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WASTEWATER CHARACTERIZATION AND  
TREATABILITY FOR AN EASTERN COAL SLURRY

BY

MARK J. FLINT  
B.S., Old Dominion University, 1980

THESIS

Submitted in partial fulfillment of the requirements  
for the degree of Master of Science  
in the Graduate Studies Program of the College of Engineering  
University of Central Florida  
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## ABSTRACT

A complete wastewater characterization study was performed on an eastern Kentucky coal slurry after a 10-day circulation period in a 40 foot (12.2 m) pilot-scale pipeline. The resulting wastewater was settled and decanted for additional lime and alum treatability studies.

Eastern coal slurries were characterized by high TDS, conductivity, sulfates and iron. Significant concentrations of a number of trace metals were also found; however, organics were very low. Wastewater quality varied considerably among several experiments and was presumed to be influenced by different properties of the coal and the addition of a corrosion inhibitor. The major treatment concern was removal of high concentrations of iron, manganese, and trace metals if wastewaters were to be discharged.

Lime treatment was found to effectively remove iron, magnesium, manganese and many other trace metals from coal slurry wastewaters. Alum treatment methods were considerably less effective for metals removal; however, alum was more effective in removing organics, color and turbidity. The addition of a corrosion inhibitor was found to reduce treatment removals for both lime and alum treatment. Several alternative uses were proposed for slurry wastewaters based on predicted water quality and volumes.



## ACKNOWLEDGEMENTS

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This thesis would not have been possible without the professional guidance of Dr. C.D. Cooper, Dr. J.D. Dietz, and Dr. J.S. Taylor. In addition, Mr. C.R. Roddy assisted in obtaining pulverized coal and laboratory analysis that was essential to this research.

The quality and success of this thesis was enhanced by the cooperation and assistance of many fellow students and friends. Mrs. Sharon Darling's excellence in typing and thesis preparation is greatly appreciated. Working with my colleague, Mr. Mike Todd, was always an enjoyable experience and his input contributed greatly to the success of this thesis.



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## CHAPTER I

### INTRODUCTION

Historically, the operation of coal slurry pipelines has proven to be an efficient and economical means of transporting coal. In the late 1950's, the Consolidated Coal Company operated a coal slurry pipeline that extended from Cadiz, Ohio to Eastlake, Ohio. Operation of the pipeline continued for about 6 years until a reduction in rail freight favored transport by the railroad system. In the late 1960's, the Black Mesa Pipeline was constructed near Kayenta, Arizona to move coal to the Mohave Power Station in southeast Nevada. The Black Mesa Pipeline operates at a capacity of 5 million tons (4.54 million MT) per year and spans 273 miles (440 Km). The Black Mesa Pipeline has operated quite successfully since its completion in 1970.

Following the completion of the Black Mesa Pipeline and an increased U.S. demand for coal power generation, considerable interest has been focused on coal slurry transport. As of 1981, more than 30 possible pipeline routes have been investigated with one major proposed system linking West Virginia and Kentucky coal mines to the Georgia and Florida power industry.

One important consideration in the development of coal slurry transport systems has been the tremendous amount of carrier water



required and the degradation of water quality during transport. Typical coal slurry systems operate at a 50 percent (by weight) solids level and require billions of gallons of water each year. A schematic diagram of coal slurry operations is presented in Figure 1. As illustrated, there is a demand for a large volume of water at the preparation plant and a need to treat and dispose of or re-use the polluted water at the pipeline terminus. Research on the effects of coal slurry transport on water quality has focused mainly on western coal slurries. The need for a more complete data base on eastern coal slurry water quality has prompted research at the University of Central Florida. In addition to characterizing the slurry water, practical treatment methods and alternative uses of coal slurry wastewaters are an essential part of understanding and dealing with the environmental impacts associated with coal slurry pipelines.

The University of Central Florida, in August of 1982, began a project to study the effects of eastern coal slurries on water quality and to investigate possible treatment methods for coal slurry wastewaters. That research was made possible by an EPA Cooperative Agreement and funds supplied by the University of Central Florida.



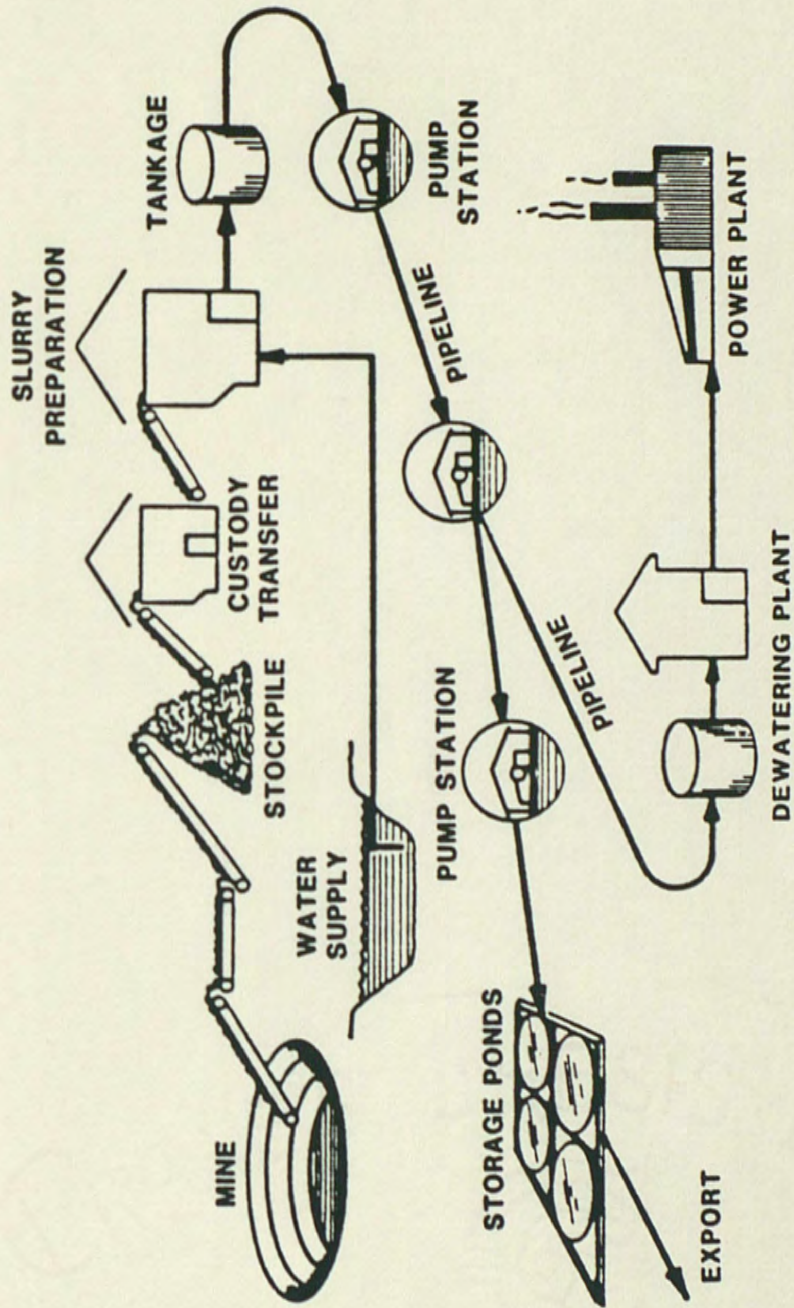


Fig. 1. Schematic diagram of a full scale coal slurry pipeline system  
(Doris 1981).



CHAPTER II  
LITERATURE REVIEW

Overview

The transport of coal by slurry pipeline requires a physical separation of coal and carrier water at the pipeline terminus. The wastewater resulting from the separation process may contain various inorganic minerals, trace metals, and organics that may render the water unacceptable for discharge or industrial uses at the power plant.

The water quality of the transport water is a function of several parameters:

1. Chemical characteristics of the coal
2. Chemical characteristics of the transport water
3. Percent or fraction of coal in the slurry media
4. Transport distance or residence time in the pipeline

Before studying the treatability of a particular coal slurry wastewater, it is important to develop a good understanding of the slurry water quality characteristics and how they may vary. Most of the treatability studies on coal slurry wastewaters have centered around coals originating from the western or interior western U.S. Chemical characteristics of these coals tend to vary considerably from



eastern coals thus wastewaters may also vary. To this date, no other pilot scale pipeline studies have been conducted on eastern coals, however, some research has been done on Kansas and Illinois coal slurries, eastern acid mine drainage, and eastern coal pile leachate. The wastewaters resulting from these processes sometimes are similar to and may be somewhat characteristic of slurry wastewaters found in eastern coal slurry systems and may require similar treatment methods.

There are various treatment methods for coal slurry and other coal industry wastewaters reported in the literature that incorporate physical, chemical and biological unit processes. Because slurry water quality varies with a number of parameters, different slurry wastewaters may require various types of treatment. Some of the treatment processes that have been studied include:

1. Physical sedimentation and separation
2. Carbon adsorption
3. Ion exchange
4. Lime and soda-ash softening
5. Alum treatment
6. Activated sludge treatment

The type and degree of treatment depends on the intended use of the wastewater as well as its characteristics. A brief review of the recent literature on water quality, treatment methods, wastewater uses, and regulations is presented here.



### Characteristics of Coal Slurry Wastewaters

Coal slurry transport requires that coal be crushed and pulverized to a range of 8-mesh to -325-mesh with no more than 20 percent by weight passing through a -325 mesh (Levence 1971). As a result, a tremendous surface area of coal is exposed to transport water for chemical interactions. It has been estimated that one ton of coal from the Black Mesa Pipeline may have as much as 55 acres of surface area (U.S. Congressional Report 1978). This tremendous surface area along with numerous impurities found in coal present a great potential for water pollution. The characteristics of coal vary with region and even with different coal seams. Peavy and co-workers (1978) studied variations in trace metal concentrations of 100 coal samples taken from 2 coal seams of the same mine in Colstrip, Montana. Variations in the two seams are presented in Table 1. These western coals typically are lower in sulfur and have a higher alkaline ash than eastern coals.

An eastern Kentucky coal composite sample of 18 unit trains was analyzed for a variety of minerals, percent ash, percent sulfur, and heating value and was reported by Todd (1983). Results of these analyses are presented in Tables 2 and 3.

Slurry transport water is another factor to consider when studying coal slurry water quality. A number of transport waters have been investigated including surface and groundwater (Todd 1983; Moore 1983 and Peavy 1980), treated municipal wastewater (Moore



TABLE 1  
COAL TRACE ELEMENT ANALYSES: AVERAGES

Element	Analyses in parts per million (ppm) of whole coal, moisture-free basis	
	Rosebud Seam (49 holes)	McKay Seam (26 holes)
Antimony	0.61	0.46
Arsenic	6.02	6.13
Beryllium	0.44	0.45
Cadmium	0.129	0.139
Chromium	5.37	5.30
Copper	12.5	14.6
Fluorine	51.0	19.0
Germanium	2.64	3.98
Lead	8.8	6.4
Manganese	66.1	22.4
Mercury	0.20	0.22
Nickel	37.3	26.5
Selenium	1.29	0.73
Zinc	49.6	15.8

SOURCE: Peavy (1978).



TABLE 2

## COAL PROXIMATE ANALYSIS (DRY BASIS)\*

Parameter	Composite (as received 18 unit trains, 1981-82)
% Ash	15.11
% Volatiles	35.09
% Fixed Carbon	49.80
Heating Value (Btu/lb)	12,378
% Sulfur	2.51

\* SOURCE: Commercial Testing and Engineering Co., test for McIntosh Power Plant.

TABLE 3

TYPICAL MINERAL ANALYSIS OF ASH \*  
(Composite of 18 Unit Trains, 1981-1982)

Component	Weight %, Ignited Basis
SiO <sub>2</sub>	49.8
Al <sub>2</sub> O <sub>3</sub>	24.95
TiO <sub>2</sub>	1.14
Fe <sub>2</sub> O <sub>3</sub>	16.80
CaO	0.90
MgO	1.34
K <sub>2</sub> O	2.82
Na <sub>2</sub> O	0.30
SO <sub>3</sub>	1.65
Other	0.3
Total	100.0

\* SOURCE: McIntosh Power Plant Chem. Lab, Department of Elec. and Water Utilities, Lakeland, Florida.



1981) and saline water (Moore 1981; Peavy 1980). Although the water quality of these different source waters may vary somewhat, the overall impacts on coal slurry water quality are not as significant as the composition and characteristics of the coal used in the slurry with the exception of highly saline transport water.

Generally, slurries with higher solids concentrations produce higher concentrations of pollutants in the slurry wastewater. Increases in parameter concentrations are generally not linear with solids concentrations (Moore 1980). Coal slurries range from 30-70% solids (by weight) with a practical operating range of 40 to 60 percent (Brown 1983).

Coal slurry residence time is a function of transport distance and velocity. Typical residence times for coal slurries range from 10 to 15 days with slurry velocities of 4 to 6 ft/s (1.22 to 1.83 m/s) (Sandu 1982). Coal slurry at this velocity is in the turbulent flow regime and particulate coal is kept in suspension. The turbulent flow induces good mixing for coal-water interactions in the slurry pipeline. Plummer et al. (1982) found that the major exchanges between coal and water occurs within a 24 hour period. The changes in concentrations of different water quality parameters have been found to be parameter specific (Moore 1980). Concentrations may increase or decrease with time depending upon the parameter. Cooper and his co-workers (1983) found that most parameters reach an equilibrium value by the fourth day of operation.



Numerous investigators have studied water quality resulting from western or interior western coal slurries. An in-depth literature review conducted by Anderson, et al. (1978) reported on 21 water quality parameters studied on the 439 km Black Mesa Pipeline. Water quality parameters included pH, total dissolved solids, sulfates, and a number of trace metals. Results for a 3-day residence period indicated that trace metal concentrations were very low and pH was 9.0. Sulfate concentrations were low at 132 mg/l and total dissolved solids were reported at 1392 mg/l. Anderson and his co-workers (1978) conducted additional research on Utah bituminous coal slurries with several different carrier waters. A 50 percent by weight coal was mixed for a 10-day period and filtered for analyses of 16 water quality parameters. Trace metals were reported to be extremely low, however, sulfates were found to increase slightly. No chemical oxygen demand was detected.

Moore (1980) conducted extensive research on several Wyoming coal slurries using different water sources. Slurries ranging from 30 to 60 percent were investigated using residence times up to 11 days in a nitrogen blanketed reactor. Sulfates ranged from 400 to 700 mg/l, total dissolved solids ranged from 1100-1200 mg/l and trace metals were relatively low. Chemical and biochemical oxygen demands were significant, however, they were different for various coals. Concentrations of COD and BOD decreased with time.

Godwin and Manahan (1979) studied two coal slurries using North Dakota and Wyoming coals at different percent solids. Residence



times were reported as 24 hours. Most trace metals reached a solubility limit before the slurry reached 30% solids, however, Na and K concentrations increased with percent of coal in the slurry. A number of trace metals were found at concentrations over 1 mg/l.

Plummer, et al. (1982) investigated various Wyoming coal slurries mixed for periods up to 15 days. Sulfates and total dissolved solids were found to increase significantly with time; BOD ranged from 92-275 mg/l and trace metals were very low. Studies were conducted under both atmospheric conditions and nitrogen blanketed atmosphere.

Peavy, et al. (1980) conducted bench-scale research using a Montana coal slurry with fresh and saline carrier waters. A 12-day residence time and approximately 50 percent solids slurry was considered. Wastewater pH was found to decrease to about 6.0, sulfates increased to 900 mg/l, turbidity increased, and dissolved organic carbon increased significantly to 20-30 mg/l. Trace metals were very low with concentrations generally less than 0.10 mg/l.

In comparison to western coals, considerably less work has been done on eastern and Appalachian coals. Moore (1981) conducted research on two eastern coals; one from Kansas and the other from Illinois. Moore reported high sulfates ranging from 1400 to 2200 mg/l, high total dissolved solids from 3600 to 6000 mg/l and BOD and COD concentrations significantly lower than western coal slurries. Significant concentrations of nickel ranging from 0.75 to 1.1 mg/l were found using the Kansas coal.



Cooper and co-workers (1983) have recently studied an eastern coal slurry using Kentucky coal in potable water. A 50 percent slurry was nitrogen blanketed and pumped in a 12 m long pipeline for a 10-day period. Twenty-nine water quality parameters were investigated. Sulfates, total dissolved solids, and conductivity were found in high concentrations initially and increased to higher concentrations with time. Some of the trace metals were found in substantial concentrations, and iron was found in very high concentrations--sometimes exceeding 500 mg/l. Organics were generally very low with phenol less than 2 ppb and THMFP concentrations less than 60 ppb for all slurry runs.

Several other coal related industrial processes may produce wastewaters comparable to coal slurry wastewaters. Acid mine drainage, coal pile leachate, and coal cleaning waste result from industrial processes that involve coal-water interactions over extended periods.

Acid mine drainage is usually characterized by highly acidic wastewater containing very high concentrations of iron, metals, and sulfates. During mining operations, coal is oxidized when exposed to atmospheric conditions. Williams (1975) studied the characteristics of acid mine drainage and the oxidation state of coal. Williams stated that the oxidized state of the coal influenced the drainage water quality. Table 4 classifies acid mine drainage according to the degree of oxidation of the coal. Wilmoth (1977)



TABLE 4  
MINE DRAINAGE CLASSES

Constituent (mg/l)	Class 1	Class 2	Class 3	Class 4
	Acid Discharges	Partially Oxidized and/or Neutralized	Oxidized and Neutralized and/or Alkaline	Neutralized and Not Oxidized
pH	2-4.5	3.5-6.6	6.5-8.5	6.5-8.5
Acidity (as CaCO <sub>3</sub> )	1,000-15,000	0-1,000	0	0
Ferrous iron	500-10,000	0-500	0	50-1,000
Ferric iron	0	0-1,000	0	0
Aluminum	0-2,000	0-20	0	0
Sulfate	1,000-20,000	500-10,000	500-10,000	500-10,000

SOURCE: (Williams 1975)



conducted research on ferrous acid mine drainage from a West Virginia coal mine. Water quality of this eastern mine drainage closely approximates findings of the eastern coal slurry study reported by Cooper, et al. (1983). Table 5 summarizes the Crown Mine water quality found during 1974-1975.

Coal pile drainage results from stormwater runoff and leaching through coal storage piles and cleaning operations. Leachate waters are typically acidic with pH values ranging from 2.1 to 6.6. Acidity may range from 720-28,970 mg/l and trace metals may be found in various concentrations (Davis and Boegly 1981).

#### Physical Treatment Methods

The generation of coal slurry wastewater begins with the dewatering operation at the pipeline terminus. Slurry dewatering operations may typically recover 60 to 70 percent of the transport water (Peavy 1981). In most proposed pipeline systems, the recovered transport water is to be used for industrial purposes such as cooling tower makeup water.

The dewatering operation may incorporate a number of physical processes along with some thermal drying, if required. A brief summary of the physical processes as proposed by Brown (1983) is as follows:



TABLE 5  
CROWN WATER QUALITY DATA, 7/74 THROUGH 6/75

Parameter	Unit	Mean	Maximum	Minimum	Standard Deviation
pH	pH	5.04	5.9	4.7	---
Specific conductance	$\mu$ mhos/cm	3760	4000	3400	260
Acidity as CaCO <sub>3</sub>	mg/l	640	1070	155	120
Calcium	mg/l	370	450	300	40
Magnesium	mg/l	110	150	55	20
Total iron	mg/l	300	380	250	39
Ferrous iron	mg/l	270	340	160	34
Sodium	mg/l	480	670	280	95
Aluminum	mg/l	15	36	6	9
Manganese	mg/l	6	8	4.3	1
Sulfate	mg/l	3040	3600	2300	300
Alkalinity	mg/l	17	100	0	25
Total dissolved solids	mg/l	4320	5170	3250	480
Temperature	°C	13.8	17	9	2.3

SOURCE: Wilmouth (1977).



- A. Screening Operations
  - 1. Dewatering
  - 2. Vibrating
- B. Hydrocycloning
- C. Thickening Operations
- D. Centrifugation
  - 1. Basket type
  - 2. Solid bowl type
- E. Vacuum Filtration Operations
  - 1. Rotary drum type
  - 2. Vacuum disc
  - 3. Horizontal rotary type
  - 4. Tilting pan type
- F. Pressure Filtration Operations
  - 1. Filter press
  - 2. Tank type
  - 3. Belt press
- G. Thermal Drying Operations
  - 1. Flash dryer
  - 2. Fluidized-bed dryer
  - 3. Rotary dryer
  - 4. Rotary tray dryer

The early methods of dewatering as used by Consolidated Coal's Cadiz, Ohio pipeline involved thickening to 60 percent solids, vacuum filtration to about 20 percent moisture, and thermal drying to about 9 percent moisture content (Brown 1983).

