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WATER QUALITY CONSIDERATIONS IN THE SLURRY PIPELINING OF COAL

by James W. Moore, Ph.D. University of Arkansas



Arkansas Water Resources Research Center

UNIVERSITY OF ARKANSAS Fayetteville

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WATER QUALITY CONSIDERATIONS IN THE SLURRY PIPELINING OF COAL

by

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August, 1981

(Contents of this publication do not necessarily reflect the views and policies of the Office of Water Research and Technology, U.S. Department of the Interior, nor does mention of trade names or commercial products constitute their endorsement or recommendations for use by the U.S. Government.)

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ABSTRACT

WATER QUALITY CONSIDERATIONS IN THE SLURRY PIPELINING OF COAL

Interest in the use of slurry pipelines for the movement of large volumes of coal over long distances has increased rapidly during the last decade. In the early 1970's, this interest involved the movement of Western coals to markets in the southwestern and western United States. In recent years, however, interest in the use of slurry pipelines for transporting Eastern coal developed.

Very little information was available concerning the water quality aspects of the slurry pipelining of Eastern coal. The research program was developed to commence building the data base in this regard. Extensive water quality investigations were conducted using two Eastern coals and various water sources to determine the coal-water relationships. Large concentrations of sulfate, hardness, sodium, and total dissolved solids were measured in slurry wastewaters prepared with the two coals. Additionally, large chloride concentrations were measured in slurry wastewaters prepared with the Illinois coal.

Ultimate biochemical oxygen demand curves were developed for several coals at selected mixing periods to determine the biodegradable organic load represented by the slurry wastewater. Laboratory studies were conducted to determine the fate of chloride when saline water is used to form the coal slurry. Mass balances were used to determine these results.

> Moore, James W. Water Quality Considerations In the Slurry Pipelining of Coal Report to Office of Water Research and Technology, August, 1981.

Keywords: Slurry Pipelining/Water Quality/Saline Water/ Biochemical Oxygen Demand/Eastern Coal/

Chapter 1

INTRODUCTION

Two relatively large volume-long distance slurry pipelines have been constructed and operated in the world. Both are located in the United States. These are the Consolidated Coal Company and Black Mesa pipelines. The Consolidated Coal Company pipeline operated for several years in the late 1950's. This pipeline extended from near Cadiz to Eastlake, Ohio transporting coal for use in Cleveland Electric Illuminating Company's Eastlake Station. Movement of coal by the pipeline continued for about six years until a reduction in the freight rate for movement by rail made the latter more economical. The technical feasibility of coal slurry pipelining was demonstrated by this project.

In the late 1960's, the Black Mesa pipeline was constructed to move coal from near Kayenta in northeastern Arizona to the Mohave Power Station in southeastern Nevada. One of the considerations involved in the development of this project was the distance from the mine to the nearest railhead. A substantial amount of new track would have been required for rail shipment of the coal. This factor contributed to the favorable economic climate for the slurry pipeline alternative. The Black Mesa pipeline is 273 miles in length with a capacity of five million tons per year. Operation of the pipeline has clearly been successful for over a decade with very high availability and reliability characteristics. The successful operation of this pipeline more completely affirmed the technical feasibility of the process.

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Following completion of the Black Mesa pipeline, interest in the use of the slurry pipelining process for the movement of coal increased rapidly. In excess of thirty possible pipeline routes have been investigated with six projects in advanced stages of development. There is little, if any, question remaining regarding the technical viability of the coal slurry pipelining process. Consequently, the major issues addressed in any particular project are usually directed at other than the technical merits of the process. Water rights and supplies, economic evaluations, right-of-way acquisition, and environmental concerns serve as examples of the issues which develop whenever a coal slurry pipeline project is proposed.

Coal slurry pipeline projects in the more advanced stages of development include the Energy Transportation Systems, Incorporated, San Marco, Northwest Integrated Coal Energy System, Allen-Warner Valley, Stream Coal and Texas Eastern pipelines. Of these, the Energy Transportation System, Inc. pipeline will probably be the first constructed.

