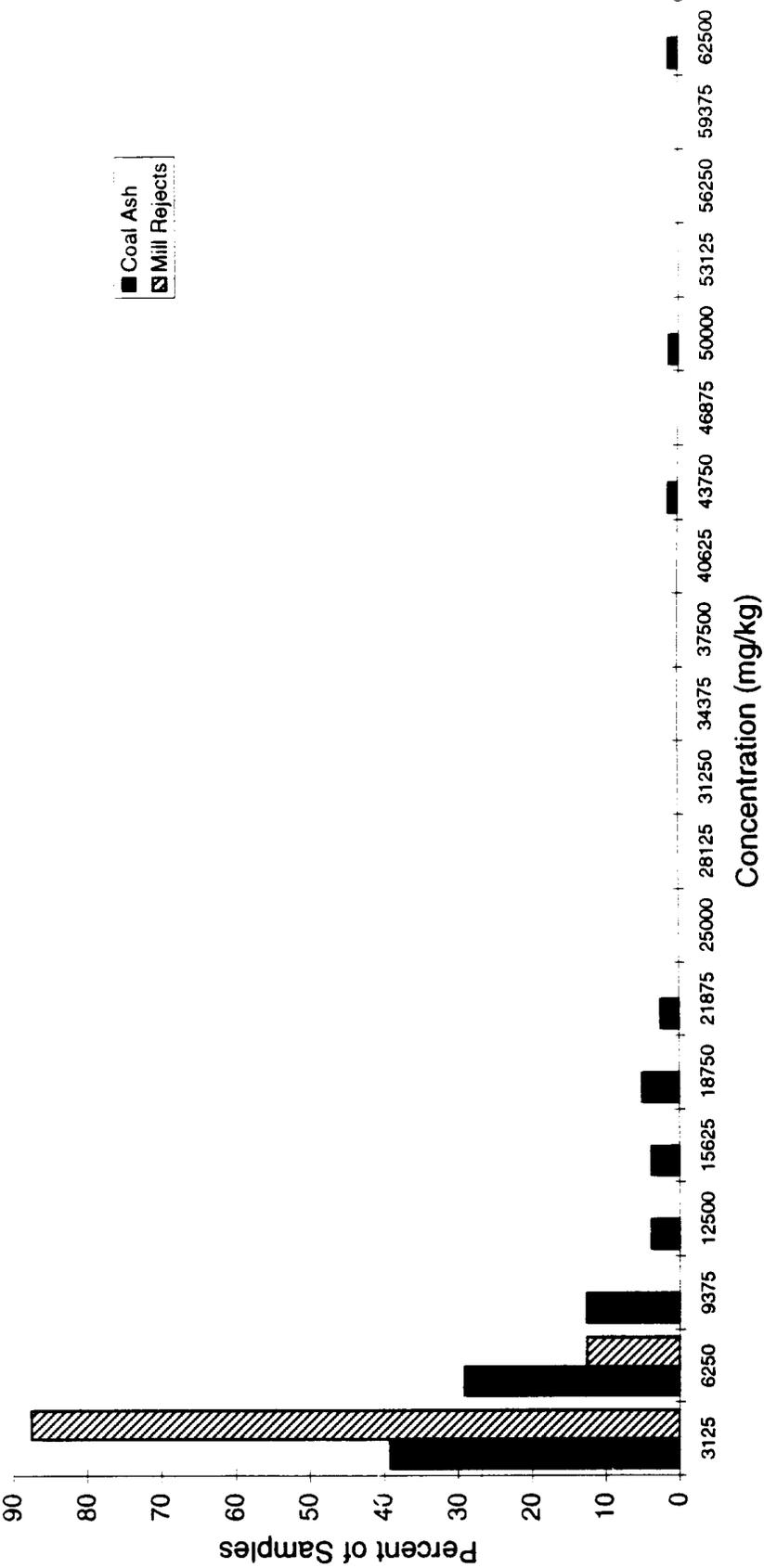
# Selenium



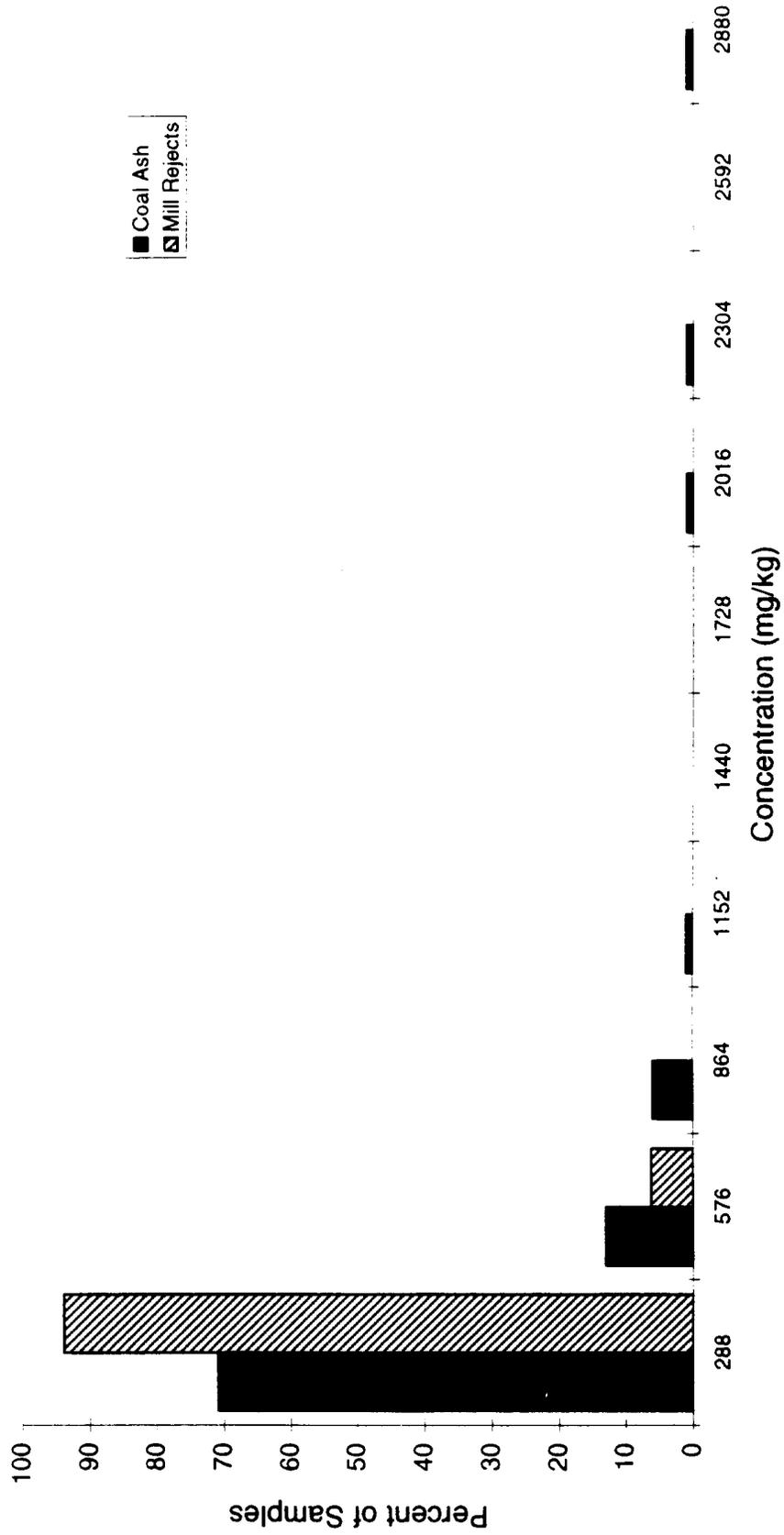