The current operation used by the Black Mesa Pipeline involves centrifugation and drying in bowl mills to 25 percent moisture content (Montfort 1972). The partially dried coal can be directly



combusted in specially designed furnaces. Most of the reported coal slurry research studies have utilized vacuum filtration (Cook 1978; Brown 1983) or centrifugation and vacuum filtration (Plummer 1983) as dewatering methods.

#### Carbon Adsorption Processes

Activated carbon has been used in advanced wastewater treatment to remove organic compounds and in industrial treatment to adsorb toxic organic compounds. The adsorption process involves physical adsorption due to Van Der Waals forces and is considered a reversible occurrence. A number of researchers have proposed the use of activated carbon treatment for coal slurry wastewaters with high organics. Plummer et al. (1982) and Cook (1978) have studied the effectiveness of powdered activated carbon for treatment of coal slurry wastewaters.

Plummer and his co-workers developed a Freundlich isotherm model for BOD removal with powdered activated carbon as a function of COD concentrations. From the isotherm studies, the adsorbability of a constituent and the dosages required were determined. Based on findings of Plummer's research, PAC was determined to be only nominally effective in removing oxygen demanding materials from coal slurry wastewaters prepared from Wyoming coals.

Cook (1978) used Wyoming coal in a 50 percent slurry at 1 to 2-day residence periods to simulate slurry wastewaters. Two activated carbon studies were conducted using powdered activated carbon



(PAC) in jar test batch analyses and granular activated carbon (GAC) in packed columns. The jar test study resulted in essentially no change in alkalinity, and calcium and total hardness. At a PAC dosage of 5 gm/l, sulfate concentrations were nominally reduced from 610 to 490 mg/l, and soluble COD was reduced from about 75 mg/l to 13 mg/l. At a dose of 3 gm/l, BOD concentrations were reduced from 40 mg/l to 10 mg/l. Concentrations of most trace metals remained constant, however, slight reductions in magnesium, lead, and aluminum were observed with increased doses of PAC. Column studies using GAC produced similar results. Soluble COD decreased from 128 to 32 mg/l, and soluble BOD was reduced from 75 to 20 mg/l. Most of the metal concentrations remained fairly constant with reductions in aluminum, titanium and magnesium. Table 6 summarizes the results of the column studies using GAC. Langmuir and Freundlich isotherm modeling was attempted, however, neither method was successful.

#### Ion Exchange Processes

Ion exchange processes have been used successfully in the past to selectively remove impurities or recover valuable chemicals otherwise lost in industrial discharges. Ion exchange has been proven to be particularly effective in the removal of many metal ions.

In the cation exchange process, positively charged ions are removed from solution through an exchange with hydrogen or sodium ions



TABLE 6  
RESULTS OF ACTIVATED CARBON COLUMN TEST

Parameter	Before Treatment	After Treatment
pH	7.0	6.8
Total Alkalinity (mg/l as CaCO <sub>3</sub> )	104	98
Calcium Hardness (mg/l as CaCO <sub>3</sub> )	223	207
Total Hardness (mg/l as CaCO <sub>3</sub> )	374	367
Sulfate (mg/l SO <sub>4</sub> )	548	467
Soluble COD (mg/l)	128	32
Soluble BOD (mg/l)	75	20
Silica (mg/l as SiO <sub>2</sub> )	17.4	14.8
Sodium (mg/l Na)	1.6	1.6
Potassium (mg/l K)	6.8	6.6
Magnesium (mg/l Mg)	52.0	46.5
Titanium (mg/l Ti)	0.50	0.36
Lead (mg/l Pb)	0.16	0.12
Aluminum (mg/l Al)	0.26	0.10

SOURCE: Cook (1978)



complexed on a resin. After the resin has been exhausted, the system is backwashed with hydrochloric acid or sodium chloride to remove the metal ions and replace the hydrogen or sodium ions.

Brown (1983) has investigated the removal of heavy metals from coal slurry wastewater using ion exchange. A 50 percent (by weight) coal slurry was prepared from Illinois coal and distilled water and mixed for a 48-hour period. Brown's work involved a two-phase study where coal slurry wastewater was dosed with known concentrations of trace metals and pure distilled water was dosed with the same trace metal concentrations. Both wastewaters were passed through an ion exchange column and analyzed for various trace metals. Ion exchange was found to effectively remove nickel to below detectable limits of the atomic absorption and meet Florida Water Quality Standards. In addition, ion exchange was effective in removing iron and lead to levels below Florida State Water Quality Standards. Mercury concentrations were reduced substantially, however, were not reduced below the Florida Water Quality Standards. Table 7 summarizes Brown's findings on the effectiveness of ion exchange for removal of certain trace metals.

#### Chemical Precipitation

Chemical precipitation and coagulation have proven to be effective methods of removing many pollutants from wastewaters. Weber (1972) has summarized the common chemicals used in chemical treatment and their application. Table 8 is a list of the chemicals noted by Weber.



TABLE 7

COMPARISON OF THE EFFECT OF ION EXCHANGE  
ON THE REMOVAL OF HEAVY METALS FROM DOSED  
DISTILLED WATER AND COAL SLURRY WASTEWATER\*

Heavy Metal	Initial Concentration	Final Concentration	
		Coal Slurry Wastewater	Dosed Distilled Water
Mercury	0.25	0.05	0.08
Mercury	0.75	0.09	0.50
Mercury	1.50	0.15	0.01
Iron	0.25	0.16	0.13
Iron	0.75	0.05	0.09
Iron	1.50	0.06	0.08
Lead	0.25	0.08	0.06
Lead	0.75	0.01	0.13
Lead	1.50	0.08	0.03
Nickel	0.25	bd1**	0.44
Nickel	0.75	bd1	0.22
Nickel	1.50	bd1	0.15

\* All concentrations are given in mg/l

\*\* bd1 - below detectable limits

SOURCE: Brown (1983).



TABLE 8

CHEMICALS COMMONLY USED IN CHEMICAL TREATMENT  
OF WATER AND WASTEWATER

Chemical	Use
Ammonium alum	Coagulation
Aluminum sulfate	Coagulation
Sodium aluminate	Coagulation
Ferric sulfate	Coagulation
Ferrous sulfate	Coagulation
Ferric chloride	Coagulation
Calcium hydroxide	Hardness, heavy metals removal
Sodium carbonate	Hardness, heavy metals removal
Sodium hydroxide	Hardness, heavy metals removal

SOURCE: Weber (1972).



Lime (calcium hydroxide) and soda ash (sodium carbonate) are typically used together to remove calcium and magnesium hardness in water supply systems. Because relatively high concentrations of both of these ions are found in coal slurry wastewaters, the use of lime-soda softening has been considered as a possible treatment method. Moore (1979) has noted that many slurry wastewaters may have significantly high concentrations of sulfates resulting in a high non-carbonate hardness and high soda ash requirements. Lime is also used in industrial processes for the hydroxide precipitation of heavy metals. Many researchers have found that metals precipitate out of solution at different pH ranges depending upon the metal ion and the solubility of the hydroxide salt that is formed. In many situations, multiple stage treatments may be required to remove several different metals.

Christoe (1976) has determined that if sulfates are present in very high concentrations, some removal of sulfates can be expected. The removal of sulfates is a result of the formation of calcium sulfate ( $\text{CaSO}_4$ ) and is limited by the solubility of this salt. Treatment with lime may effectively remove sulfates to about 1300 mg/l.

Cook (1978) investigated the use of lime-soda ash softening and hydroxide precipitation with lime on a 50 percent Wyoming coal slurry wastewater. Jar test studies were conducted using predetermined lime and soda ash dosages. Lime-soda ash softening and hydroxide precipitation studies were performed by mixing at 40 revolutions per minute for a 30 minute period followed by a 20 minute



settling period. At dosages of 136.6 mg/l lime and 313.8 mg/l soda ash, calcium and total hardness removals were reported as 55 percent and 66 percent, respectively. The magnesium concentrations were reduced by 78 percent and sulfate concentrations decreased from 615 to 525 mg/l. The hydroxide precipitation study (lime only) resulted in increased total alkalinity with increased pH values and a general increase in conductivity. When lime was added to pH 11.0, a sudden increase in calcium and total hardness was observed. Lead concentrations were observed to initially decrease around pH 9.0 and increase from pH 9.5 to 11.0. Sulfates remained constant with changing pH.

Alum in the form of aluminum sulfate is another common chemical used in coagulation processes. When alum is added to wastewater under controlled pH, long chain polymers form and settle out removing many impurities. Often, alum may be added along with another polymer to enhance flocculation and settling. Peavy (1982) has suggested the use of alum for the removal of turbidity in coal slurry wastewaters.

Plummer and others (1982) have investigated the use of alum and lime as treatment methods for slurry wastewaters. A coal slurry was prepared from a biologically treated effluent and crushed coal and was used in the treatability studies. Alum addition was found to significantly lower pH, however, samples were readjusted to pH 6-7 with quicklime (CaO). Neutralized alum treated samples



flash mixed for one minute and slow mixed for 20 minutes to allow formation of alum floc. The treated wastewater was settled and decanted for analyses of BOD, COD, TDS, conductivity, suspended solids, and sulfates. No trace metals analyses were performed on the decantate, however, metal concentrations were initially very low in the raw wastewater. Results of Plummer's investigation are presented in Table 9.

Brown (1983) investigated the removal of heavy metals from 50% Illinois coal slurry using lime addition. Brown prepared a coal slurry from the Illinois coal and pure distilled water and mixed the slurry for 48 hours. The decanted wastewater was filtered and dosed with additional known concentrations of various trace metals including lead, mercury, nickel and iron. Samples of distilled water were also dosed with these same concentrations and measured along with the dosed wastewater samples. A jar test batch analysis was performed by adding lime and rapid mixing at 100 rpm for 1 minute. Treated samples were flocculated for 15 minutes at 20 rpm. After settling for 30 minutes, samples were withdrawn and analyzed for trace metals. Lead, nickel and iron were found to be effectively removed to levels below Florida State Water Quality Standards.

Brown also studied the removal rates of these metals at different pH values. Figure 2 illustrates the response of 3 concentrations of mercury to varied pH. Brown found that concentrations were lowest for all 3 doses at around pH 10.0. Figure 3 illustrates the behavior



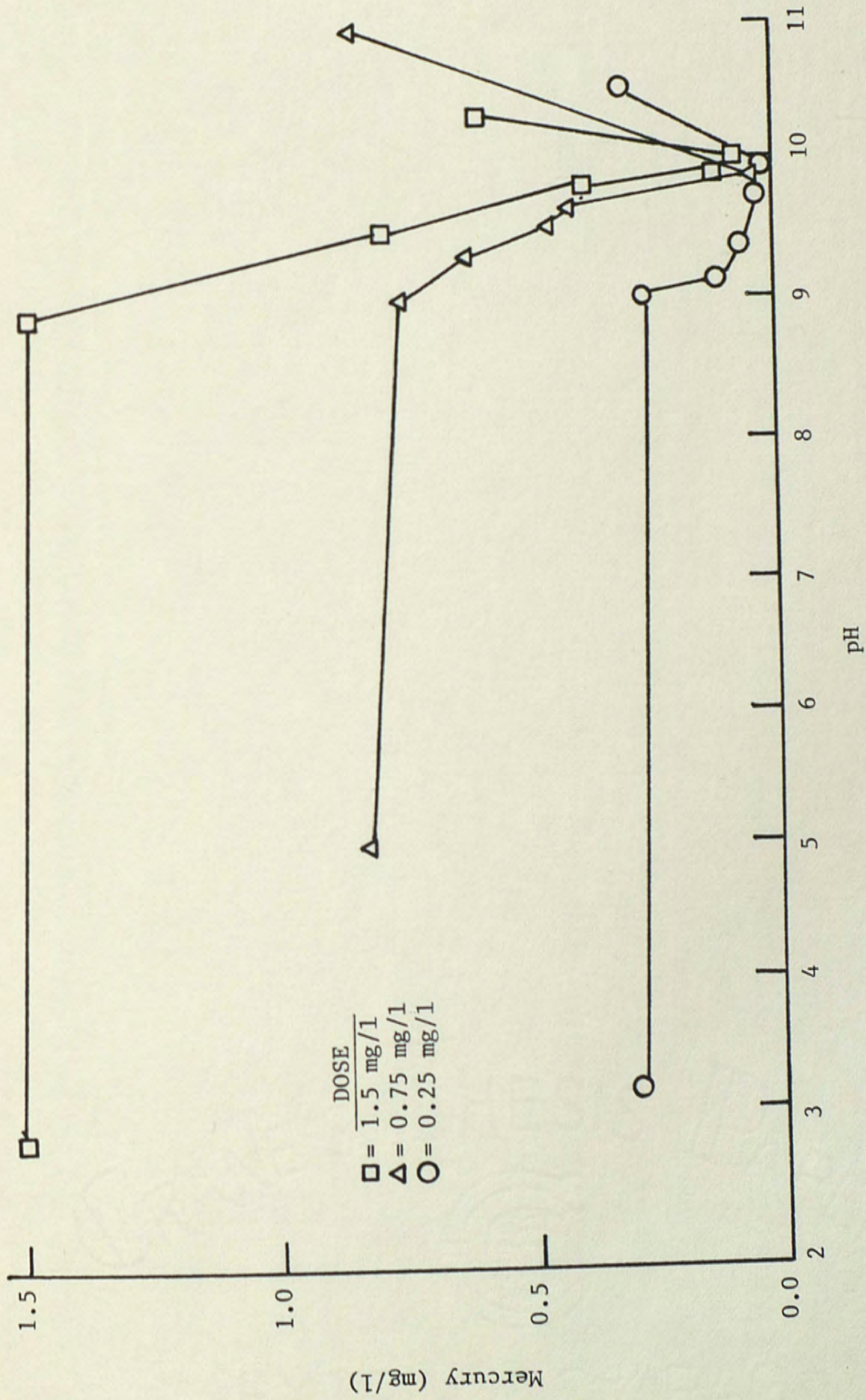


Fig. 2. Comparison of mercury concentrations with pH for coal slurry wastewater (Brown 1983).



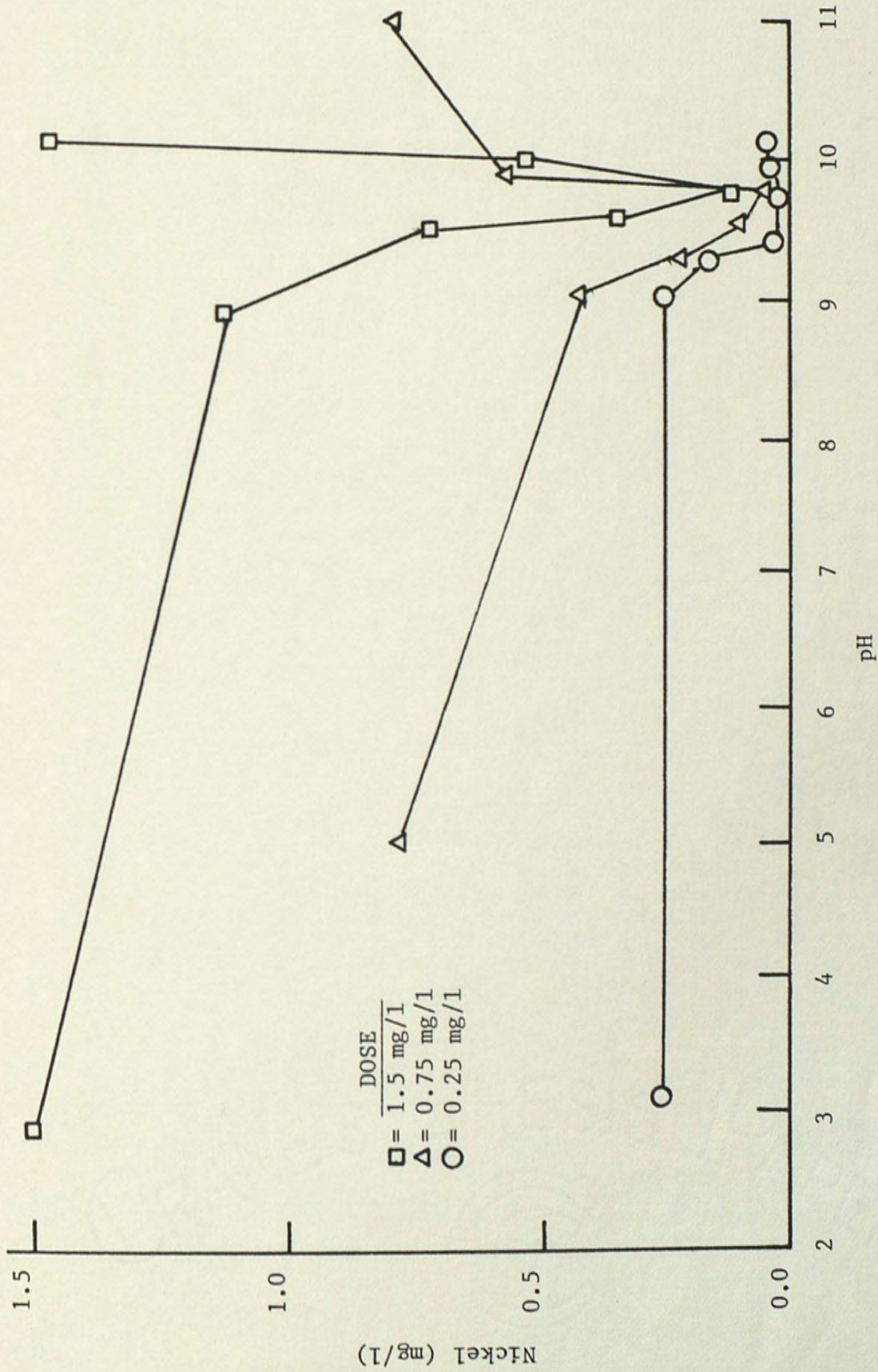


Fig. 3. Comparison of nickel concentrations with pH for coal slurry wastewater (Brown 1983).



TABLE 9  
 SELECTED RESULTS OF PLUMER'S ALUM TREATABILITY ANALYSIS

Alum Dosage (mg/l)	COD (unfiltered) (mg/l)	Total Organic Carbon (mg/l)	Total Dissolved Solids (mg/l)	Specific Conductance ( $\mu$ mhos/cm)	Total Suspended Solids (mg/l)	Sulfates (mg/l)
0	400	83	1130	768	72	770
30	260	85	1150	768	8	400
40	300	74	1100	878	8	490
60	290	52	-----	1024	--	540
80	260	81	1320	1115	<4	610
0	310	83	1080	768	54	260
75	270	71	1280	950	<4	580
75	230	86	1380	950	1	560
60	260	74	1160	950	<4	530
60	300	61	1300	950	3	530
40	300	71	1180	914	<4	450
40	300	74	1220	933	9	460

SOURCE: Plumer 1981.



of 3 concentrations of nickel at varied pH. Minimum concentrations of nickel were found between about pH 9.5-9.8. Figure 4 illustrates a similar response for iron doses. Brown found minimum concentrations of iron to occur around pH 9.8-10.0. Figure 5 illustrates the behavior of lead to varied pH. Minimum concentrations of lead were found to occur around pH 9.3-9.5.

Numerous studies have focused on the treatment of acid mine drainages with lime or limestone precipitation. Wilmoth (1977) studied the effective removal of high concentrations of ferrous and ferric iron by lime and limestone addition. The mine drainage studied by Wilmoth approximates coal slurry wastewater characterized by Cooper, et al. (1983). Experiments with sludge recycle and aeration were performed to determine the most economical treatment alternative. Wilmoth concluded that limestone addition with aeration and recycle was economically unfeasible. The optimum treatment scheme for iron removal was determined to be precipitation with lime at pH 8.0 and oxidation of all iron in the ferric state. This conclusion followed from the pH-iron concentration relationship illustrated in Figure 6.