One of the considerations involved in the slurry pipelining of coal involves the water quality aspects of the pipelining process. Because the interest in coal slurry pipelining was initially concentrated in the west, the data base on the coal-water relationships which occur during movement of Western coal by slurry pipeline is more developed than for Eastern coals. Similarly, data concerning water quality upgrading requirements and the treatment measures suitable for quality restoration are increasing with respect to the movement of Western coal. However, little information is available concerning the coal-water relationships which occur during transportation of Eastern coal by pipeline. The research program on which this report is based was designed

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primarily to commence building the data base regarding the water quality aspects of the shipment of Eastern coal by slurry pipeline. Additionally, several specific objectives dealing with various aspects of coal slurry pipelining were included in the research program.

PURPOSE

The purpose of this report is to present the data developed during imple-These data correspond with the nine spementation of the research program. 1) to determine the type and cific objectives of the program. These were: extent of water quality changes which will occur as a result of slurry pipe-2) to determine the treatment procedures lining of high-sulfur Eastern coal; applicable for restoration of the wastewater resulting from the slurry pipelining of high-sulfur Eastern coal; 3) to develop the ultimate biochemical oxygen demand curves for coal samples from several sources to determine their similarities and differences, and to determine if the curves are predictable; 4) to identify and assess the significance of the factor inhibiting biological treatment of the slurry wastewater; 5) to identify the type and extent of organic materials present in the slurry wastewater; 6) to assess the significance of these organic materials; 7) to determine the treatment measures suitable for removal of the organic materials, if necessary; 8) to develop a procedure whereby the chemical parameter concentrations can be predicted for a given coal and water quality, and; 9) to investigate the feasibility of using saline water as the slurry medium.

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The report includes data on the characteristics of slurry wastewater with respect to alkalinity, biochemical oxygen demand, boron, calcium, chemical oxygen demand, dissolved solids, fluoride, iron, lead, manganese, magnesium, nickel, pH, potassium, silica, sodium, sulfate, titanium, total hardness and zinc. Comparisons of the slurry wastewater characteristics from slurries prepared with coal from two sources and distilled water are presented to indicate the effects of coal source on wastewater characteristics. Similar comparisons of water quality parameters for slurries prepared with distilled water and other water sources are provided to show indications of the effects of influent water quality on the slurry wastewater characteristics.

Ultimate biochemical oxygen demand curves are presented to indicate the effect of coal source on the magnitude of this parameter. Treatment techniques applicable for water quality restoration are identified and data developed during the treatment studies are included.

The results of linear and multiple regression analyses on slurry wastewater data developed with both Eastern and Western coals are presented. These results indicate trends with respect to parameter concentrations as a function of detention time.

SCOPE

Chapter 2

SUMMARY OF FINDINGS AND CONCLUSIONS

The following findings and conclusions were derived from the data developed during the research program:

- The characteristics of the slurry wastewater resulting from the pipelining of Eastern coal are dependent on the source of coal used. Consequently, definitive data for a specific pipeline project must be developed using the specific coal to be transported in the pipeline.
- The characteristics of the water used to form the slurry influence the concentrations of certain parameters in the slurry wastewater. The significance of this influence is clearly parameter specific.
- 3. High concentrations of sulfate, hardness, sodium and total dissolved solids were measured in slurry wastewaters prepared with Eastern coals. Additionally, large concentrations of chloride were measured in slurry wastewaters prepared with the Illinois coal.
- 4. The large concentrations of sulfate, chloride and total dissolved solids will increase the complexity and expense of restoration of the slurry wastewater quality, should restoration be required.

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- 5. The hardness concentrations in the slurry wastewaters preapred with the Eastern coals are primarily significant from the viewpoint of larger treatment costs and sludge disposal requirements. Conventional lime or lime-soda ash softening can reduce these concentrations to acceptable levels.
- 6. Treatment requirements for reduction of the biochemical oxygen demand in slurry wastewaters prepared with both coals will probably be site specific, because of the relatively low concentrations.
- 7. The biochemical oxygen demand concentrations in slurry wastewaters prepared with both Eastern coals were considerably less than in slurry wastewaters prepared with Western coals previously investigated.
- 8. With acclimated microorganisms used as seed, the ultimate biochemical oxygen demand is developed in about a twelve-day period as compared with 25-30 days for typical domestic wastewater.
- 9. The use of saline water as the slurry medium should be employed only after very careful evaluation of the potential adverse effects on furnace and flue gas processing equipment.
- 10. The alkalinity concentrations in slurry wastewaters prepared with the Eastern coals were all low and tended to decrease with increasing detention time.