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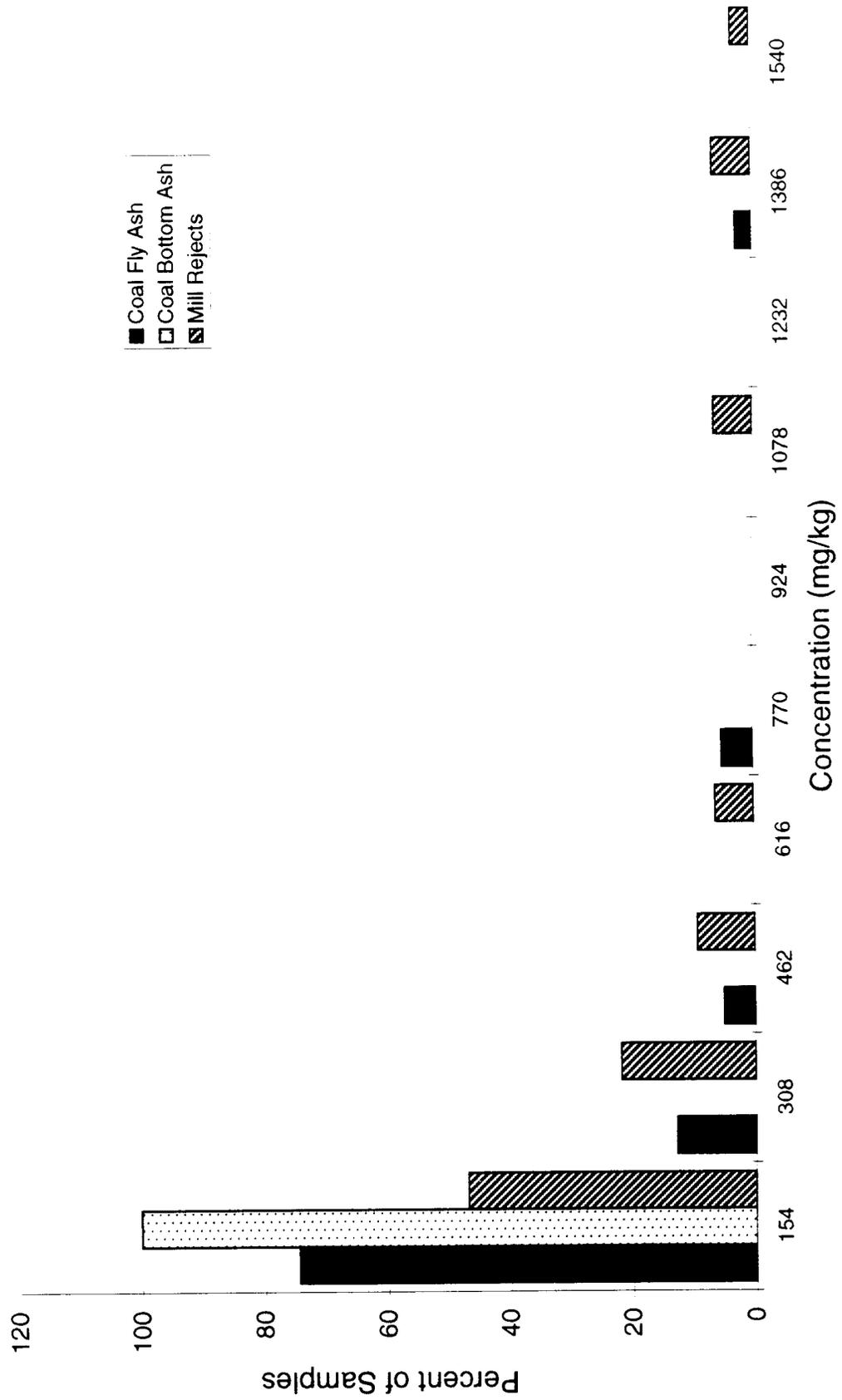
# Sodium