#### Biological Treatment Processes

Significant biochemical and chemical oxygen demands have been reported in western and interior western coal slurries. The need for biological treatment of slurry wastewater is site specific and can only be determined from a complete wastewater characterization



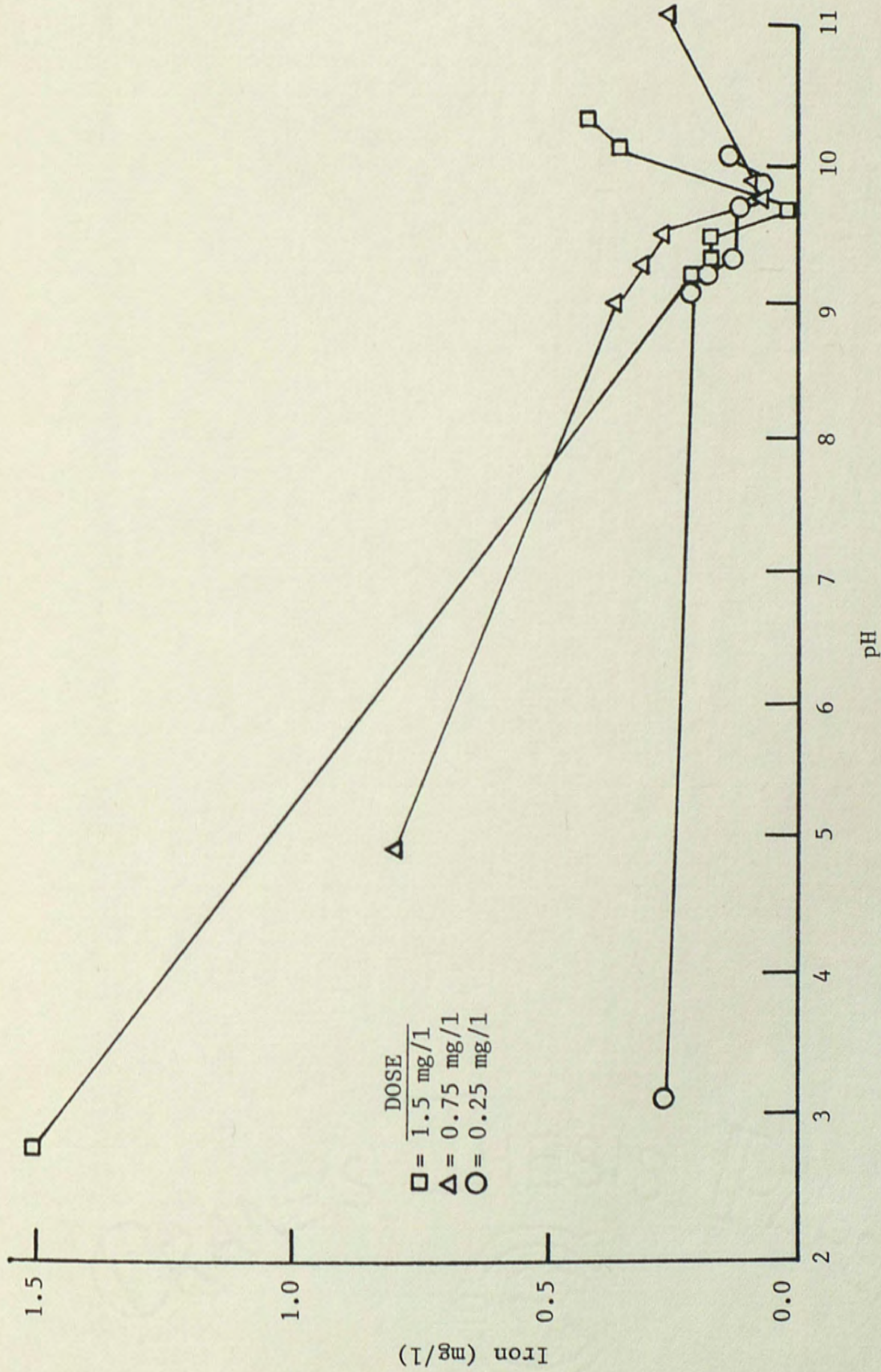


Fig. 4. Comparison of iron concentrations with pH for coal slurry wastewater (Brown 1983).



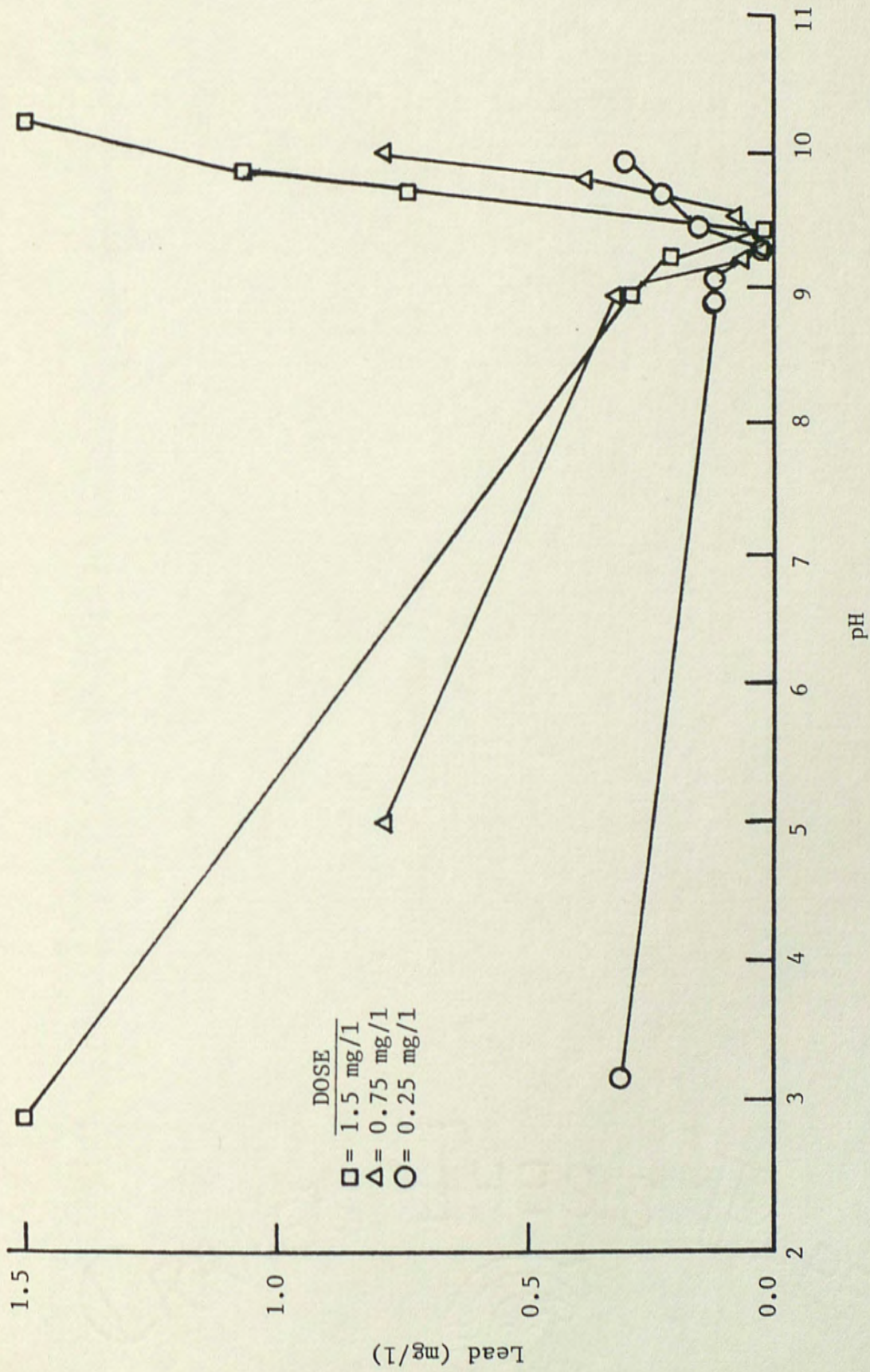


Fig. 5. Comparison of lead concentrations with pH for coal slurry wastewater (Brown 1983).



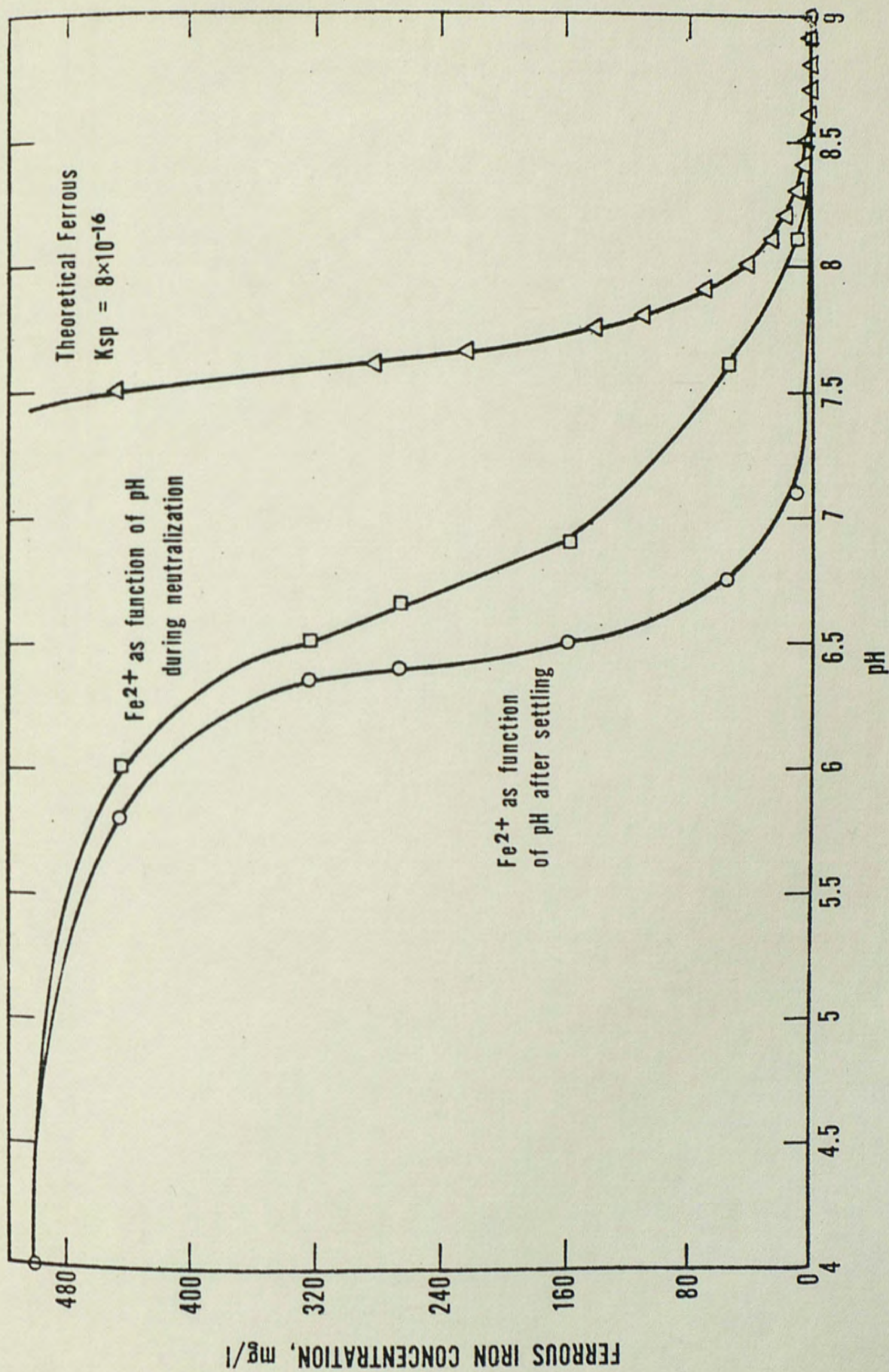


Fig. 6. Effect of pH on iron on solubility (Wilmouth, 1977).



study. Although eastern coal slurries have been shown to produce low organic wastewaters, there may be a need for biological treatment of some eastern slurry wastewaters. Several researchers have studied the feasibility of using activated sludge for BOD reduction in western coal slurries (Cook 1978; Moore 1981; and Plummer, et al. 1982). Additionally, Moore (1981) has included studies of Kansas and Illinois coal slurries.

Moore (1981) performed bench scale treatability studies using batch fed activated sludge units acclimated with Illinois and Kansas coal slurry wastewaters. Moore used an activated sludge obtained from a Fayetteville, Arkansas sewage treatment plant as a seed for his laboratory batch fed units. The units were filled with sludge and aerated for 23 hours, settled, and fed 1 liter of slurry wastewater. This procedure was continued until the units operated on 100 percent slurry wastewater. Moore also used a soil/coal sample containing endogenous microorganisms to seed the laboratory batch units. Both procedures proved to be successful. Moore concluded that eastern coal slurries from Illinois and Kansas coals produced wastewaters with relatively low BOD and COD concentrations, however, microorganisms could be acclimated and oxygen demanding wastes could be degraded.

Cook (1978) conducted similar research under the direction of Moore. Cook used a Wyoming coal slurry wastewater and the same activated sludge as mentioned above. The acclimation of slurry wastewater was done to maintain an appropriate food to microorganism



ratio and no coal/soil seeding was attempted. Cook concluded that the Wyoming coal slurry contained some toxic materials that inhibited bacterial growth, however, acclimation was found to overcome these toxic affects.

Plummer and co-workers (1982) performed bench scale studies using activated sludge and extended aeration on Powder River Basin coal slurry. A total of 3 laboratory units were operated at various food to microorganism ratios, mixed liquor suspended solids, and detention times. Based on a review of the results, biological treatment appeared to be successful in reducing the BOD<sub>5</sub> concentrations to the 20 to 30 mg/l range under laboratory conditions. A number of biological treatment parameters were estimated including rate constants, endogenous decay rate, and sludge production values. The total sludge production per day was estimated to be about 0.7 times the pounds of BOD<sub>5</sub> removed. Plummer concluded that biological treatment processes can reduce the total BOD<sub>5</sub> concentration in simulated slurry wastewater to the 20 to 40 mg/l range in laboratory conditions.

#### Alternative Uses of Coal Slurry Wastewater

The coal power industry uses water for a number of industrial processes, maintenance cleaning, and fly ash and bottom ash transport. The single major use of water is in condensor cooling, however, other major uses include cooling tower make-up, ash transport and flue gas desulfurization water. Cooling water blowdown



from closed cycle cooling towers may amount to 1 to 3 billion gallons of water per year nation-wide (Matson, et al. 1979). These waters are typically highly polluted with corrosion inhibitors and algaecides and require treatment, evaporative storage, or recycle. A typical water budget for a 415 MW coal fired power plant is illustrated in Figure 7.

Most researchers to date have speculated using the coal slurry wastewater as cooling water makeup or alternatively treating and discharging to a receiving stream. Little attention has been focused on other industrial uses.

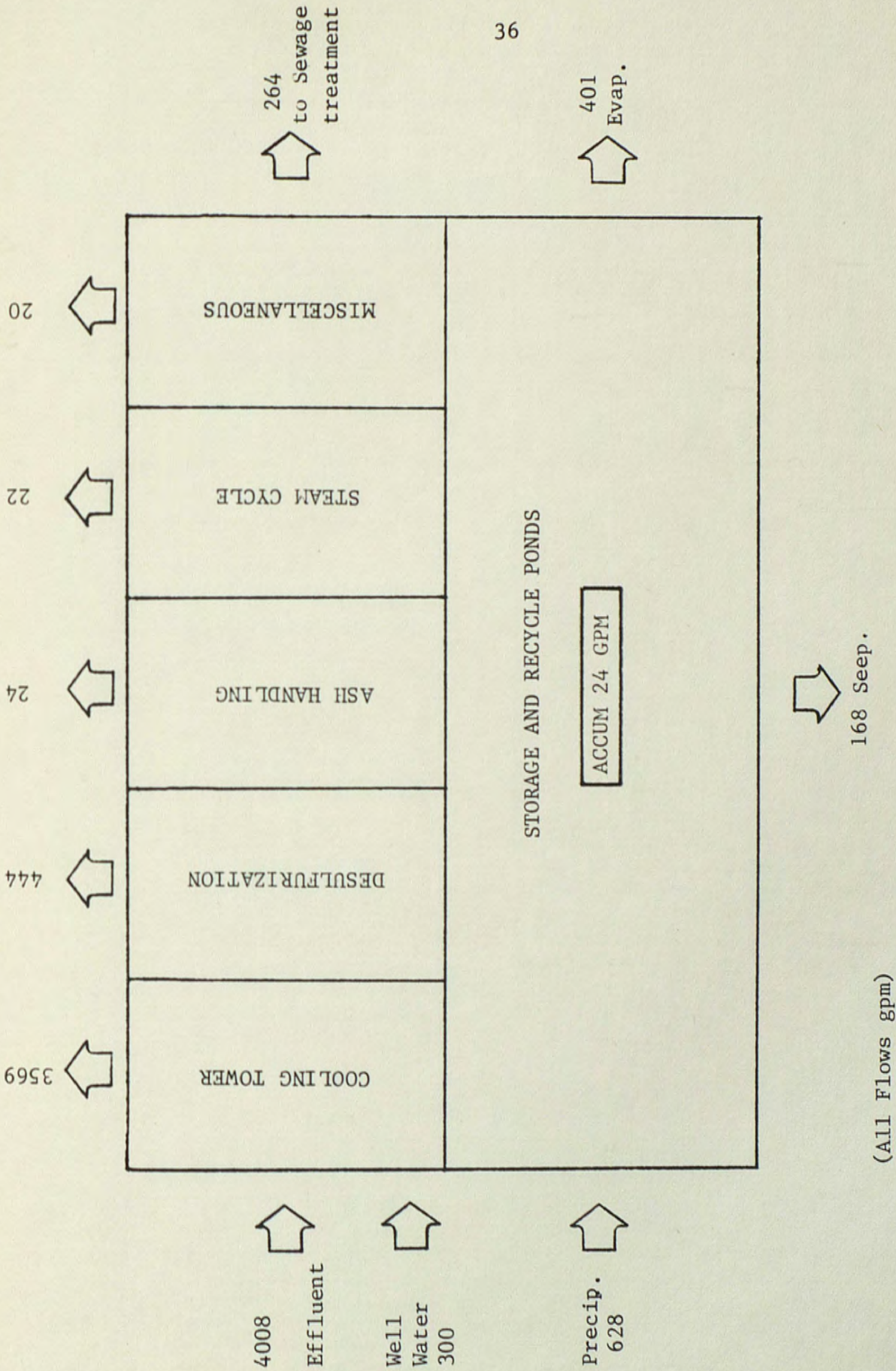
#### Federal and Florida State Regulations

The United States EPA has not established specific guidelines and regulations for coal slurry discharges. Point source discharges into U.S. receiving waters are regulated under the Federal Water Pollution Control Act Amendments of 1972 and subsequent amendments. Section 402 of this Act addresses discharge permits in accordance with the National Pollutant Discharge Elimination System (NPDES).

Under Section 301 of FWPCA, the effluent limitations for categories and classes of any point sources other than publicly operated treatment facilities must conform to "best available technology economically achievable" for that source.

Section 304 of the Act requires the EPA to periodically update and publish water quality criteria for a list of 65 specified toxic





(All Flows gpm)

Fig. 7. Water mass balance for unit 1, Stanton Energy Center (OUC 1981).



pollutants (Federal Register, March 16, 1979). Although Section 304 criteria are not enforceable as water quality standards, they can be used to implement standards under different sections of the Act.

A number of identified toxic pollutants are addressed by Section 304 criteria for establishing a numerical maximum value (i.e., not to be exceeded at any time) and a 24-hour average value.

In establishing stream standards, several factors are likely to be considered. These could include the technological and economical capacity to control the pollutant discharge; the toxicity, frequency and concentration of discharge; and the breadth of the data base used to develop the Section 304 criteria (Federal Register, November 28, 1980).

The National Interim Primary Drinking Water Standards are enforceable and control the permissible quality in finished drinking water. These standards differ from Section 304 criteria in that they protect human health. The states have an option to use Section 304 criteria to supplement or modify existing safe drinking water standards in the future if these modifications exceed the SDWA limits. These standards would not likely affect coal slurry discharges, unless ultimately used for potable sources.

The EPA has proposed regulations for a list of 299 "hazardous" substances under Section 311 of the FWPCA. These include levels for accidental discharges. Continuous discharges would be regulated



under an NPDES permit of Section 402 and would be exempt from these criteria. Accidental spills would be regulated under Section 311 regardless of whether they occurred at the NPDES permitted facility or some other point (Federal Register, August 29, 1979).