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- 11. Total alkalinity concentrations in slurry wastewaters prepared with the Kansas coal were larger than in slurry wastewaters prepared with the Illinois coal.
- 12. Although the alkalinities were low, the pH values remained within an acceptable range for all of the experimental runs.
- 13. The five-day biochemical oxygen demand concentrations in slurry wastewaters prepared with both coals were relatively low.
- 14. The chemical oxygen demand concentrations in slurry wastewaters prepared with the two Eastern coals were relatively low.
- 15. The chemical oxygen demand concentrations in slurry wastewaters prepared with the Illinois coal were significantly less than in those prepared with the Kansas coal. This may be attributable to the use of washed Illinois coal (as lump coal) and unwashed Kansas coal.
- 16. The relatively high five-day biochemical oxygen demand to chemical oxygen demand ratios indicate that, once microorganisms are acclimated, the wastewaters are readily biodegradable.
- 17. Calcium and total hardness concentrations were very high in slurry wastewaters prepared with both Eastern coals.

- 18. The calcium to total hardness ratios in slurry wastewaters prepared with the two Eastern coals were significantly different. Slurry wastewaters prepared with the Illinois coal had much higher calcium to total hardness ratios.
- 19. The high hardness concentrations in the slurry wastewaters prepared with the two coals tended to minimize the influence of the hardness in the water used as the slurry media on the hardness concentrations in the slurry wastewater.
- 20. The effect of detention time on the calcium and total hardness concentrations in the slurry wastewaters was clearly different for the two Eastern coals. For slurry wastewaters prepared with the Kansas coal, the initial concentrations were generally representative of those for the remainder of the experimental run. For slurry wastewaters prepared with the Illinois coal, the hardness concentrations clearly increased with increasing detention time.
- 21. The chloride concentrations in slurry wastewaters prepared with the two coals were substantially different. The average concentrations were 90 and 1,500 milligrams per liter for slurry wastewaters prepared with the Kansas and Illinois coals, respectively.

- 22. The chloride concentrations tended to increase with increasing detention time in slurry wastewaters prepared with both coals.
- 23. Measureable quantities of fluoride were present in slurry wastewaters prepared with both Eastern coals. The fluoride concentrations were in the one to two milligrams per liter range.
- 24. A general tendency for increasing fluoride concentrations with increasing detention time was evident from the data.
- 25. Measureable quantities of lead were present in the slurry wastewaters prepared with both Eastern coals. Although these concentrations were considerably less than one milligram per liter, lead may be significant because of very low allowable lead concentrations specified in some water quality standards. Project and site specific factors will determine the significance of this parameter.
- 26. A slight tendency for decreasing lead concentrations with increasing detention time was apparent from the data.
- 27. Relatively large concentrations of manganese were present in slurry wastewaters prepared with the Kansas coal. These concentrations clearly decreased with increasing detention time.

- 28. Manganese concentrations were clearly a function of coal source. The data indicated less manganese was present in slurry wastewaters prepared with Illinois coal than in those prepared with the Kansas coal.
- 29. Significant nickel concentrations were present in slurry wastewaters prepared with both Eastern coals. Surface water quality standards ordinarily contain very low allowable discharge limits for this parameter.
- 30. The nickel concentrations in slurry wastewaters prepared with both coals decreased with increasing detention time indicating removal from the aqueous phase.
- 31. The pH values of the slurry wastewaters clearly increased with increasing detention time.
- 32. The potassium concentrations in slurry wastewaters prepared with both coals were all low and would not be significant other than for a very minor contribution to dissolved solids.
- 33. The potassium concentrations clearly increased with increasing detention time.
- 34. The silica concentrations in slurry wastewaters prepared with the Illinois coal were significantly less than in slurry waste-

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waters prepared with the Kansas coal. However, the silica concentrations were nominal in slurry wastewaters prepared with both coals.

- 35. Substantial differences in sodium concentrations were observed in slurry wastewaters prepared with the two coals. The sodium concentrations in slurry wastewaters prepared with the Illinois coal were greater than those prepared with the Kansas coal.
- 36. The sodium concentrations in slurry wastewaters prepared with the Kansas coal were significant both because of the relatively high concentrations (for fresh water) and because sodium is relatively expensive to remove.
- 37. The sulfate concentrations were high in slurry wastewaters prepared with both coals. Since sulfate is a parameter usually included in surface water quality standards, this parameter is significant both directly and because of the contribution to dissolved solids.