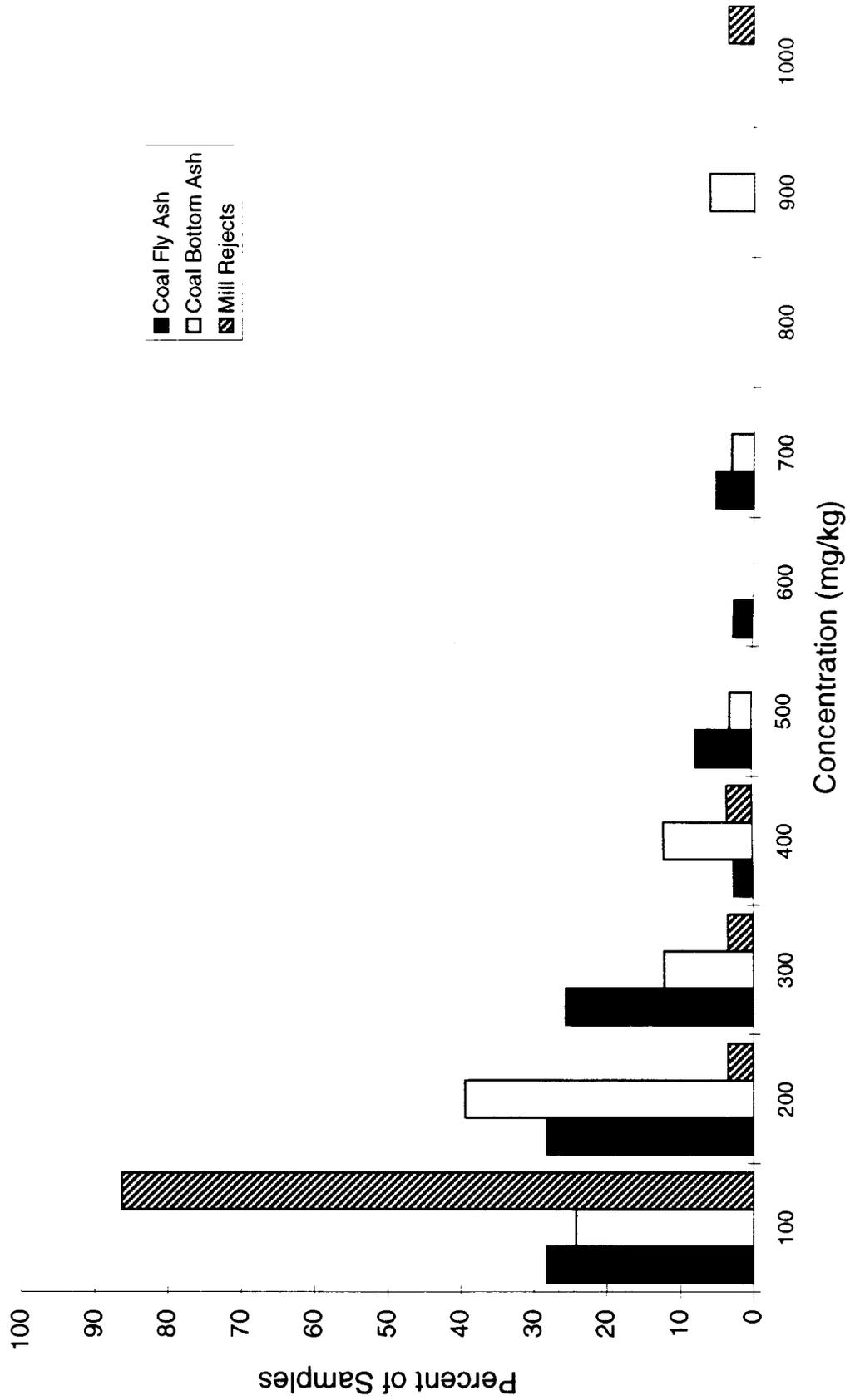
# Zinc



# Arsenic