Chapter 17-6.300 of the rules of the Florida State Department of Regulation (DER) states that dischargers must meet federal guidelines for industrial effluents unless otherwise noted by the DER. Table 10 is a list of the Florida State Water Quality Standards.



TABLE 10

FLORIDA STATE WATER QUALITY STANDARDS FOR CLASS III WATERS  
(Recreation and Wildlife Management)

Parameter	State Criteria
Arsenic	0.05 mg/l
Cadmium	0.7 µg/l (5.0 µg/l marine)
Chlorides	less than 10% above ambient
Chlorine	0.01 mg/l (residual)
Chromium	1.0 mg/l in effluent
Copper	0.03 mg/l (0.015 mg/l marine)
Dissolved O <sub>2</sub>	at least 5.0 mg/l (24 hour average)
Iron	1.0 mg/l (0.3 mg/l marine)
Lead	0.03 mg/l
Mercury	0.02 µg/l (0.10 µg/l marine)
Nickel	0.10 mg/l
pH	6.0-8.5
Selenium	0.025 mg/l
Silver	0.07 µg/l (0.05 µg/l marine)
Zinc	0.03 mg/l

SOURCE: Chapter 17.3 of the Rules of the Florida Department of Environmental Regulation.



## CHAPTER III

### RESEARCH METHODOLOGY

#### Design and Construction of Model Pipeline

As part of an EPA funded research project at the University of Central Florida, a pilot scale coal slurry pipeline was designed and constructed in the fall of 1982. A 70-gallon (265 l) cylindrical reactor was constructed from 10 gauge steel and fitted with a 0.25 inch (0.64 cm) reinforced steel cover plate. A 1.5 horsepower (1.1 KW) Hazelton VNL model submersible slurry pump was mounted on the reactor cover plate and was used for slurry pipeline circulation. To ensure complete mixing in the reactor, a 14-lb thrust (62N) electric trolling motor was installed through the cover plate and pressure sealed.

The model pipeline consisted of a "U" shaped loop constructed from 1 inch (2.54 cm) diameter schedule 80 steel pipe having a total length of 40 feet (12.2 m). Appropriate sampling and coal loading ports were installed to facilitate easy sampling and transfer of coal slurry without the introduction of air into the pipeline system.

The temperature of the coal slurry was monitored by a thermometer installed on the cover plate and controlled by water cooled sleeves installed on the pipeline loop. Water obtained from the



university supply was used for counter current cooling and wasted to the sewer. The temperature of the coal slurry was controlled by regulating the flow through the heat exchangers.

A nitrogen rich atmosphere was maintained in the reaction vessel by supplying low pressure nitrogen gas. A compressed nitrogen cylinder and low pressure regulator were used to maintain a pressure of about 0.5 psi in the pipeline system. The complete pipeline system was pressure sealed to exclude atmospheric oxygen during down periods.

Figure 8 illustrates schematically the final design of the pilot scale coal slurry pipeline. The entire pipeline project was housed in an outdoor shelter located on university property. A mobile water quality laboratory was available for sample preparation and storage and was suitable for some general water quality analyses. A more detailed description of the design and construction of the pipeline project is given by Todd (1983).

#### Operation of the Model Pipeline

The initial operation of the pipeline project began in May of 1983. Pulverized coal used in this research was donated by the C.D. McIntosh Coal Fired Power Station in Lakeland, Florida. The origin of the coal was reported to be eastern Kentucky and was transported to Lakeland by rail. Coal was collected indirectly from the plant pulverizers by means of a specially designed 55 gallon (208 L) steel drum and metallic hoses (see Todd 1983).



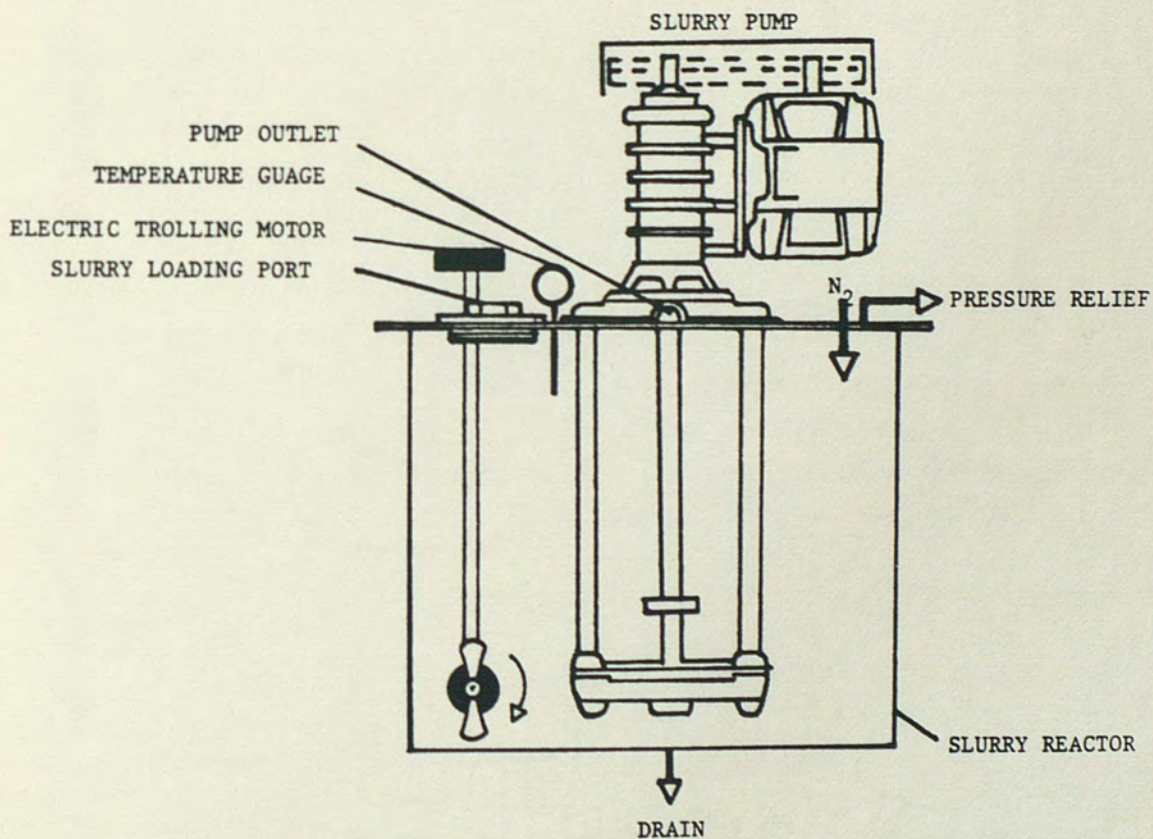
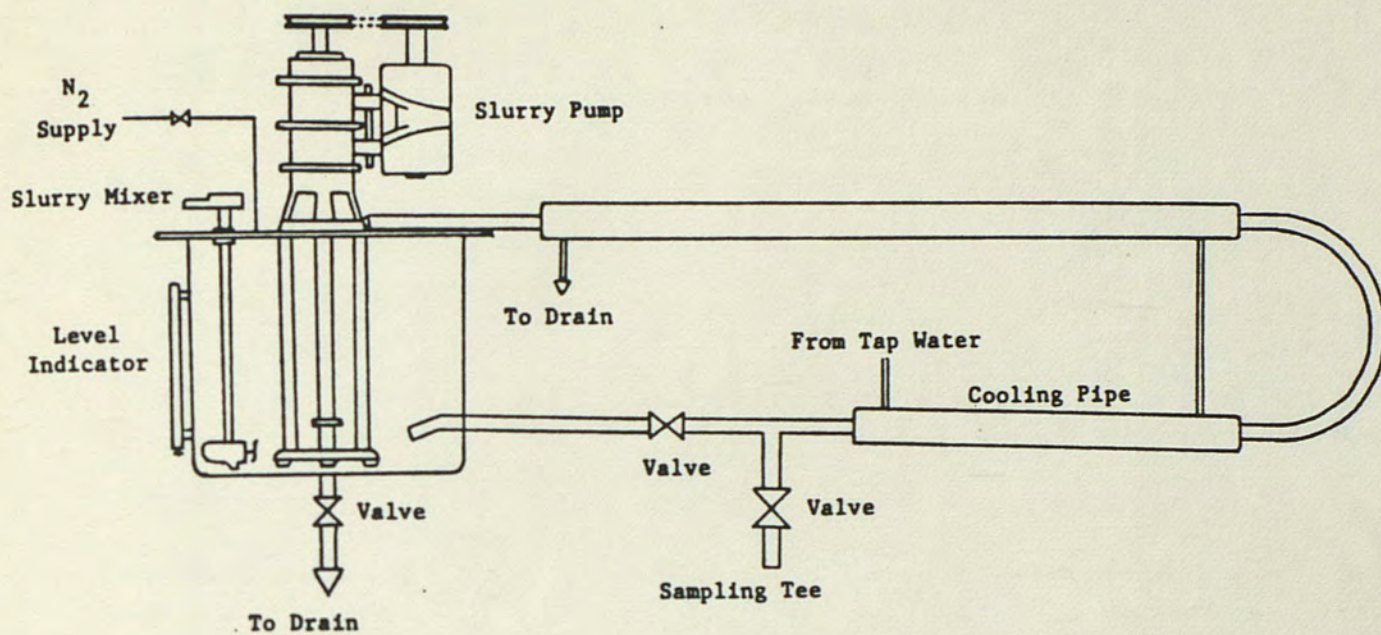


Fig. 8. Schematic diagram of pilot scale pipe loop used for coal slurry experiments.



The coal filled drum was sealed and stored for a 1-3 week period before use in the coal slurry pipeline.

A fifty percent (by weight) coal slurry was prepared using the collected pulverized coal and tap water from the university's potable water system. The coal and water were initially mixed in the coal collection drum by hand mixing and an auxiliary electric trolling motor. Once a homogenous coal slurry was achieved, it was manually transferred to the reactor tank by hand scooping with one gallon (3.8 L) plastic containers. When the coal slurry was completely transferred, the reactor was sealed and pressurized with nitrogen gas. Mixing and slurry circulation was then initiated and this marked the beginning of a 10-day sampling period. On the tenth day of operation, the slurry was sampled for total solids to determine any changes in percent solids.

Pumping speed (coal slurry flowrate), mixing and slurry temperature were monitored and controlled over the 10-day sampling period. Pump speed was adjusted to maintain a flowrate of approximately 60 L per minute. The pumping speed was adjusted at the beginning of each 10-day sampling period and checked for variation on the tenth day of operation. Mixing intensity was adjusted as needed to maintain a uniform slurry suspension in the reactor tank. Slurry temperature was controlled by regulating water flow to the pipeline heat exchangers.

Upon termination of a 10-day sampling period, the remaining coal slurry was collected and stored for treatability studies.



The reactor and pipeline were flushed with fresh water several times for cleaning purposes and the system was nitrogen blanketed until the next sampling period. Any minor maintenance was also performed during this down period.

A total of five 10-day sampling runs were made from May to August of 1983. The first of these sampling runs was mainly used to determine any operational problems; therefore, no results from this run are reported in this study. Two of the remaining four sampling runs included the addition of a corrosion inhibitor at the beginning of the sampling periods.

#### Slurry Sampling Operations

The slurry sampling schedule was designed to serve two purposes. First, a 10-day sample period was chosen to approximate the pipeline residence time of the proposed Coalstream slurry system to link Kentucky and West Virginia coal mines to the Florida power industry. Secondly, the sample intervals were spaced to allow time dependent coal-water interactions to be monitored effectively. The 10-day sampling periods were followed by one week of down time to complete all water quality analyses and treatability studies.

To ensure a representative sample, the slurry was withdrawn from a valve located in the pipeline loop. During sampling operations, the slurry reactor was purged with nitrogen gas to prevent the introduction of atmospheric oxygen into the pipeline system.



Samples were collected in 1 gallon (3.79 L) plastic containers or 1 liter glass bottles, if specified by EPA sampling procedures (EPA 1974). With the exception of dissolved oxygen, pH and redox potential, the samples were immediately dewatered by vacuum filtration through a 10 inch (25 cm) Whatman qualitative filter pad under a strong vacuum. The slurry filtrate was then passed through a 0.45 micron glass fiber filter to remove particulate coal.

Filtered samples were preserved and stored in accordance with the EPA recommended procedures (EPA 1974). On the tenth day of operation, a raw slurry sample was collected and stored under refrigeration for later treatability studies. Bench scale treatability studies were performed in the laboratory. Details of the analytical and laboratory procedures are presented in the following chapter.



## CHAPTER IV

### ANALYTICAL PROCEDURES

#### Water Quality Analyses

The filtered coal slurry wastewaters were analyzed for a total of 26 water quality parameters. In addition, DO, pH and redox potential were measured on unfiltered coal slurry samples immediately after collection. A summary of these water quality parameters and the methods of analyses is presented in Table 11. All analyses were performed in accordance with Standard Methods for the Examination of Water and Wastewater, 14th ed. (APHA 1975), and the Supplement to the 15th Edition of Standard Methods for the Examination of Water and Wastewater: Selected Analytical Methods Approved and Cited by the United States EPA (EPA 1974), with the exception of trace metals analyses which were performed using plasma emission spectrophotometry. A brief description of methods used for trace metals analyses is presented below. All other methods are described in detail by Todd (1983).

#### Trace Metals Analyses

Dissolved metals were analyzed by use of an SMI Spectrospan III Plasma Emission Spectrophotometer. Filtered coal slurry samples were collected in plastic containers and acidified to pH 2.0 by the



TABLE 11  
METHODS OF WATER QUALITY ANALYSIS

	Parameter	Equipment
General Water Quality	Dissolved Oxygen pH Redox Potential Turbidity Conductivity Color Total Dissolved Solids Acidity Alkalinity Chlorides Sulfates	DO Probe-Meter pH Meter Meter-Redox Probe Turbidometer Conductivity Bridge Spectrophotometer Gravimetric (208C) Titration (401) Titration (401) Titration (408C) Turbidometer (427C)
Organics	Total Organic Carbon Trihalomethanes  Phenols	Beckman TOC Analyzer EPA* Liquid-liquid Extract Extraction (501A, B)
Trace Metals	Mercury Selenium Cadmium Zinc Arsenic Manganese Copper Aluminum Iron Lead Nickel Chromium Barium Magnesium Silver	Plasma Emission Plasma Emission Plasma Emission Plasma Emission Plasma Emission Plasma Emission Plasma Emission Plasma Emission Plasma Emission Plasma Emission Plasma Emission Plasma Emission Plasma Emission Plasma Emission Plasma Emission

NOTE: All analyses done in accordance with Standard Methods except trace metals and those marked with an asterisk (\*).



addition of nitric acid. All filtered and preserved samples were transferred to 50 ml disposable styrene containers and sealed with Parafilm wax covering. Because of the relatively high concentrations of metals found in slurry wastewaters, the samples were measured by direct aspiration. Standards were prepared from commercially available stock matrix solutions (1 ml = 1 mg). The concentrations of standards were determined from the expected concentration ranges of the samples. Blanks and standards were prepared with distilled and deionized water obtained from a Corning distillation unit.

The plasma emission spectrophotometer was given an initial 30-45 minute warm-up period and then was peaked on the nickel channel using a 100 mg/l nickel peaking solution. Once the instrument had been peaked, a multiple metal standard and blank were used for calibration as directed by the manufacturer. The metal standards and blank were initially analyzed followed by six samples and re-analyses of the standards and blank. This sampling procedure enabled the analyst to check and correct for instrument drift. Multiple sample aspirations were performed when necessary. Measurements of arsenic and selenium resulted in some analytical problems. A hydride generation technique was recommended for analyses of arsenic and selenium, however, when this method was attempted, instrument response was very poor.



The SMI spectraspan provided a direct printout of metals concentrations in mg/l, however, these values had to be corrected for instrument drift. Raw data were input into a FORTRAN computer program to correct for instrument drift. An additional FORTRAN computer program was available for data reduction of solid coal samples. These programs are described in the following section.

#### Solid Coal Analyses

Prior to each coal slurry 10-day sampling run, a representative sample of the pulverized coal was taken for laboratory analysis. Pulverized coal was analyzed for moisture content, ash content, total sulfur, heating value, and trace metals. Many of these analyses were routinely performed at the C.D. McIntosh Power Station where the coal was obtained. Moisture content, ash content, total sulfur, and heating values were determined at the McIntosh Laboratory. The remainder of the coal analyses were performed by the author at the University of Central Florida.

Ash content was determined gravimetrically after combustion at 750°C, in accordance with methods presented by Bosshart, Price and Ford (1980). Coal samples were oven-dried in porcelain crucibles and weighed prior to combustion in a muffle furnace. Combustion involved placing the dried, pre-weighed coal samples in a cold muffle furnace and heating to 500°C. The furnace was periodically opened to allow for air circulation. After one hour, the temperature was increased to 750°C for an additional 2 hours. The ashed



samples were cooled and re-weighed to determine the percent ash of the pulverized coal samples. Triplicate dry coal samples were analyzed for percent ash.

Ashed coal samples were prepared for trace metal analysis by a modified method described by Bosshart, Price and Ford (1980). An ashed coal sample was prepared by acid digestion using concentrated nitric acid and gentle heating. A forty ml aliquot of concentrated nitric acid was mixed with the ashed coal sample in a wide mouth 250 ml erlenmeyer flask. The samples were gently heated until all but about 6 ml of samples had evaporated and then brought back to a 20 ml volume with the addition of distilled and deionized water. Samples were then analyzed for trace metals as described in the previous section. Data reduction was performed with the aid of two FORTRAN computer programs. METALS was the general FORTRAN program required to correct for instrument drift. The SOLIDS program was used to calculate the trace metals concentrations by weight of ashed coal samples. A listing of these programs is included in the Appendix.

#### Treatability Studies

A bench scale treatability study was conducted on the 10-day coal slurry wastewaters. The procedure used in this research simulated actual dewatering and treatment methods proposed for coal slurry pipelines and involved the following steps:

1. Storage/sedimentation
2. Dewatering of the coal slurry by vacuum filtration



3. Chemical treatment with lime or alum
4. Flocculation/sedimentation
5. Clarification and filtration

Figure 9 schematically illustrates the treatment processes described above.

The 10-day raw coal slurry samples were collected as outlined earlier and stored under refrigeration until use. When treatability tests were conducted, the raw samples were resuspended by agitation and allowed to settle at room temperature. After complete settling, samples were decanted and dewatered under vacuum filtration.

Two methods of slurry decanting were employed in order to recover the maximum volume of decantate. The first method consisted of siphoning the clarified wastewater from the settling container into clean sampling containers. This method proved to be very slow and in many cases coal was siphoned along with the clarified water. As an alternative method, clarified samples were carefully poured off from the sedimentation container into clean sampling containers. This second method was much faster and produced about the same results as siphoning. The pouring method was thought to better represent actual clarification processes because the clarified water was removed from the water surface rather than the sediment-water interface.