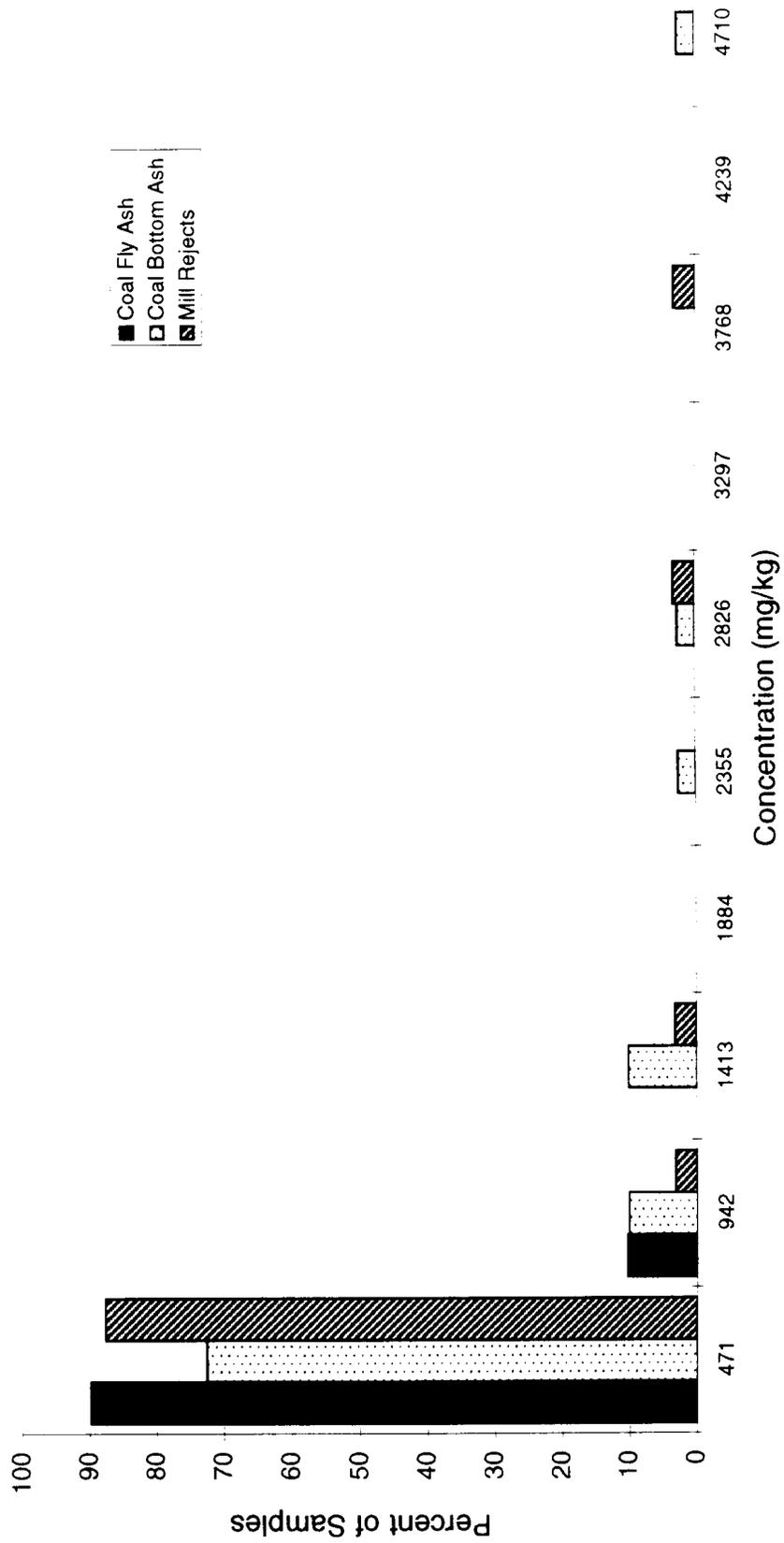


# Chromium

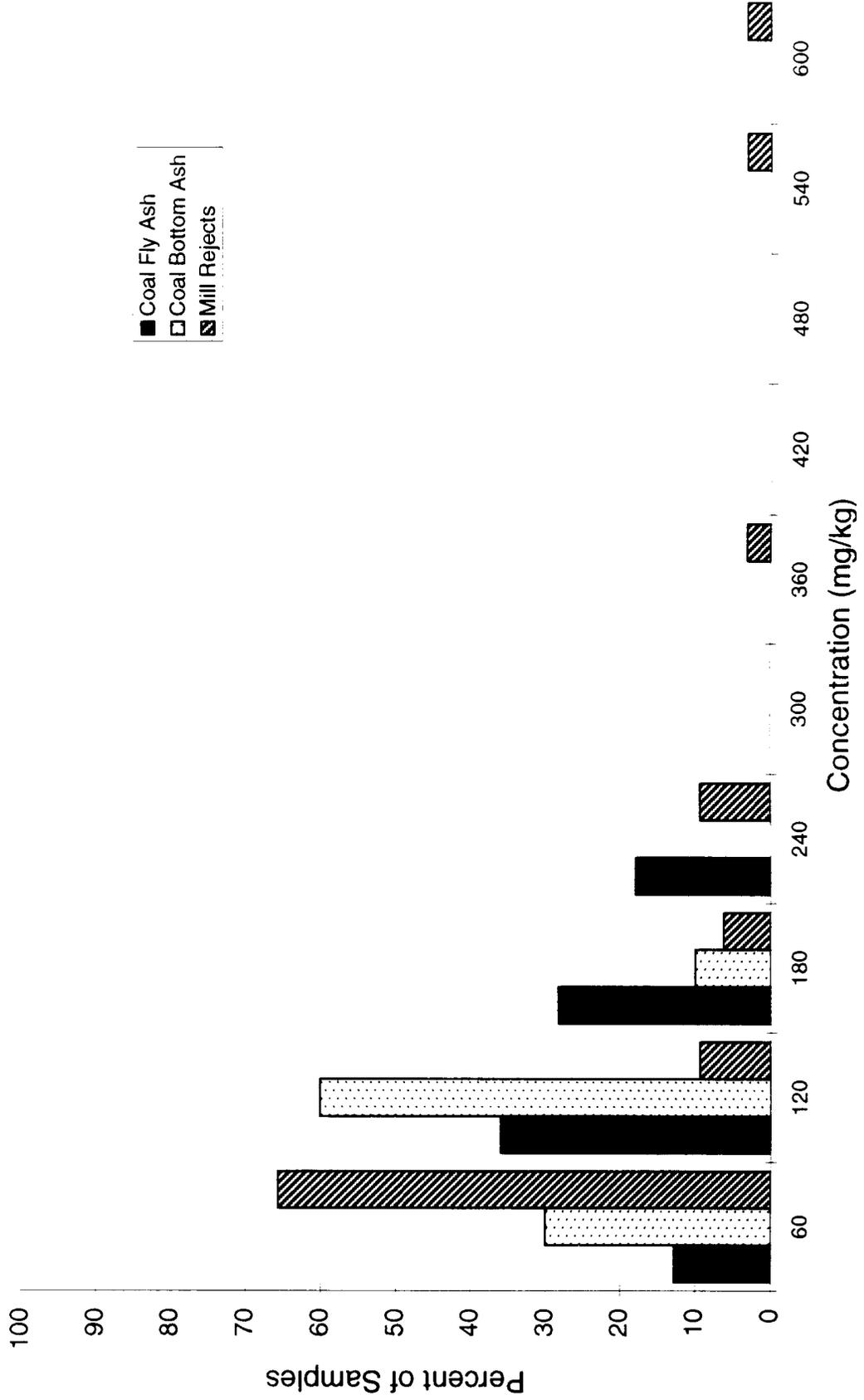


Chromium values above 1,000 mg/kg not shown in plot.