Before any lime or alum treatment was performed, an optimum dosage was determined by tests on 200 ml aliquot samples of decanted



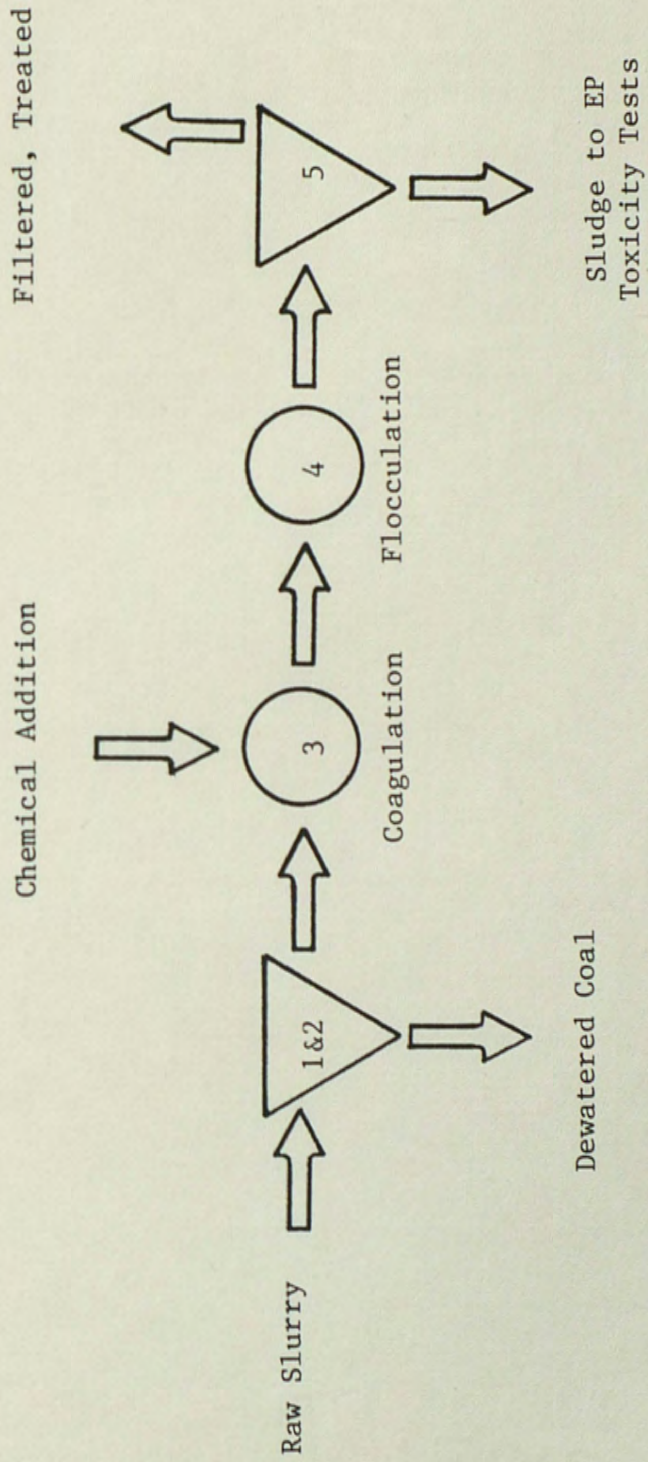


Fig. 9. Schematic diagram of coal slurry treatment process.



slurry water. In determining the optimum alum dose, turbidity was initially measured by use of the Hach 2100 turbidometer and samples were adjusted to pH 5.5 by the addition of sulfuric acid or sodium hydroxide. A standard alum stock solution was prepared (1 ml = 1 mg) and used for dosing the wastewater samples. Various pre-determined alum doses were applied by pipetting the stock solution into the samples. The dosed samples were then stirred by magnetic stirrers and allowed to settle for a 15-minute period. The pH of each sample was readjusted to 5.5 and again measured for turbidity. The optimum alum dose was defined as the lowest practical dose that removed the greatest percentage of turbidity.

Optimum lime dosage was determined in a similar fashion. Again, the clarified wastewater samples were measured for turbidity and dosed to pre-determined pH values with a lime slurry. The lime slurry was prepared from lime,  $\text{Ca(OH)}_2$ , and distilled water to about 10,000 mg/l. The clarified sample was stirred on a magnetic stirrer while pH was monitored with a Corning research pH meter. Lime slurry was added slowly with a dropper while pH was carefully monitored. Samples were removed from stirring and allowed to settle for 15 minutes. Turbidity was again measured and used to determine the optimum dosage. As with the alum dosage, optimum lime dose was defined as the lowest dose (according to pH) that removed the greatest percentage of turbidity.



Lime and alum treatment required collection of approximately 6 liters of decanted coal slurry. The decanted slurry water was transferred to four 1.5 liter beakers and placed on a Phillips-Byrd jar test machine. Optimum doses of lime and alum were applied in duplicate samples under rapid mix conditions of 100 rpm until the proper dose was achieved. After one minute, the mixer was slowed to 35 rpm and samples were allowed to flocculate for 15 minutes. After the 15 minutes of slow mixing, the samples were removed and allowed to settle for another 15 minutes. The resulting lime and alum treated samples were clarified with filtration through a 0.45 micron glass fiber filter under vacuum. The filtrate was collected and preserved for water quality analyses as described earlier. The lime and alum sludges were collected on the filter pads and stored for later toxicity studies.

#### EP Toxicity Studies

Following lime and alum treatability studies, the sludges were collected and used to determine the toxicity as defined by the EP toxicity test. A solid waste exhibits the characteristic of EP toxicity if, using the test methods described in the Federal Register, Volume 45, Number 98 (Monday, May 19, 1980), Appendix II, the extract from a representative sample of the waste contains any of the contaminants listed in Table 12 at a concentration equal to or greater than the values listed.



TABLE 12  
MAXIMUM CONCENTRATION OF  
CONTAMINANTS FOR CHARACTERISTICS OF EP TOXICITY

EPA Hazardous Waste Number	Contaminant	Maximum Concentration (milligrams per liter)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin	0.02

SOURCE: Federal Register 45, No. 98 (May 19, 1980):  
33122.



The separate lime and alum sludges were combined in order to attain a large enough sample to perform the toxicity tests. The lime and alum sludges were weighed and placed in a beaker with 16 times the solids weight of deionized water. The beakers were placed on a shaker table and well agitated. The pH of each extract was periodically measured and if the pH was above  $5.0 \pm 0.2$ , 0.50 N acetic acid was added to adjust the pH back to 5.0. If the total amount of acid required reached 4 ml of acid per gram of solid, no additional acid was added.

The extraction procedure continued for a 24-hour period at room temperature. The pH was monitored for 6 hours until the solutions were considered stable. At the end of the 24-hour extraction period, deionized water was added as defined by the equation:

$$V = (20)(W) - 16(W) - A$$

where:

V = ml of deionized water to be added

W = weight of solids charged to beaker, in grams

A = ml of 0.5 N acetic acid added during extraction

The solid residue was separated from the liquid component by vacuum filtration through a 0.45 micron glass fiber filter. The resulting liquid extract was measured for arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver.



## CHAPTER V

### RESULTS

Results of coal slurry wastewater characterization and treatability studies are presented in this chapter. Chapter VI presents a detailed discussion of results and implications pertaining to treatment alternatives for coal slurry pipeline systems.

A total of five pilot scale pipeline studies were performed, however, only four of these studies produced valid results. Wastewater characterization and treatability results are presented only for these valid experiments. Water quality parameters were studied by the author and by Todd (1983) as a function of pipeline residence time over a period of 10 days and were reported in detail by Todd. Since the focus of the research reported here is on treatability, only a summary of the characterization work is reported.

A number of variables may influence slurry water quality as reported in the literature, thus, these parameters were monitored during pipeline operations and are presented in Table 13. Other factors that reportedly influence water quality include the characteristics of the source water and coal. A brief description of the transport water and the coal is presented in the next section.



TABLE 13  
SLURRY PIPELINE OPERATING CONDITIONS

Operating Conditions *	Slurry Sampling Run			
	2	3	4	5
Pumping Speed (rpm)	910	980-1100	1130-1200	~1200
Approx. Velocity (m/s)	1.7	1.8-2.0	2.0-2.2	2.2
Temp. Range (°C)	27.7-31.1	27.7-30	28.3-30.5	30-31.1
Percent Solids	53	47	34	48
Corrosion Inhibitor	no	no	yes	yes

\* All slurries under anaerobic pipeline conditions

#### Transport Water Quality

Coal slurry transport water was typical of a Central Florida groundwater. Aerated and chlorinated groundwater was obtained directly from the university's potable water supply. Water quality tests were conducted on the tap water and a three day field blank to determine background concentrations. Results of these analyses are summarized in Table 14. Trace metal concentrations were generally very low for both the tap water and field blank, however, some metals such as iron, chromium, and magnesium were found in increased concentrations in the field blank samples. The THMFP and TOC concentrations were relatively high for both tap and field blanks, however, previous studies suggest that these values are normally lower (Taylor 1984). Dissolved oxygen



TABLE 14

## UCF HOSE WATER, FIELD BLANK, AND DISTILLED WATER ANALYSES

Parameter*	Distilled	Field Blank	Hose Water
Sulfates	< 2	3.8	< 2
Chlorides	< 5	19.5	19
TDS	34	184	207
Conductivity, $\mu\text{mho/cm}$	14	243	366
Dissolved Oxygen	8.3	0.7	7.9
Redox Potential, mV	164	121	526
pH, units	5.0	7.4	7.0
Acidity, mg/l as $\text{CaCO}_3$	46	-115	-96
Alkalinity, mg/l as $\text{CaCO}_3$	2	108	120
Color, cpu	4	7	6
Turbidity, JTU	4.2	0.7	5.3
THMFP, ppb	< 5	53.9	60
TOC	2	22	6
Phenols, ppb	< 1.0	N.R.	N.R.
Metals			
Hg	< 0.050	< 0.050	0.076
Se**	0.121	0.264	0.242
Cd	< 0.005	0.004	0.006
Zn	0.021	0.080	0.071
As**	0.064	0.057	0.045
Mn	< 0.001	0.146	0.009
Cu	0.018	0.017	0.016
Al	0.019	0.104	0.033
Fe	0.100	23.1	1.28
Pb	< 0.015	0.041	0.029
Ni	0.006	0.028	0.002
Cr	< 0.001	0.004	0.004
Ba	< 0.001	0.023	0.015
Mg	< 0.001	11.0	11.0
Ag	< 0.002	0.006	0.002

\* All concentrations are in mg/l unless otherwise stated.

\*\* Instrumentation problems, validity of data suspected.

See Analytical Procedures.

N.R. - not reported



and redox potential were lower in the three day field blank samples. The above mentioned differences indicate that some changes in water quality resulted from pumping operations; however, these changes were minimal.

#### Solid Coal Characterization

An eastern Kentucky coal was obtained from the McIntosh Power Plant by methods previously described. The pulverized coal was reported to pass 70% through a 200 mesh Tyler sieve. The McIntosh laboratory reported the coal to average about 16% ash, 35% volatiles, and 49% fixed carbon on a dried basis. The heating value averaged about 12,000 BTU/lb with a sulfur content of about 1.9% (Table 15).

Trace metals analyses were performed on ashed coal samples and these results are summarized in Table 15. The major elements were found to be iron, magnesium and aluminum. Considerable concentrations of various other metals were also found. The metal concentrations varied with the coal used in each run.

#### Characterization of 10-Day Slurry Water

A 10-day pipeline operational period was chosen to simulate the typical residence times expected in actual pipeline operations. Most water quality parameters varied considerably with different sampling runs and were considered a function of the chemistry of the pulverized coal and pipeline residence time. Many of the water quality parameters exhibited increased concentrations with time until



TABLE 15

## SELECTED RESULTS OF PULVERIZED COAL ANALYSIS

Component	ppm in Ignited Ash, as the element unless noted				
	Run 2	Run 3	Run 4	Run 5	Average
% Ash	15.28	14.39	15.37	18.50	15.89
% Volatile	32.85	36.79	36.49	35.13	35.32
% Fixed Carbon	51.87	48.82	47.63	46.37	48.67
Heating Value	11,632	12,830	11,922	11,500	11,971
% Sulfur					2.51
Hg	56	47	63	59	56
Se	92	83	72	63	78
Cd	3.5	4.3	4.2	4.2	4.1
Zn	106	311	228	219	216
As	156	238	379	421	298
Mn	163	541	408	505	404
Cu	221	139	154	110	156
Pb	122	101	109	104	109
Ni	90	136	133	135	124
Cr	231	133	150	123	159
Ba	585	837	797	720	735
Mg	8,490	15,900	8,190	9,610	10,550
Ag	4.0	2.0	7.0	2.5	3.9



some equilibrium was attained. Once at equilibrium, the concentrations of most parameters remained constant for the remainder of the sampling period. In many cases, the 10-day samples represented maximum observed concentrations; however, some parameters such as DO and redox potential were at a minimum on the tenth day of operation.

Table 16 illustrates the observed maximum, minimum and 10-day concentrations of measured water quality parameters for slurry run 2. In most cases, dissolved metals were at a minimum value on the tenth day. Exceptions were nickel, aluminum, copper, arsenic, zinc, and selenium. Maximum concentrations of sulfates (about 1700 mg/l), chlorides (80 mg/l), TDS (3500 mg/l), and conductivity (2500  $\mu\text{mho/cm}$ ) were observed in the 10 day samples. The 10-day pH had stabilized at 6.2 and acidity was reported at about 1500 mg/l. Alkalinity was 14 mg/l. Organics were found in very low concentrations throughout run 2, with TOC averaging about 6.0 mg/l.

Table 17 corresponds to observed variations in water quality over the 10-day sampling period of run 3. In general, water quality varied considerably from the data collected in run 2; however, the trends of increased concentrations over time remained consistent. Again, most dissolved metals were found in maximum concentrations on the tenth day of sampling with the exception of barium, nickel, aluminum, copper, arsenic, and zinc. Maximum concentrations of sulfates (about 1000 mg/l), chlorides (about 150 mg/l), TDS (about 1900 mg/l) and conductivity (about 2400  $\mu\text{mho/cm}$ ) were again observed



TABLE 16  
 VARIATIONS IN COAL SLURRY WATER QUALITY FOR RUN 2

Water Quality Parameter	10-Day	Maximum	Minimum
Sulfates, mg/l	1680	1683	1090
Chlorides, mg/l	78.1	78.1	24.1
TDS, mg/l	3494	3494	1952
Conductivity, $\mu\text{mho/cm}$	2510	2510	1665
Dissolved Oxygen, mg/l	< 0.10	4.7	< 0.10
Redox Potential, mV	-192	277	-192
pH	6.2	6.2	3.5
Acidity, mg/l $\text{CaCO}_3$	1450	1450	805
Alkalinity, mg/l $\text{CaCO}_3$	14	23	13
Color, cpu	483	483	12
Turbidity, JTU	74	74	0.90
TOC, mg/l	5.7	6.1	3.9
THMFP, $\mu\text{g/l}^*$	23	23	23
Phenols, $\mu\text{g/l}$	1.8	< 1.0	< 1.0
Metals, mg/l			
Se**	0.534	0.576	0.265
Cd	0.084	0.084	0.031
Zn	0.238	2.29	0.238
As**	0.771	0.863	0.382
Mn	15.0	15.0	4.23
Cu	0.047	0.398	0.012
Al	0.780	21.2	0.516
Fe	529.0	529	114
Pb	0.569	0.569	0.388
Ni	0.225	1.57	0.111
Cr	0.060	0.060	0.030
Ba	0.120	0.120	0.067
Mg	91.2	91.2	80.4
Ag	0.038	0.038	0.028
Hg	0.801	0.801	0.324

\* Data available for 10-day sample only.

\*\* Analytical problems data suspect (see Analytical Procedures).



TABLE 17  
 VARIATIONS IN COAL SLURRY WATER QUALITY FOR RUN 3

Water Quality Parameter	10-Day	Maximum	Minimum
Sulfates, mg/l	1005	1005	735
Chlorides, mg/l	154	154	48
TDS, mg/l	1896	1896	1207
Conductivity, $\mu\text{mho/cm}$	2395	2395	1246
Dissolved Oxygen, mg/l	< 0.10	0.30	< 0.10
Redox Potential, mV	-200	145	-200
pH	6.2	6.2	4.9
Acidity, mg/l $\text{CaCO}_3$	254.2	304.8	29.4
Alkalinity, mg/l $\text{CaCO}_3$	12.4	27.8	12.4
Color, cpu**	78	78	2
Turbidity, JTU **	33.5	102.5	6.8
TOC, mg/l	5.6	9.4	2.3
THMFP, $\mu\text{g/l}^*$	< 5	< 5	< 5
Phenols, $\mu\text{g/l}$	< 1.0	1.3	< 1.0
Metals, mg/l			
Hg	0.087	0.087	< 0.050
Se**	0.200	0.200	0.112
Cd	0.005	< 0.005	< 0.005
Zn	0.066	0.290	0.066
As**	0.488	0.493	0.279
Mn	6.86	6.86	3.90
Cu	0.019	0.033	0.015
Al	0.162	0.234	0.128
Fe	188	188	2.25
Pb	0.226	0.226	0.148
Ni	0.066	0.473	0.045
Cr	0.014	0.015	0.006
Ba	0.083	0.144	0.066
Mg	65.8	65.8	50.1
Ag	0.005	0.007	0.002

\* 10-day only.

\*\* Analytical problems, data suspect (see Analytical Procedures).



on the tenth day of operation. The pH was stabilized at 6.2 and acidity was about 250 mg/l. Alkalinity was again observed to be low. Organics were also very low for run 3, with TOC averaging 6 mg/l.

Run 4 data (with corrosion inhibitor) are presented in Table 18. Most water quality parameters for run 4 were considerably higher than values found in run 3, and a number of parameters were much higher than both runs 2 and 3. In many instances, the maximum observed dissolved metal concentrations did not occur on the tenth day of operation. Mercury, selenium, cadmium and arsenic, however, did reach maximum values on the tenth day of operation. Sulfates reached a maximum concentration of about 4500 mg/l, the maximum chlorides concentration reached 175 mg/l, TDS reached a maximum concentration of about 7400 mg/l, and conductivity reached a maximum value of about 6500  $\mu\text{mhos/cm}$ . All of these values are considerably higher than previous slurry runs, and with the exception of chlorides, maximum concentrations did not occur on day 10. The pH stabilized at 6.0 and acidity reached about 1700 mg/l as  $\text{CaCO}_3$ . Alkalinity was higher than previous runs at 34 mg/l, however, organics were again very low, with TOC about 4 mg/l.

Table 19 corresponds to the recorded variations in water quality for run 5. Run 5 water quality data was similar to run 4 data in many respects. High sulfate concentrations (3400 mg/l), high chlorides (180 mg/l), high TDS (4500 mg/l), and high conductivity



TABLE 18  
 VARIATIONS IN COAL SLURRY WATER QUALITY FOR RUN 4

Water Quality Parameter	10-Day	Maximum	Minimum
Sulfates, mg/l	3940	4510	2330
Chlorides, mg/l	175.0	175.0	66.3
TDS, mg/l	6890	7407	4974
Conductivity, $\mu$ mho/cm	6290	6475	5420
Dissolved Oxygen, mg/l	< 0.005	0.81	< 0.05
Redox Potential, mV	-130	175	-130
pH	6.0	6.5	5.8
Acidity, mg/l CaCO <sub>3</sub>	1336	1688	504
Alkalinity, mg/l CaCO <sub>3</sub>	34	276	20
Color, cpu	6	13	5
Turbidity, JTU**	58.5	68.5	4.8
TOC, mg/l	3.5	4.6	2.0
THMFP, $\mu$ g/l*	< 5	< 5	< 5
Phenols, $\mu$ g/l	1.0	1.9	< 1.0
Metals, mg/l			
Hg	0.256	0.256	< 0.05
Se**	0.444	0.444	0.255
Cd	0.015	0.016	0.006
Zn	0.222	0.286	0.107
As**	0.478	0.478	0.249
Mn	25.5	25.5	5.43
Cu	0.023	0.034	0.019
Al	0.597	0.629	0.293
Fe	470.0	485.0	0.981
Pb	0.483	0.497	0.408
Ni	0.455	0.455	0.101
Cr	0.037	0.366	0.031
Ba	0.008	0.184	0.008
Mg	198.0	268.0	151.0
Ag	0.017	0.023	0.001

\* 10-day only.

\*\* Analytical problems, data suspect (see Analytical Procedures).



TABLE 19  
 VARIATIONS IN COAL SLURRY WATER QUALITY FOR RUN 5

Water Quality Parameter	10-Day	Maximum	Minimum
Sulfates, mg/l	3420	3420	1340
Chlorides, mg/l	180	180	65.8
TDS, mg/l	4534	4534	3332
Conductivity, $\mu\text{mho/cm}$	4435	4435	3345
Dissolved Oxygen, mg/l	< 0.05	0.30	< 0.05
Redox Potential, mV	-143	-193	108
pH	6.7	7.2	6.4
Acidity, mg/l $\text{CaCO}_3$	374	374	143
Alkalinity, mg/l $\text{CaCO}_3$	81	269	59
Color, cpu	5	11	2
Turbidity, JTU **	132	161	1.0
TOC, mg/l	33.8	33.8	2.0
THMFP, $\mu\text{g/l}^*$	8	8	8
Phenols, $\mu\text{g/l}$	< 1.0	< 1.0	< 1.0
Metals, mg/l			
Hg	0.052	0.076	< 0.05
Se**	0.167	0.229	0.167
Cd	< 0.05	< 0.05	< 0.05
Zn	0.073	0.079	0.010
As**	0.274	0.403	0.133
Mn	7.60	7.60	0.789
Cu	0.012	0.116	0.004
Al	0.291	0.291	0.173
Fe	69.3	69.3	0.055
Pb	0.358	0.358	0.211
Ni	0.180	0.180	0.025
Cr	0.019	0.024	0.014
Ba	0.064	0.182	0.042
Mg	128	128	51.6
Ag	0.014	0.014	0.002

\* 10-day only.