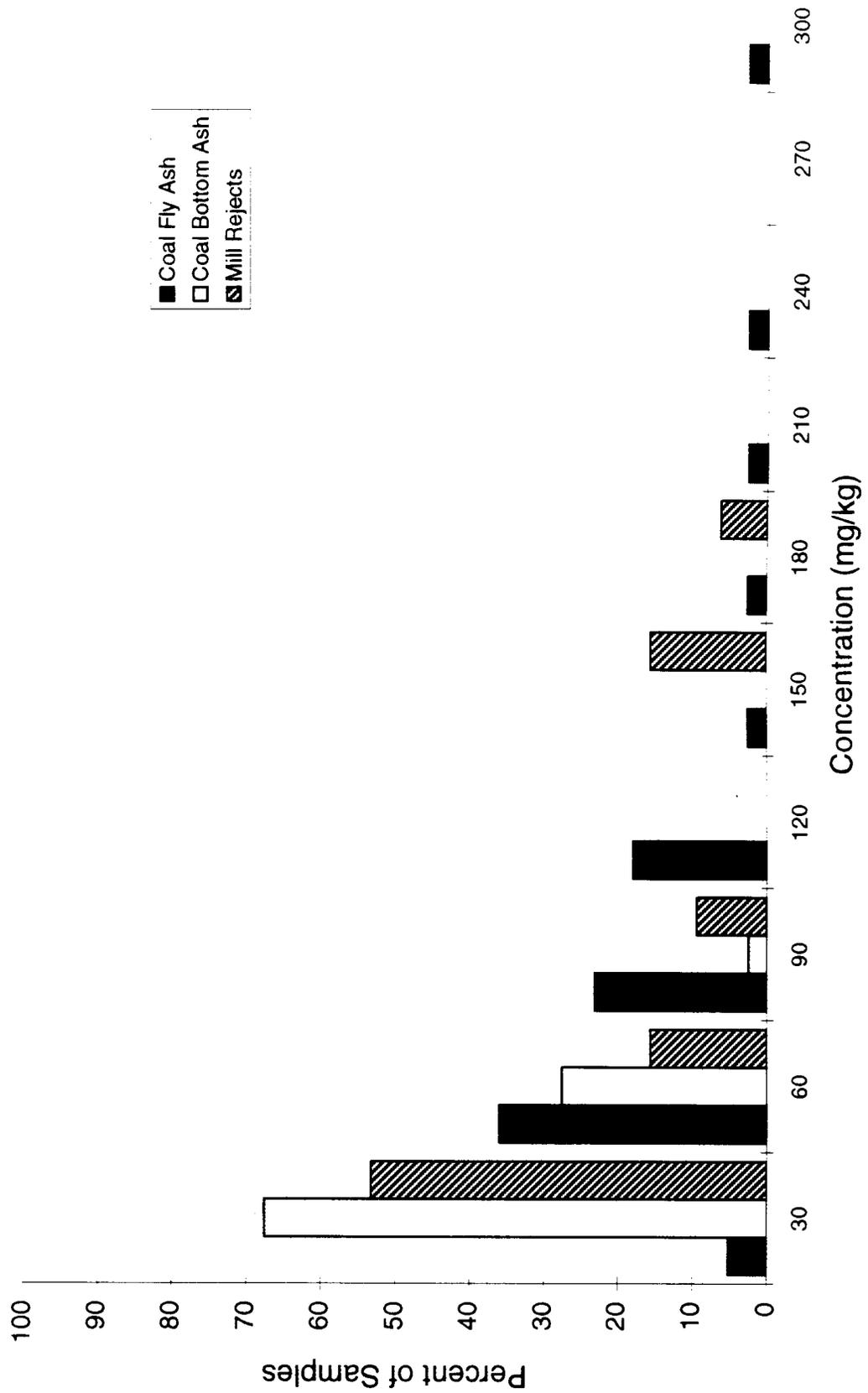
# Chromium



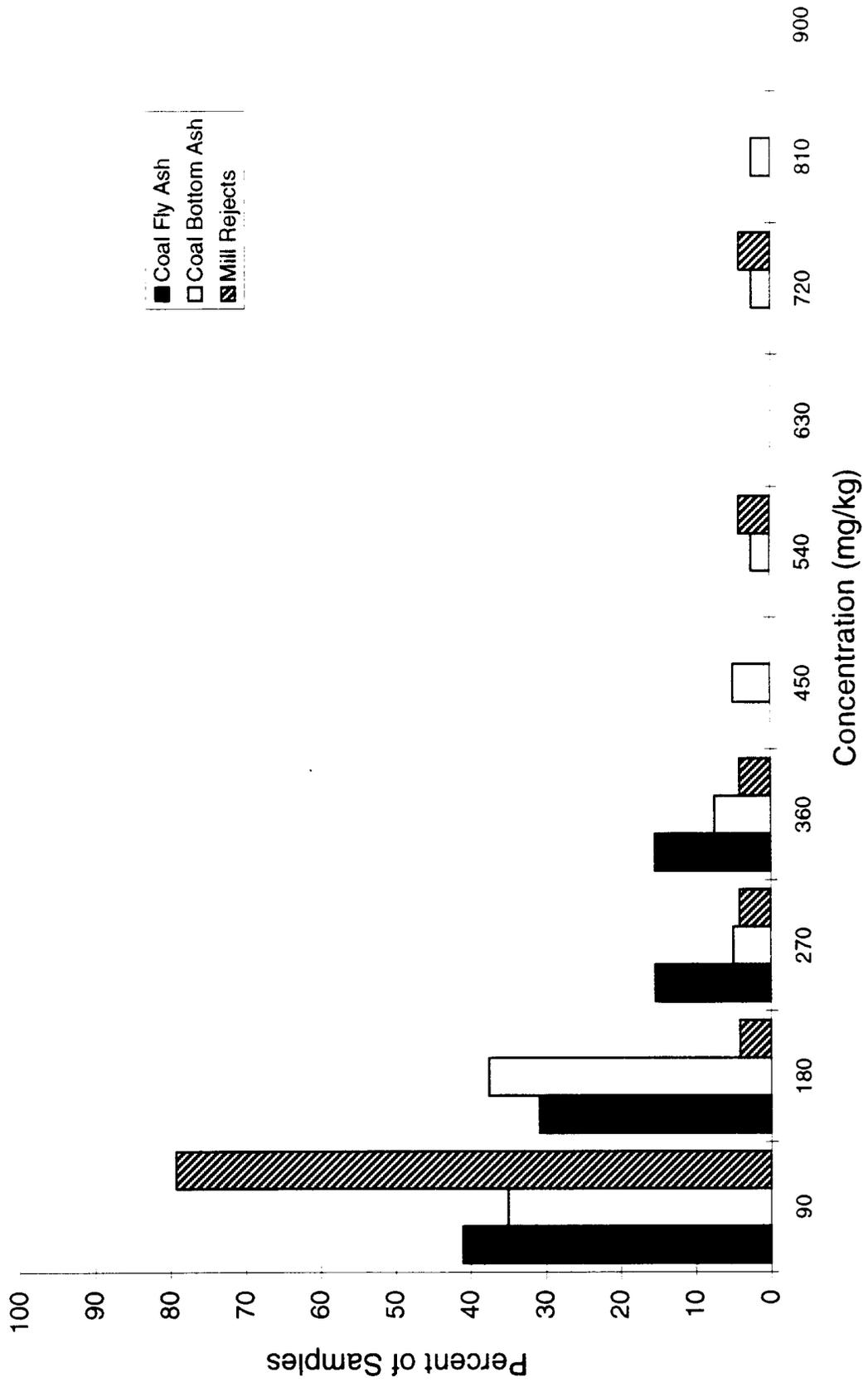
**Copper - (Outliers of 1047 and 1452 mg/kg for coal fly ash not included.)**