\*\* Analytical problems, data suspect (see Analytical Procedures).



(4400  $\mu\text{mhos/cm}$ ) were observed for run 5. On the other hand, acidity was much lower (370 mg/1 as  $\text{CaCO}_3$ ) and many dissolved metals were lower than run 4. Most measured water quality parameters did exhibit maximum concentrations for the 10-day samples. Organics were somewhat higher, with TOC about 34 mg/1.

As previously mentioned, slurry runs 4 and 5 included the addition of a commercial corrosion inhibitor. The general effects of the corrosion inhibitor on water quality can be studied by averaging data from runs 2 and 3, and runs 4 and 5. Table 20 lists the average 10-day water quality for slurry with and without corrosion inhibitor. Sulfates, chlorides, TDS and conductivity were shown to be considerably higher for coal slurries when corrosion inhibitor was added. Dissolved metals did not seem to follow these same trends.

Overall results of the wastewater characterization study indicate that these eastern Kentucky coal slurries produce waters high in dissolved solids, sulfates and metals. In addition, the properties of the source coal and wastewater may vary considerably depending on many influencing factors. The inclusion of a corrosion inhibitor altered a number of characteristics of the wastewater. Details of these results and their implications regarding treatment needs are presented in detail in the following chapter.

#### Treatability Studies

Optimum dose studies were performed with lime and alum treatment on the 10-day settled coal slurry samples. Turbidity removal



TABLE 20

AVERAGED 10-DAY SLURRY WATER QUALITY FOR  
COAL SLURRIES WITH AND WITHOUT CORROSION INHIBITOR

Parameter, Units	Without Corrosion Inhibitor	With Corrosion Inhibitor
	10-days	10-days
<u>General</u>		
Sulfates, mg/l	1342	3680
Chlorides, mg/l	116	178
TDS, mg/l	2695	5712
Conductivity, $\mu$ mho/cm	2452	5362
Dissolved Oxygen, mg/l	< 0.05	< 0.05
Redox Potential, mV	-196	-136
pH	6.2	6.3
Acidity, mg/l as CaCO <sub>3</sub>	852	855
Alkalinity, mg/l as CaCO <sub>3</sub>	13.2	58
Color, cpu*	280	6
Turbidity, JTU*	53.8	96
<u>Organics</u>		
TOC, ppm	5.6	18.6
THMFP, ppb	23	8
Phenols, ppb	1.4	< 1.0
<u>Metals (mg/l)</u>		
Hg	0.45	0.15
Se**	0.37	0.31
Cd	0.04	0.01
Zn	0.15	0.15
Ag**	0.63	0.38
Mn	10.9	16.6
Cu	0.03	0.02
Al	0.47	0.45
Fe	358	270
Pb	0.40	0.42
Ni	0.14	0.32
Cr	0.04	0.03
Ba	0.10	0.03
Mg	78	163
Ag	0.02	0.016

\* 10 day only.

\*\* Analytical problems, data suspect (see Analytical Procedures).



was greatest for lime doses ranging from pH 8.5 to pH 11.0 and alum doses were optimum at ranges of 100 to 250 mg/l. Removal of turbidity did not necessarily correlate with metals removal as evidenced by further water quality analyses of the treated samples.

Results of lime and alum treatment for runs 2, 10-day samples are presented in Table 21. The effectiveness of treatment on metals removal is illustrated in Figure 10. Lime treatment at pH 8.5 removed at least 90% of turbidity, color, acidity, mercury, cadmium, zinc, manganese, iron and nickel. In addition, significant reductions in most other metals and TOC were observed. Slight decreases in sulfates, chlorides, and TDS were also observed with lime treatment. Alum treatment at 100 mg/l was not as effective as the lime treatment for most parameters. Color and turbidity, however, were reduced by 90% or more, 87% of the cadmium was removed, and chromium was reduced by 85%. Some increases in concentrations were observed with alum treatment. The alum was more effective in removing TOC, lead and chromium than lime treatment, however, all other constituents were better removed with the lime treatment.

Run 3 treatability studies were conducted at a lime dose of pH 10.8 and alum dose of 200 mg/l. Results of the run 3 treatability study are presented in Table 22 and metals removals are illustrated in Figure 11. With the lime dose increased to pH 10.8, iron, manganese, cadmium and magnesium were reduced at least 90% and mercury, copper, nickel, chromium and barium were significantly reduced. Most



TABLE 21

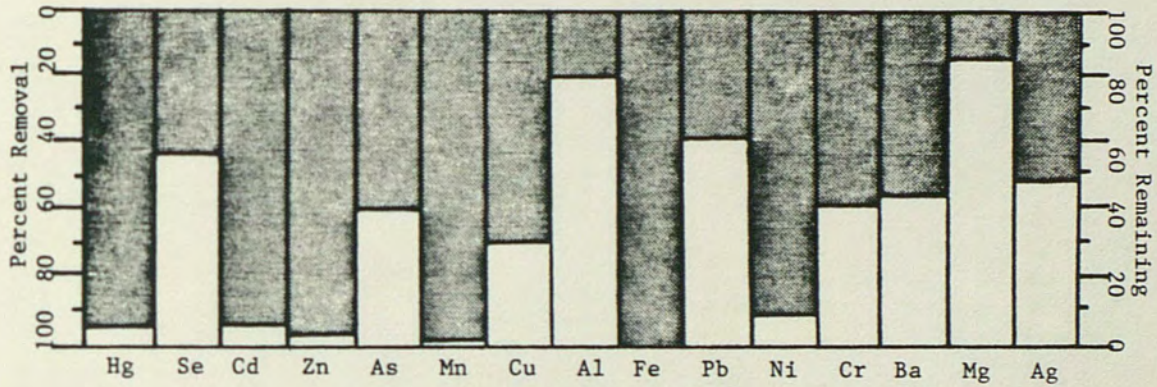
## TREATABILITY RESULTS - RUN 2

Parameter, Units	Untreated 10-day Sample	Treated Filtrate			
		Lime		Alum	
		Dose: pH=8.5	Percent Removal	Dose: 100mg/1	Percent Removal
<u>General</u>					
Sulfates, mg/l	1680	1500	11	1660	1
Chlorides, mg/l	78	69	12	72	8
TDS, mg/l	3494	2959	15	3286	6
Conductivity, $\mu$ mho/cm	2510	3225	inc	3280	inc
Dissolved Oxygen, mg/l	< 0.05	3.8	inc	4.2	inc
Redox Potential, mV	-192	113	inc	154	inc
pH	6.2	8.5	inc	4.3	23
Acidity, mg/l as CaCO <sub>3</sub>	1450	0	100	972	33
Alkalinity, mg/l as CaCO <sub>3</sub>	14	23	inc	13	7
Color, cpu	483*	22	95	11	98
Turbidity, JTU	74*	5.3	93	6.7	91
<u>Organics</u>					
TOC, mg/l	5.7	3.1	46	2.8	51
THMFP, $\mu$ g/l	23	N.R.	---	N.R.	---
<u>Metals (mg/l)</u>					
Hg	0.801	< 0.05	94	0.200	75
Se**	0.534	0.303	43	0.374	30
Cd	0.084	0.006	93	0.011	87
Zn	0.283	0.011	96	0.151	47
As**	0.771	0.306	60	0.532	31
Mn	15.0	0.189	99	10.3	33
Cu	0.047	0.014	70	0.150	inc
Al	0.780	0.630	19	2.54	inc
Fe	529	0.288	100	422	20
Pb	0.569	0.353	38	0.249	56
Ni	0.225	0.017	92	1.37	inc
Cr	0.060	0.025	58	0.009	85
Ba	0.120	0.054	55	0.090	25
Mg	91.2	78.4	14	96.7	inc
Ag	0.038	0.019	50	0.019	50

NOTES: inc = increase; N.R. = not reported; \* = turbidity high because precipitation occurred after filtration; \*\* = data suspect, instrument problems, see quality assurance section for explanation.



## LIME TREATMENT (Dose = pH 8.5)



## ALUM TREATMENT (Dose = 100 ng/l)

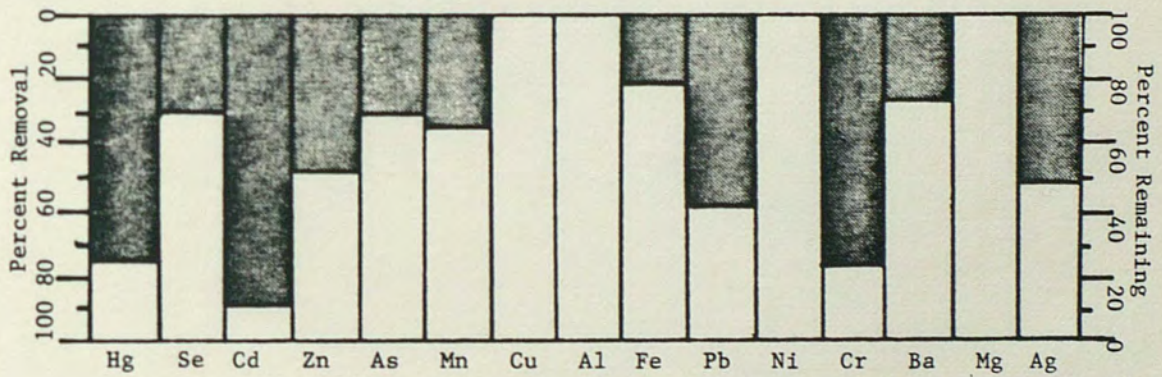


Fig. 10. Effective removals of heavy metals using lime and alum treatment (run 2).



TABLE 22

## TREATABILITY RESULTS - RUN 3

Parameter, Units	Untreated 10-day Sample	Treated Filtrate			
		Lime		Alum	
		Dose: pH=10.8	Percent Removal	Dose: 200mg/1	Percent Removal
<u>General</u>					
Sulfates, mg/l	1005	1150	inc	1290	inc
Chlorides, mg/l	154	161	inc	160	inc
TDS, mg/l	1896	1933	inc	N.R.	---
Conductivity, $\mu$ mho/cm	2395	2530	inc	2555	inc
Dissolved Oxygen, mg/l	< 0.05	2.42	inc	3.20	inc
Redox Potential, mV	-200	-41	inc	+175	inc
pH	6.2	10.8	inc	5.1	23
Acidity, mg/l as CaCO <sub>3</sub>	254.2	0	100	290	inc
Alkalinity, mg/l as CaCO <sub>3</sub>	12.4	81	inc	42	inc
Color, cpu	78*	21	73	7	91
Turbidity, JTU	33.5*	7.5	78	14.3	57
<u>Organics</u>					
TOC, mg/l	5.6	3.0	46	2.4	57
THMFP, $\mu$ g/l	< 5***	34	***	14	***
<u>Metals (mg/l)</u>					
Hg	0.087	0.020	77	0.067	23
Se**	0.200	0.216	inc	0.197	2
Cd	< 0.005	< 0.005	---	0.008	inc
Zn	0.066	< 0.005	92	0.074	inc
As**	0.488	0.465	5	0.489	inc
Mn	6.86	< 0.001	100	7.97	inc
Cu	0.019	0.004	79	0.003	84
Al	0.162	0.298	inc	0.719	inc
Fe	188	< 0.002	100	130	31
Pb	0.226	0.207	8	0.172	24
Ni	0.066	0.011	83	0.397	inc
Cr	0.014	0.005	64	0.013	7
Ba	0.083	0.015	82	0.037	55
Mg	65.8	4.39	93	72.3	inc
Ag	0.005	0.017	inc	0.017	inc

NOTES: inc = increase; N.R. = not reported; \* = turbidity high because precipitation occurred after filtration; \*\* = data suspect, instrument problems; \*\*\* = untreated sample THMFP probably in error.



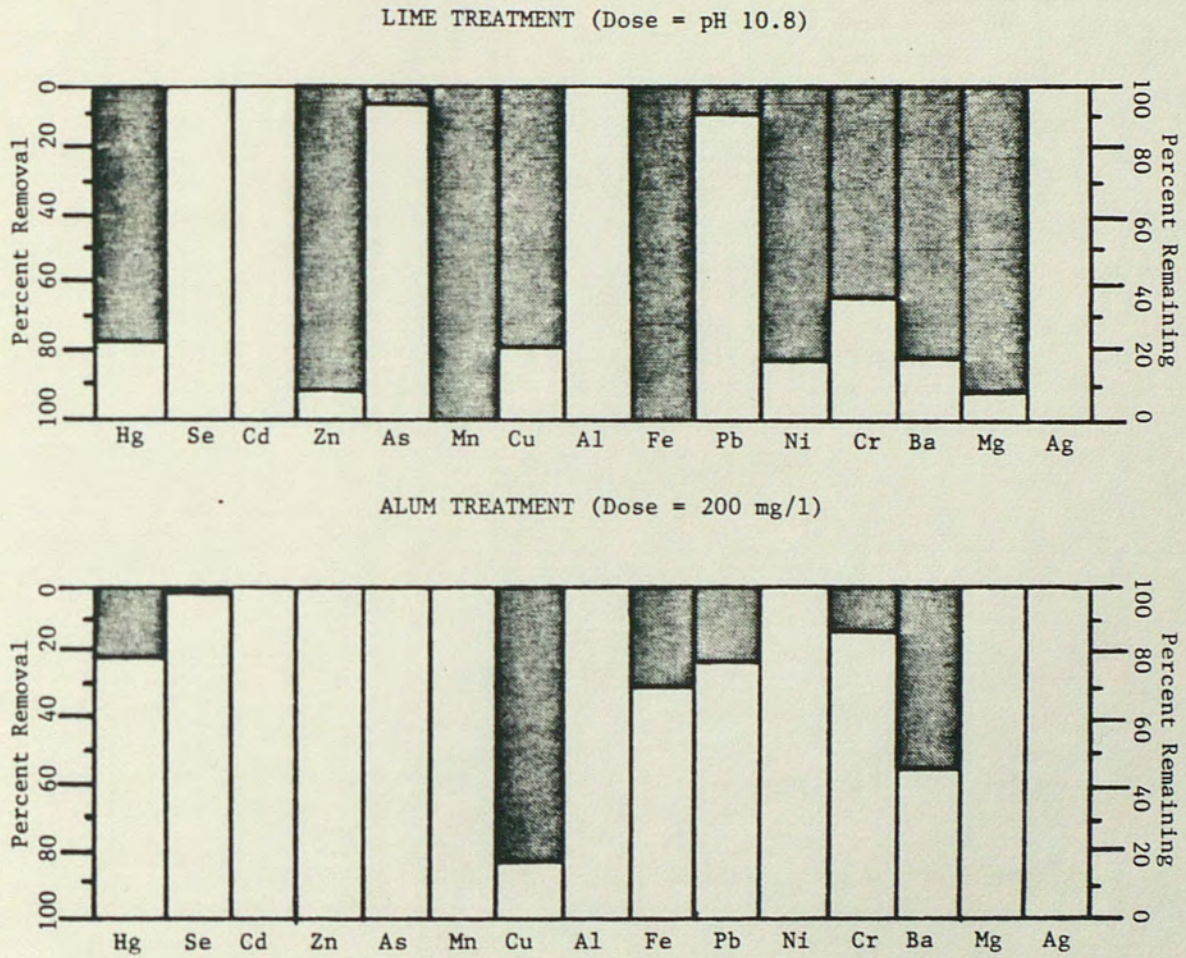


Fig. 11. Effective removals of heavy metals using lime and alum treatment (run 3).



other metals exhibited some reductions but there were some increased concentrations reported. Alum treatment at 200 mg/l resulted in less favorable results than run 2 alum samples. Although 91% of the color was removed, many parameters exhibited increased concentrations.

Run 4 samples were dosed with lime to pH 10.3 and with alum to 200 mg/l. Results of these studies are presented in Table 23 and metals reductions are illustrated in Figure 12. Lime was effective in removing 90% or more of acidity, turbidity, manganese, iron and magnesium. In addition, significant reductions in mercury, zinc, and nickel were observed. Alum at a dose of 200 mg/l was generally not effective in removal of any constituents for run 4 samples. Many of the measured parameters exhibited increased concentrations with alum treatment.

Treatability studies were performed on run 5 samples dosed at pH 10.8 for lime and 250 mg/l for alum. The results of run 5 treatability studies are presented in Table 24 and corresponding metals removal efficiencies are illustrated in Figure 13. Lime removed 90% or more of the acidity, turbidity, manganese, iron and substantially reduced TOC and nickel. Many other parameters were reported to increase. Alum removed 90% or more TOC and turbidity and substantially reduced alkalinity and iron concentrations.

Overall results of the treatability studies suggest that the commercial corrosion inhibitor had considerable impacts on the treatability of coal slurry wastewaters. The treatability



TABLE 23

## TREATABILITY RESULTS - RUN 4

Parameter, units	Untreated 10-Day Sample	Treated Filtrate			
		Lime		Alum	
		Dose: pH=10.3	Percent Removal	Dose: 200mg/1	Percent Removal
<u>General</u>					
Sulfates, mg/l	3940	3700	6.1	3745	4.9
Chlorides, mg/l	175	187	inc	165	5.7
TDS, mg/l	6890	8128	inc	6858	.46
Conductivity, $\mu$ mho/cm	6290	5480	13	5740	8.7
Dissolved Oxygen, mg/l	< 0.05	9.8	inc	11	inc
Redox Potential, mV	-130	-50	inc	185	inc
pH	6.0	10.3	inc	4.6	23
Acidity, mg/l as CaCO <sub>3</sub>	1336	0	100	1236	6.0
Alkalinity, mg/l as CaCO <sub>3</sub>	34	1420	inc	31.5	6.8
Color, cpu	6	42	inc	46	inc
Turbidity, JTU	58.5*	0.25	99	11.3	60
<u>Organics</u>					
TOC, mg/l	3.5	3.2	9	1.7	51
THMFP, $\mu$ g/l	< 5***	10	***	< 5	***
<u>Metals, mg/l</u>					
Hg	0.256	0.089	65	0.294	inc
Se**	0.444	0.837	inc	1.16	inc
Cd	0.015	0.016	inc	0.023	inc
Zn	0.222	0.034	85	0.391	inc
As**	0.478	0.730	inc	0.779	inc
Mn	25.5	0.030	100	21.8	15
Cu	0.023	0.014	39	0.057	inc
Al	0.597	0.653	inc	0.811	inc
Fe	470.	7.82	98	269.	43
Pb	0.483	0.859	inc	0.690	inc
Ni	0.455	0.053	88	0.888	inc
Cr	0.038	0.060	inc	0.046	inc
Ba	0.008	0.028	inc	0.012	inc
Mg	198.	4.95	98	80.0	60
Ag	0.017	0.035	inc	0.049	inc

NOTES: inc = increase; \* = turbidity high because precipitation occurred after filtration; \*\* = data suspect, instrument problem; \*\*\* = untreated sample THMFP probably in error.



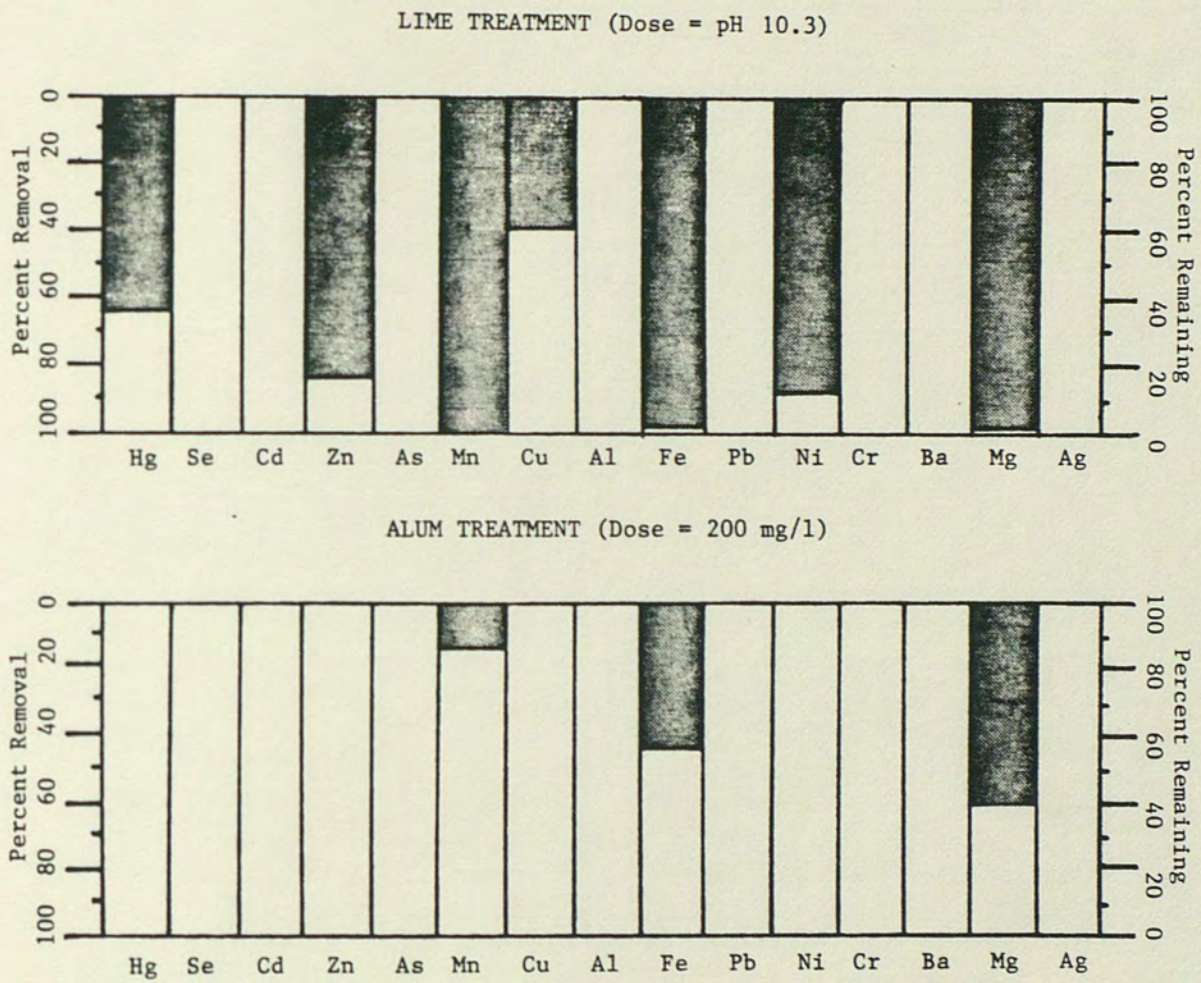


Fig. 12. Effective removals of heavy metals using lime and alum treatment (run 4).



TABLE 24

## TREATABILITY RESULTS - RUN 5

Parameter, units	Untreated 10-Day Sample	Treated Filtrate			
		Lime		Alum	
		Dose: pH=11	Percent Removal	Dose: 250mg/1	Percent Removal
<u>General</u>					
Sulfates, mg/l	3420	2310	33	2565	25
Chlorides, mg/l	180	183	inc	185	inc
TDS, mg/l	4535	5999	inc	4166	8.1
Conductivity, $\mu$ mho/cm	4435	5450	inc	3805	14
Dissolved Oxygen, mg/l	< 0.05	6.0	inc	8.9	inc
Redox Potential, mV	-143	-39	inc	254	inc
pH	6.7	10.8	inc	4.6	31
Acidity, mg/l as CaCO <sub>3</sub>	374	0	100	265	29
Alkalinity, mg/l as CaCO <sub>3</sub>	81	1426	inc	28	65
Color, cpu	5	3	40	5	0
Turbidity, JTU	132*	0.12	100	0.28	100
<u>Organics</u>					
TOC, mg/l	33.8	6.8	80	1.6	95
THMFP $\mu$ g/l	8	6	25	< 5	37.5
<u>Metals, mg/l</u>					
Hg	0.052	0.103	inc	0.099	inc
Se**	0.167	1.07	inc	0.947	inc
Cd	< 0.005	0.023	inc	0.025	inc
Zn	0.074	0.047	36	0.097	inc
As**	0.274	0.920	inc	0.613	inc
Mn	7.6	0.008	100	6.66	12
Cu	0.012	0.021	inc	0.038	inc
Al	0.291	0.624	inc	0.348	inc
Fe	69.3	6.21	91	3.75	66
Pb	0.358	0.830	inc	0.510	inc
Ni	0.180	0.048	73	0.555	inc
Cr	0.019	0.081	inc	0.048	inc
Ba	0.064	0.077	inc	0.067	inc
Mg	128	0.621	100	79.9	38
Ag	0.014	0.037	inc	0.041	inc

NOTES: inc = increase; \* = turbidity high because precipitation occurred after filtration; \*\* = data suspect, instrument problems.



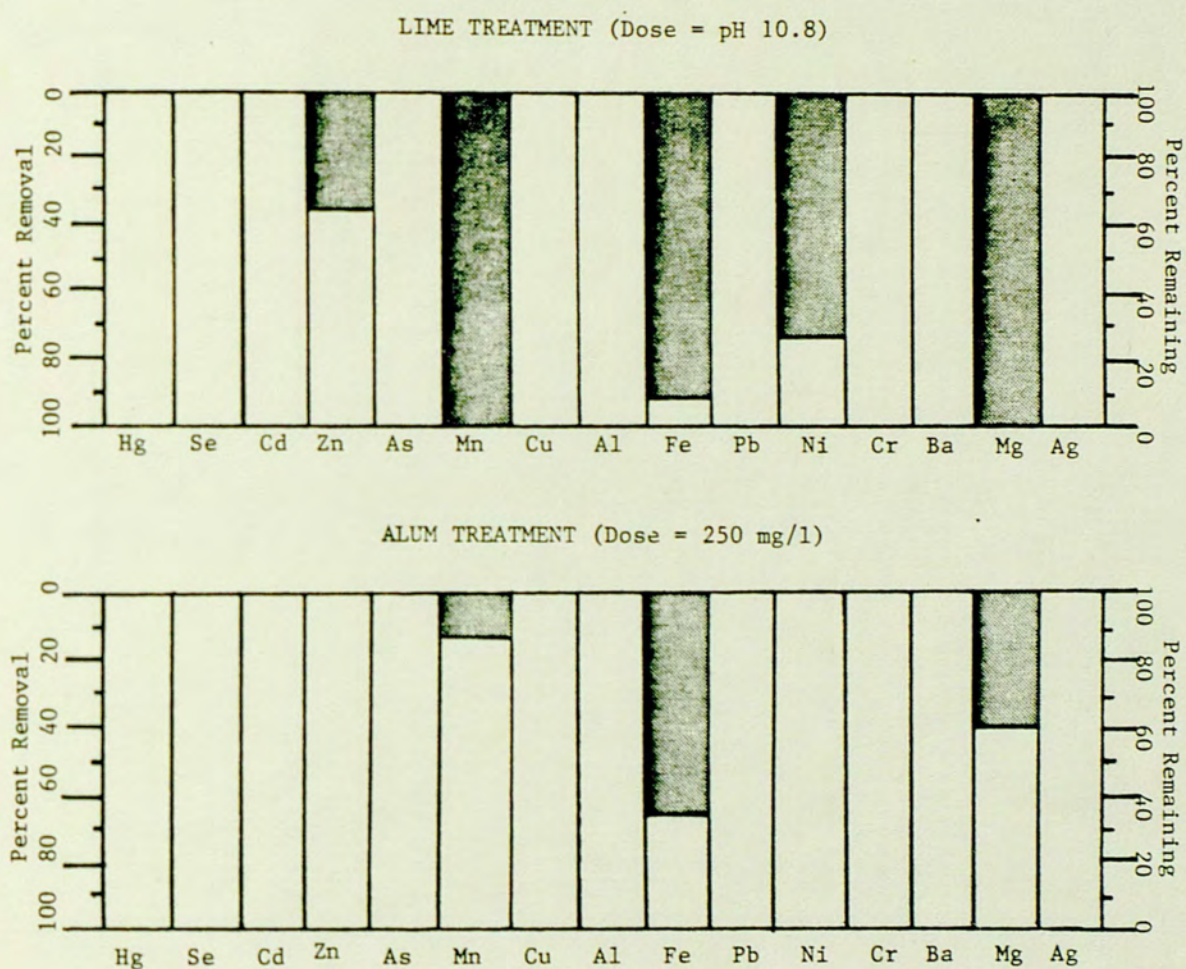


Fig. 13. Effective removals of heavy metals using lime and alum treatment (run 5).



studies conducted for runs 2 and 3 (without inhibitor) yielded similar results with overall removal efficiencies greater than runs 4 and 5 (with inhibitor). Therefore, slurry runs 2 and 3 are difficult to compare with runs 4 and 5. Despite these difficulties, some general observations were made and are addressed in detail in the following chapter.

#### Settling Characteristics

During the course of this research, qualitative observations were made on the settling characteristics of raw coal slurry. One general observation was that when corrosion inhibitor was added to the slurry pipeline, slurry settling characteristics were altered considerably. The addition of corrosion inhibitor appeared to hinder settling and dewatering characteristics of the raw slurry. Attempts were made to quantify these observations by running settling tests on 1 liter samples in the laboratory; however, pipeline conditions were not adequately simulated in the lab.

Although the laboratory settling tests were unsuccessful, the decanted coal slurry with corrosion inhibitor exhibited a higher turbidity than the samples without inhibitor. These observations were also noted in lime and alum treatability studies.



EP Toxicity Tests

The lime and alum sludges that resulted from treatment were collected on filter pads and tested for toxicity in accordance with the EPA recommended procedures. The results of this EP toxicity study are presented in Table 25. The lime sludge from runs 4 and 5 was found to contain high concentrations of mercury, however lime sludge from runs 2 and 3 was well below the maximum EPA limit. There was considerable variability in results for the EP toxicity study. Because very small volumes of sludges were produced from treatability studies, the EP toxicity analysis required procedural modifications. These modifications may have led to some errors in measurement.



TABLE 25  
RESULTS OF EP TOXICITY TESTS ON TREATMENT SLUDGES

Contaminant	Maximum Limit*	Concentrations, mg/liter			
		Runs 2 and 3		Runs 4 and 5	
		Lime**	Alum	Lime	Alum
Arsenic	5.0	0.419	0.194	1.56	0.341
Barium	100.0	0.206	0.296	0.717	0.468
Cadmium	1.0	0	0	0.045	0
Chromium	5.0	0	0.030	0.016	0
Lead	5.0	0.090	0.028	1.405	0.051
Mercury	0.2	0	0.057	1.126	0.011
Selenium	1.0	0	0	0.874	0
Silver	5.0	0	0	0.05	0

\* From Federal Register 45, No. 98 (May 19, 1980).

\*\* Lime and alum refer to the sludges obtained from the lime treatment process and the alum treatment process, respectively.



## CHAPTER VI

### DISCUSSION OF RESULTS

#### General Observations

The addition of an "oxygen scavenging" corrosion inhibitor was shown to significantly alter the characteristics of the raw coal slurry and decanted wastewaters. With regards to treatability, use of the inhibitor presented two problems. First, the settling characteristics of the raw slurry were adversely affected. Second, metals removal of the decanted wastewater was not as effective when corrosion inhibitor was used. One plausible explanation for settling differences is that the corrosion inhibitor may alter the surface characteristics of the coal particles, enhancing the stability of the suspension. The manufacturer of the inhibitor reported that nitrites and borates were the major ingredients in the inhibitor. The deterioration in treatability caused by the corrosion inhibitor may be linked to the increased buffering (more free available anions) and formation of more soluble and stable metal species. With altered pH, these more stable complexes may not allow formation of hydroxide precipitates. In actual practice, the advantages of using corrosion inhibitors (longer pipeline life) may be overshadowed by reduced settling and treatment effectiveness.

In many instances, treated 10-day samples exhibited concentrations higher than untreated 10-day samples. The reasons for these



differences may be explained by a combination of the variability of the analytical instruments and/or by sample handling. Because of a rigorous sampling and analytical schedule, 10-day filtered samples were preserved and analyzed after 5 days. However, 10-day raw slurry samples were stored under refrigeration for at least one week before treatability tests were performed. This raw slurry was not re-tested before performance treatability studies. Apparently, some additional increases in concentrations of trace metals occurred during storage. The observed increases in metal concentrations were reported as apparent increases and were not considered relevant to the overall results of lime and alum treatment.

#### Slurry Wastewater Quality

Coal slurry pipelines behave as long chemical reactor systems for coal and water interactions. The wastewater quality at the pipeline terminus is ultimately affected by acid-base interactions, redox reactions, and precipitation-dissolution phenomena that occur over the course of the pipeline transport. Treatment requirements depend on the degree of water quality degradation and the intended use or discharge of the water. Results of wastewater characterization studies indicate that considerable concentrations of dissolved solids, sulfates and certain metals are present in eastern Kentucky coal slurries. Dissolved metals present the major treatment concern if the wastewaters are to be discharged.

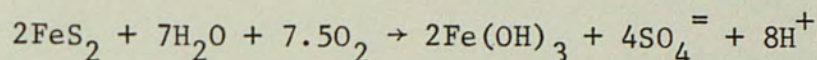


The concentration of dissolved metals in solution depends on the pH of the solution. Acidic conditions are associated with dissolution of metals, whereas basic conditions usually result in the formation of insoluble metal hydroxide precipitates. The pH of coal slurry is mainly governed by reactions involving sulfur, water and oxygen. The presence of sulfate, chloride, or bicarbonate ions may raise or lower the pH of the solution through acid-base reactions.

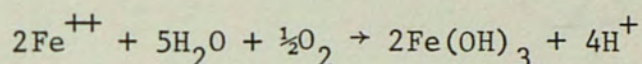
In addition to pH, the solubilities of metals may be dependent on the activity of ions in solution. Theoretically, as the concentration of ions in solution increases, the electrostatic interactions between ions also increase and the activity of the ions in solution become somewhat less than the measured concentrations. In such cases, the chemical equilibriums of various metals must be adjusted. Complex ionic interactions may occur due to high concentrations of sulfates, chlorides and other ions. The complex chemistry associated with coal slurry wastewaters may not be modeled adequately with simple solubility equilibria and stoichiometric relationships. In cases of such complex wastewaters, the affects of ionic strength on solubilities may best be modeled by computer programs.

Oxidation-reduction reactions may result in depletion of dissolved oxygen, altered solubilities, and changes in pH. Reactions involving iron pyrites in coal slurries are common and result in oxygen consumption and sulfate production according to the reaction:





Reactions involving iron are particularly dependent on the available oxygen. In an oxygen limited environment, the ferrous form predominates, however, some oxidation of iron will occur such as the overall reaction:



Similar reactions may occur with other metals resulting in the additional consumption of oxygen and liberation of free ions.

The overall complexity of coal slurry water chemistry requires that actual wastewater characterization studies be performed on each coal slurry to determine unique characteristics and problems that may be associated with treatment.

#### Effectiveness of Lime and Alum Treatment

Regardless of the intended use or discharge of coal slurry wastewater, some treatment will inevitably be required at some point in coal slurry processes. If stream discharge is required, water quality must meet guidelines set forth for class III waters in Section 17-3.121 of the DER Water Quality Standards. If the water is to be used as cooling tower makeup, some treatment may be required to reduce dissolved solids and high concentrations of iron and other metals.



Treatability results suggest that lime treatment is effective in removing many problem metals associated with the wastewater, however, the optimum pH for removal of different metals may vary. These observations are confirmed by treatability results at pH 8.5 and 10.8 (Figures 10, 11 and 13) and the solubility diagram presented in Figure 14. Removal of all metals to meet Florida Water Quality Standards may require multiple stage treatment strategies at different pH ranges.

Alum is not as effective at removing metals as is lime, yet alum may be considered effective in removal of organics. Characteristics of eastern Kentucky coal slurries studied here suggest that organics are not a problem of concern.

The effectiveness of both lime and alum treatment appeared to be adversely affected by the addition of a corrosion inhibitor. The use of corrosion inhibitors may warrant additional research and considerations.

Lime is an attractive treatment alternative because of availability, low cost, and it is widely used for scrubber operations (desulfurization of flue gases). Brown (1983) has shown that lime treatment is as effective as reverse osmosis or ion exchange for the removal of certain metals.

Some of the more important considerations for effective lime or alum treatment include: (1) an appropriate dose must allow enough excess ions to drive the precipitation reaction to completion, (2) the proper pH must be maintained throughout precipitation,



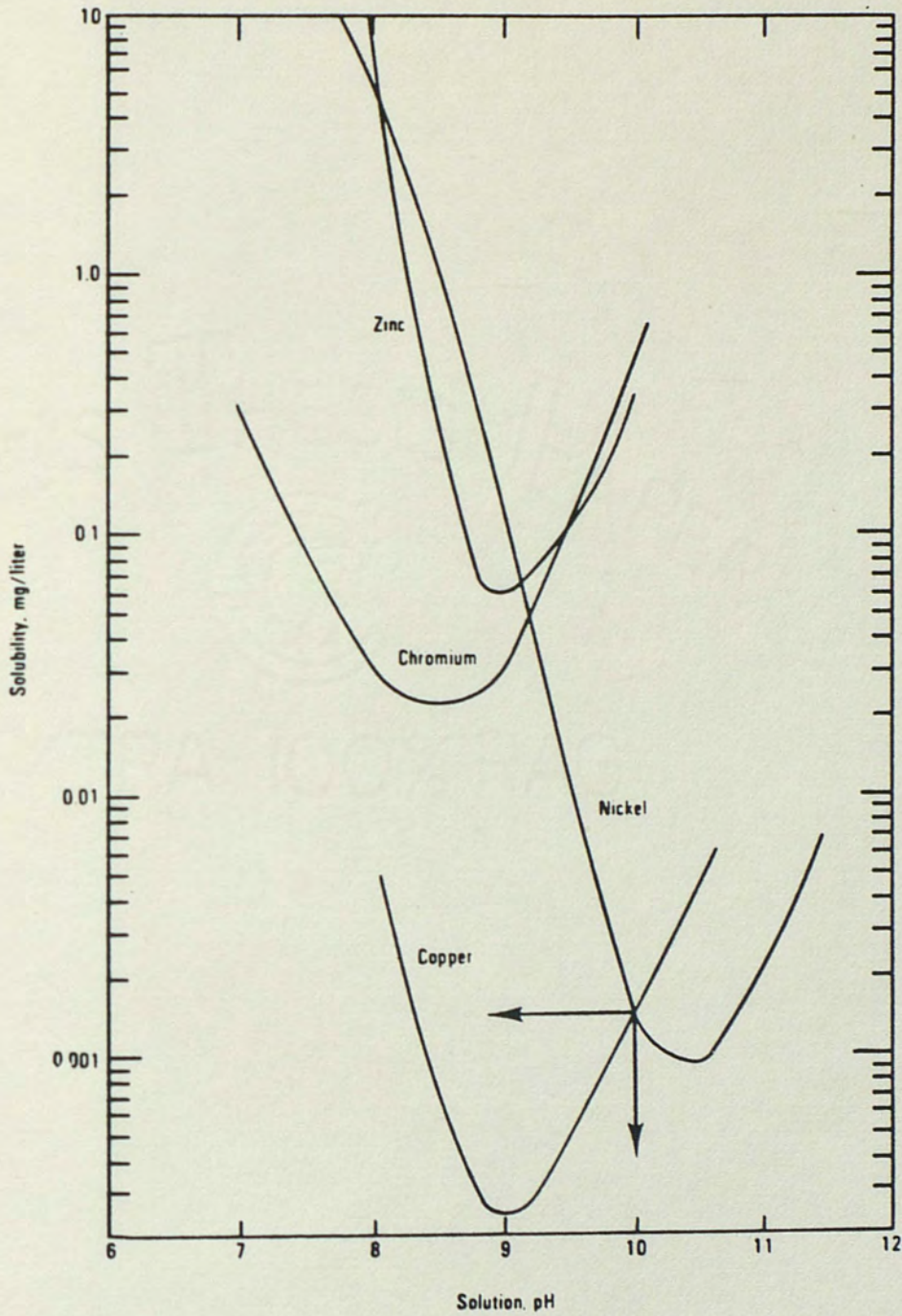


Fig. 14. Solubilities of heavy metals as a function of pH (Cherry 1982).



and (3) after precipitation, the solids must be effectively separated.