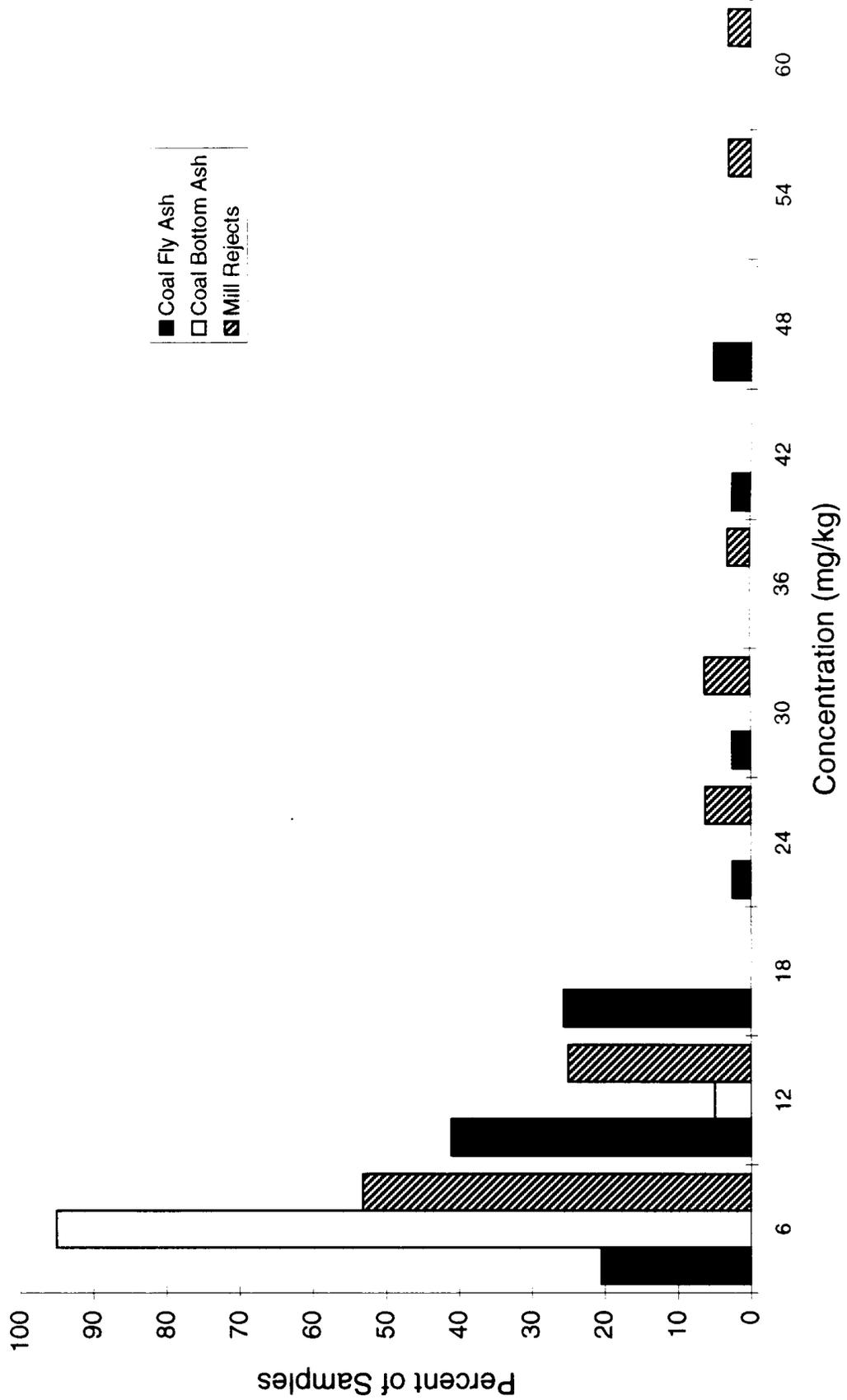
Lead - (Outliers of 843 mg/kg for coal bottom ash and 1340 and 2120 mg/kg for coal fly ash not included.)



Nickel - (Outlier of 1267 mg/kg for coal bottom ash not included.)



# Selenium



# C

## TIME-SERIES PLOTS FOR SELECTED WELLS AT FA SITE

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The following time-series plots illustrate groundwater quality at selected up and downgradient wells at the FA Site. Available water quality data are plotted for each well, so the time periods included may differ.