#### Wastewater Treatment and Reuse Strategies

Coal slurry water quality was found to vary according to a number of influencing pipeline conditions. Slurry handling and pipeline operations are variables which may be controlled to some extent. As an example, the age and degree of oxidation of pulverized coal is directly related to the soluble iron available for chemical interactions. Reactions involving pyritic iron are responsible for sulfate production and lowered pH. Oxidation of coal may occur during mining, grinding and pulverizing, and storage. Any precautions to reduce oxidation during these operations would reduce the oxidized coal available for chemical interactions. Surface and groundwater sources have both been suggested for use as transport waters. Groundwater sources are generally lower in dissolved oxygen and, thus, may be more favorable for coal slurry transport.

A typical coal fired power plant requires large volumes of water for industrial processes. The main use of water in a coal fired plant is for cooling purposes. As water is used for cooling in a cooling tower, evaporation occurs and, thus, makeup water must be supplied to balance the loss. Other major uses for water include ash sluicing and flue gas desulfurization processes. Both of these processes recycle wastewater, however, a significant portion

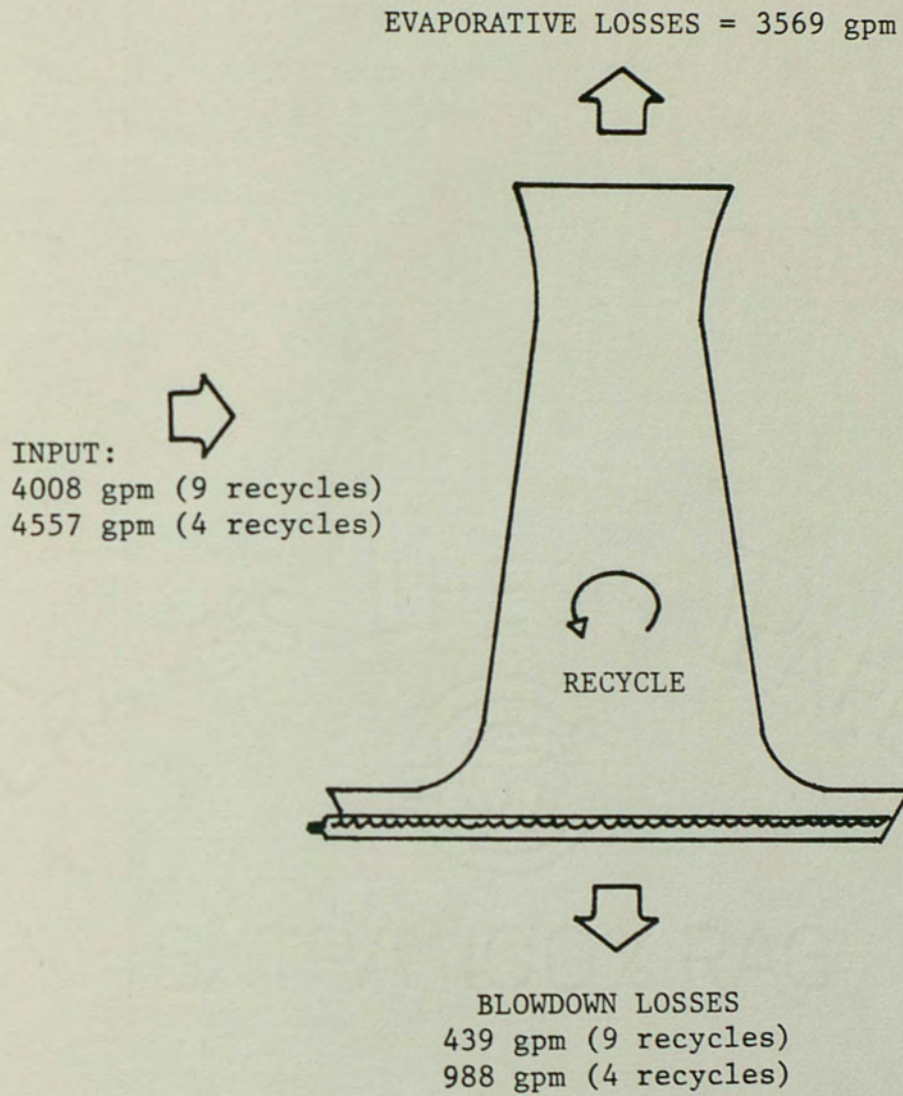


is also lost to evaporation. The use of coal slurry wastewaters for industrial purposes may reduce or possibly eliminate treatment requirements.

An industrial water balance was performed on a proposed 415 MW (NET) power plant to be sited in the Central Florida area (Orlando Utilities Commission 1981). According to plans, 4008 gpm ( $1.52 \times 10^4$  l/min) of makeup cooling water is required. Ash sluicing requires 24 gpm (91 l/min) of makeup and flue gas desulfurization equipment requires 444 gpm (1681 l/min) of makeup water. The same coal fired plant would produce 534 gpm (2021 l/min) of coal slurry wastewater assuming peak power production, 70% recovery of wastewater and 50% coal slurry. Practical uses of coal slurry wastewater include cooling tower makeup, ash sluicing makeup, or desulfurization process makeup.

The most accepted potential use for coal slurry wastewater is for cooling tower makeup. In normal coal plant operations, various sources for cooling tower makeup have been utilized, including treated sewage effluents. The water quality constraints for cooling waters are based on the scaling effects in the tower and the number of times the water can be recycled before blowdown. Generally, cooling waters characterized by high concentrations of dissolved minerals require more frequent blowdown. Typically, cooling tower water may be recycled from 4 to 9 times before blowdown is required. Figure 15 illustrates the water balance around the proposed Stanton





$$\text{Makeup} = \text{Evaporation} + \text{Blowdown} + \text{Minor Losses}$$

Fig. 15. Water mass balance around a natural draft cooling tower for a 415 MW (net) coal plant.



Energy Station 415 MW plant cooling tower. The normal 9 cycle cooling water circulation results in considerably less blowdown than the 4 cycle schedule. If untreated coal slurry wastewater is used for cooling tower makeup, the recycle schedule may be reduced, resulting in increased blowdown. The subsequent increase may require that the additional blowdown be treated. The decision to treat slurry wastewaters before use as cooling tower makeup may depend on the anticipated recycle schedule required.

Other potential uses for coal slurry wastewaters include ash transport and flue gas desulfurization makeup. There are no water quality constraints for ash transport water, however, flue gas desulfurization water must be pre-treated with lime or limestone before use in the desulfurization unit. Use of coal slurry wastewater would increase limestone demands and result in solids precipitation. The excess solids in the limestone slurry should not pose any operational problems with desulfurization processes. Although the volume of water required for ash transport makeup is relatively small, this option represents a viable treatment alternative for coal slurry wastewaters and should be given some consideration.

The projected treatment strategy for the coal power industry is to achieve zero discharge of industrial effluents. From the brief review of these treatment alternatives, coal slurry wastewaters may be used in typical industrial applications to avoid stream discharges and reduce treatment requirements. If treatment is required before industrial use, stringent state regulations will not have to be met and treatment costs will be minimized.



## CHAPTER VII

### CONCLUSIONS

1. Wastewater characterization of an eastern Kentucky coal slurry revealed that eastern slurries typically exhibit high sulfates, varied pH, and high concentrations of iron, magnesium and manganese. Other trace metals are present in various concentrations. Organics are considered very low with TOC in the 15 to 30 mg/l range.

2. Wastewater quality may vary considerably and is related to the composition of the coal along with several other pipeline operations parameters. It may be possible to control some of these influencing factors at the mine and in the pipeline before treatment.

3. The addition of a commercial corrosion inhibitor was found to increase conductivity, total dissolved solids and sulfate concentrations in coal slurry wastewaters.

4. The settling characteristics and treatability of coal slurry wastewaters are adversely affected by the addition of a corrosion inhibitor in the pipeline. These adverse reactions are thought to be related to the increased number and concentrations of anions to the slurry media, thus affecting the surface characteristics of pulverized coal and solubilities of various metals.



5. Lime treatment is a technologically feasible means of treatment and effectively removes many metals from solution. The optimum pH for removal of different metals varies and a multiple stage treatment strategy may be required to meet stream standards.

6. Alum treatment removes some metals effectively and is effective in removal of turbidity, color and organics.

7. The resulting alum sludges from this study would not be classified as hazardous substances as defined by the EP Toxicity (Leachability) Test. One lime sludge was found to contain a high concentration of mercury, however, this value is thought to be in error.

8. A review of a typical water budget for a coal fired power plant suggests that there may be feasible alternative uses for coal slurry wastewater in everyday power plant processes. Some of these uses, including ash transport, may not require prior treatment of the wastewater. Other uses may require varying degrees of treatment.

9. Costs for slurry wastewater treatment can be reduced by a reduction in the required volumes of discharged effluent and optimum uses of untreated slurry wastewater.



CHAPTER VIII  
RECOMMENDATIONS

The results of this research have suggested that the following areas should be further investigated to provide a better understanding of eastern coal slurries:

1. The variability of coal slurry wastewater quality with respect to the oxidation state of eastern coals.
2. The effects of different corrosion inhibitors on slurry settling and water quality.
3. The effects of various corrosion inhibitors on lime and alum treatability.
4. Optimum lime treatment strategies based on pH and multiple stage precipitation.
5. Further investigation on potential uses for coal slurry wastewaters.



APPENDIX



## SOLIDS PROGRAM

```

*SAUF77 • V W I N T E G E R   S A M
I N T E M S I O N   D A T ( 1 2 , 1 5 ) , S O L ( 1 2 ) , R E S ( 1 2 , 1 5 )
R E A D ( 1 5 , * )   M E T
R E A D ( 1 5 , * )   S A M
D O 1 0 0   I = 1 , S A M
  R E A D ( 1 5 , * )   ( C A T ( I , J ) , J = 1 , M E T )
  W R I T E ( 1 6 , 7 0 )   ( C A T ( I , J ) , J = 1 , M E T )
  F C R M A T ( 1 X , " D A T A = " , 1 5 ( F 5 . 3 , 2 X ) )
  C O N T I N U E
R E A D ( 1 5 , * )   ( S O L ( I ) , I = 1 , S A M )
D O 3 0 0   I = 1 , S A M
  D O 4 0 0   J = 1 , M E T
    R E S ( I , J ) = C A T ( I , J ) * 0 . 0 2 / S O L ( I )
  C O N T I N U E
D O 5 0 0   I = 1 , M E T
  W R I T E ( 1 6 , 8 0 )   I
  F O R M A T ( 1 X , " M E T A L   N O . = " , I 2 / )
  W R I T E ( 1 6 , 5 0 )   ( R E S ( J , I ) , J = 1 , S A M )
  F C R M A T ( 1 X , 1 2 ( F 1 0 . 9 , 2 X ) )
  C O N T I N U E
E N D $
V U . B
L I B * S A U L 7 7 * L I B E R Y
$ X E

```







## METALS PROGRAM (Continued)

```

130 WRITE (16,130) ELEM(I), TRUSTD(I), BGNSTD(I), ENDSTD(I), BGNBLK(I),
* ENDBLK(I)
* 3)
140 FORMAT(10,13X,1A3,13X,1F7.3,13X,1F7.3,14X,1F7.3,11X,1F7.3,10X,1F7
CONTINUE
WRITE (16,1)
WRITE (16,105)
170 READ (15,170) (DATE(J),J=1,2),(SAMPLE(J),J=1,2)
FORMAT(2A6,2A6)
WRITE (16,170) DATE,SAMPLE
172 READ (15,172) (SMPTIM(N),N=1,NSAMPLE)
FORMAT(10(A6,2X))
WRITE (16,174)
174 FORMAT (//30X,'SAMPLE TIME FROM START OF RUN',//)
176 WRITE (16,176) (SMPTIM(J),J=1,NSAMPLE)
FORMAT(2X,'ELEMENT',5X,8(A5,4X)//)
DO 190 N=1,NSAMPLE
190 READ (15,*) (CONC(N,I),I=1,NELEM)
CONTINUE
DO 250 N=1,NSAMPLE
DO 250 I=1,NELEM
IF (BGNSTD(I).EQ.0.0) GO TO 250
PSCORR (I) = (BGNSTD(I) - ENDSTD(I)) / (NSID)
SCORR (I) = (TRUSTD(I)) / (BGNSTC(I) - (PSCORR(I)*N))
PBCORR (I) = (BGNBLK(I) - ENDBLK(I)) / (NBLK)
BCORR (I) = BGNBLK(I) + (PBCORR(I)*N)
ACONC (N,I) = ((CONC(N,I) - BCORR (I)) * SCORR(I)) / (CCNCF)
CONTINUE
DO 252 I=1,NELEM
253 WRITE (16,253) ELEM(I), (ACONC (N,I),N=1,NSAMPLE)
252 FORMAT (5X,A3,4X,8(F8.4,2X))
CONTINUE
STOP
END
EOF..

```



## REFERENCES

- American Public Health Association. Standard Methods for the Examination of Water and Wastewater. 14th ed., Washington, D.C., 1975.
- Anderson, O.L.; Rogozen, M.B.; Margler, L.W.; Mankiewicz, P.; and Axelrod, M.H. Water Pollution Control for Coal Slurry Pipelines. Prepared for the U.S. Department of Energy. NTIS SAI-068-79-516. Springfield, VA: National Technical Information Service, 1978.
- Bosshart, R.D.; Price, A.A.; and Ford, C.T. Evaluation of Coal Cleaning on Fugitive Elements - Part II, Analytical Methods. Washington, D.C.: U.S. Department of Energy, COO-4427-35, 1980.
- Brown, Cynthia. "The Removal of Heavy Metals from Coal Slurry Wastewater," M.S. Thesis, University of Arkansas, Fayetteville, AR, 1983.
- Cherry, K.F. Plating Waste Treatment. Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1982.
- Christoe, J.R. "Removal of Sulfate from Industrial Wastewaters." Journal Water Pollution Control Federation 48 (December 1976): 2804.
- Cook, K.W. "A Study of the Treatability of Coal Slurry Pipeline Wastewater." M.S. Thesis, University of Arkansas, Fayetteville, AR, 1978.
- Cooper, C.D.; Dietz, J.D.; Taylor, J.S.; Flint, M.J.; and Todd, M.R. "Water Quality Characterization of an Eastern Coal Slurry." Presented at the Second Conference on Municipal, Hazardous and Coal Wastes Management, Miami Beach, FL, December 5-7, 1983.
- Davies, E.C., and Boegly, W.J. "Coal Pile Leachate Quality." Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers 107, EE2 (1980): 399.



- Doris, Allen D. "Statement of Allen D. Doris, President, Coal-Stream Pipeline Company, A Subcommittee on Energy, Nuclear Proliferation and Government Processes," U.S. Senate, June 8, 1981.
- "EPA Announces Availability and Provides Summaries of Water Quality Criteria for Toxic Pollutants." Federal Register 45, No. 231 (November 28, 1980): 79302.
- "EPA Announces Availability for Public Comment of Water Quality Criteria for 27 of the 65 Toxic Pollutants." Federal Register 44, No. 52 (March 15, 1979): 15926.
- "EPA Issues Rules on Designated Hazardous Substances Under the Clean Water Act." Federal Register 44, No. 69 (August 29, 1979): 50766.
- Godwin, J., and Manahan, S.E. "Interchange of Metals and Organic Matter Between Water and Sub-bituminous Coal or Lignite Under Simulated Coal Slurry Pipeline Conditions." Environmental Science and Technology 13 (September 1979): 1300.
- Hanson, V.D. "Coal Pipeline Nears Completion." Power Engineering 60 (October 1956): 86-88.
- "Hazardous Materials Transportation." Federal Register 45, No. 98 (May 19, 1980): 33821.
- Levence, H.D. "The Longest, Largest Coal Slurry Pipeline Ever Built." Coal Mining and Processing 8 (February 1971): 127.
- Matson, J.V., and Harris, T.G., III. "Zero Discharge of Cooling Water by Side Stream Softening." Journal Water Pollution Control Federation 51 (November 1979): 2602.
- Montfort, J.G. "Black Mesa Coal Slurry Line is Economic and Technical Success." Pipe Line Industry 36 (May 1972): 42.
- Moore, J.W. Water Quality Aspects of Coal Transportation by Slurry Pipeline. Arkansas Water Resources Research Center, University of Arkansas, Fayetteville, AR, 1979.
- Moore, J.W. "Quality Characteristics of Slurry Wastewater Resulting from the Slurry Pipelining of Eastern Coal." In Proceedings of the Fifth International Technical Conference on Slurry Transportation, Las Vegas, NV, March 26-28, 1980, Washington, D.C.: Slurry Transport Association, 1980.



- Moore, J.W. Water Quality Considerations in the Pipelining of Coal. Arkansas Water Quality Resources Research Center, University of Arkansas, Fayetteville, AR, 1981.
- Moore, J.W. "The Effects of Coal Slurry Pipelining of Eastern Coal on Water Quality." In Proceedings of the Sixth International Technical Conference on Slurry Transportation, Las Vegas, NV, March 24-27, 1981, Washington, D.C.: Slurry Transport Association, 1981.
- Orlando Utilities Commission. "Curtis H. Stanton Energy Center Unit 1." Site Certification Application, Volumes 1, 2, and 3, 1981.
- Peavy, H.S.; Murgel, G.A.; Axelberg, T.A.; and Curtis, M.R. "Chemical Interaction of Water and Coal in Slurry Pipelines." In Proceedings of the Third International Technological Conference on Slurry Transportation, Las Vegas, NV, 1978.
- Peavy, H.S.; Jennings, P.W.; and Murgel, G.A. Water Pollution Potential for Coal Slurry Pipelines. Prepared for Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Final Report, Contract No. R-805176-01. Reproduced by Montana State University, 1980.
- Peavy, H.S. Water Pollution Potential of Coal-Slurry Pipelines, Project Summary. Cincinnati, OH: Center of Environmental Research Information, U.S. Environmental Protection Agency, EPA-600/57-81-082, June 1981.
- Peavy, H.S. "Water Quality as a Function in the Reuse and Disposal of Coal Slurry Wastewater." In Proceedings of the Seventh International Technical Conference on Slurry Transportation, Lake Tahoe, NV, March 23-26, 1982, Washington, D.C.: Slurry Transport Association, 1982.
- Plumer, A.H.; Derammelaere, R.H.; and Eiserman, F.M. "Effluent Characteristics and Discharge Permit Considerations for the ETSI Coal Slurry Pipeline." In Proceedings of the Sixth International Technical Conference on Slurry Transportation, Las Vegas, NV, March 24-27, 1981, Washington, D.C.: Slurry Transport Association, 1981.
- Plumer, A.H.; Jordan, B.; Derammelaere, R.; and Sandhu, A. "Coal Slurry Dewatering Operations, Wastewater Treatability Studies." In Proceedings of the Seventh International Technical Conference on Slurry Transportation, Lake Tahoe, NV, March 23-26, 1982, Washington, D.C.: Slurry Transport Association, 1982.



- Sandhu, A.S., and Gandhi, R.L. "Water Quality Simulation for the Design of the ETSI Wastewater Treatment Facility." In Proceedings of the Seventh International Conference on Slurry Transportation, Lake Tahoe, NV, March 23-26, 1982, Washington, D.C.: Slurry Transport Association, 1982.
- State of Florida, Department of Environmental Regulation. "Rules of the Department of Environmental Regulation," Chapter 17-3 Water Quality. Public Document published by Florida State DER, Tallahassee, FL, 1982.
- Taylor, J.S. Professor of Engineering, University of Central Florida, Orlando, FL. Personal communication, April, 1983.
- Todd, M.R. "The Simulation and Water Quality Characterization of a Coal Slurry Involving Eastern Coal." M.S. Thesis, University of Central Florida, Orlando, FL, 1983.
- U.S. Congress, Office of Technology Assessment. A Technology Assessment of Coal Slurry Pipelines. Washington, D.C.: Library of Congress, 77-600023, March 1978.
- U.S. Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Washington, D.C.: Office of Technology Transfer, U.S. Environmental Protection Agency, EPA-625/6-74-003, 1974.
- Weber, W.J., Jr. Physiochemical Processes for Water Quality Control. New York: John Wiley and Sons, 1972.
- Williams, R.E. Waste Production and Disposal in Mining, Milling and Metallurgical Industries. San Francisco, CA: Miller Freeman Publications, Inc., 1975.
- Wilmoth, R.C. Limestone and Lime Neutralization of Ferrous Iron Acid Mine Drainage. Prepared for Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency. NTIS EPA-600/2-77-101, Springfield, VA: National Technical Information Service, May 1977.