Chapter 3

BACKGROUND

The coal-water mixture in a slurry pipeline is a complex environment in which numerous physical, chemical and biological activities may occur. These reactions involve both the transfer of impurities in the coal into the liquid phase and impurities in the water into the solid phase. A variety of factors determine the type and extent of changes which may result from mixing water with coal. Among others, these factors include detention time, mixing rate, the relative proportions of water and coal, the quality of water used as the slurry media, and the source and type of coal used (1,2). Because of the variety of factors which may affect the coal-water relationship, a brief review and description of the coal slurry pipelining process is appropriate.

GENERAL DESCRIPTION OF THE COAL SLURRY PIPELINING PROCESS

The process of transporting coal in a slurry pipeline is basically the same as for transporting any other solid material with a specific gravity greater than that of the suspension fluid in a pipeline. Several slurry pipelines have been constructed and operated around the world for transporting various solid materials. Copper concentrate, iron ore, limestone and coal are currently transported by slurry pipeline, for example.

Basically, the coal slurry pipelining process consists of crushing and grinding the coal to a size that will allow suspension in water, mixing of the coal and water (slurry formation), movement of the slurry through the pipeline by pumping, and separation of the coal solids from the liquid at the receiving station. Figure 1 shows a typical flow diagram of a long distance pipeline.

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Figure 1: Flow Diagram Of A Long Distance Coal Slurry Pipeline System (Reprinted From Pipeline Industry, May, 1975 (3))

HISTORY OF COAL SLURRY PIPELINING

The concept of transporting coal by slurry pipeline is an old one. A working model of a slurry pipeline was built in 1880. A 13-mile pipeline has operated successfully for over twenty years in France (4). However, the first major coal slurry pipeline was not constructed until the mid-1950's. This pipeline, constructed by the Consolidated Coal Company, transported coal from Cadiz, Ohio, to Cleveland Electric Illuminating Company's Eastlake Station (5). Disagreement with existing rail freight rates apparently was the motivation for developing the slurry pipeline project. The slurry pipeline was used for delivering coal for only about six years because a subsequent reduction in freight rates made rail shipment more economical (5). However, the pipeline was maintained in a "ready" status for several years in case the rail freight rates increased sufficiently that pipeline shipment would be more economical. The pipeline was small by current standards both in size and length. Pipeline length was 108 miles with a diameter of ten inches (5).

The second major coal slurry pipeline project constructed was the Black Mesa pipeline which delivers coal from the Black Mesa mine near Kayenta in northeastern Arizona to the Mohave Power Station in southeastern Nevada. This pipeline has been in operation since 1970 and has displayed excellent operational characteristics. Reliability and availability values for this pipeline have been very high. Attainment of availability values exceeding 99 percent was accomplished very early in the operational period (6). The Black Mesa slurry pipeline is 273 miles in length and is eighteen inches in diameter for most of its length. Pipeline size was reduced to twelve inches for the purpose of dissipating head as the line descends into the Colorado River valley. Annual throughput capacity of the pipeline is about five million tons.

These two pipelines are the only long distance - large volume coal slurry pipelines which have been constructed in the world. However, in excess of thirty pipeline corridors have been evaluated in the United States alone since construction of the Black Mesa system. Others have been evaluated around the world.

Several coal slurry pipeline projects are under development in the United States. Of these, six have been under development for several years. These are the Energy Transportations Systems, Incorporated; Stream Coal; Northwest Integrated Coal Energy System; San Marco; Allen-Warner Valley, and; Texas Eastern pipelines.

The Energy Transporation Systems, Incorporated pipeline will be probably be the first of these constructed. This pipeline will deliver coal from the Powder River Basin in northeastern Wyoming to the Arkansas - Louisiana - Mississippi area. Pipeline capacity will be in the 25-35 million tons per year Pipeline size is projected to be 38 inches in diameter with a length range. of about 1400 miles (7). The environmental impact statement has been prepared Construction is scheduled to start within the next two for this project. years. This project will be unique compared with the two previous coal slurry pipelines because it will deliver coal to several users rather than being a single source-single delivery point system. Water for the slurry pipeline will be obtained from deep wells in the Madison formation.

The Stream Coal pipeline is the first of the projects currently under development or proposed which will move Eastern coal to markets. Although the Consolidated Coal Company pipeline delivered Eastern coal, the project was developed under conditions which do not exist today. Environmental constraints and other factors have considerably altered the difficulty of taking a project from conception to completion. Consequently, the Stream Coal pipeline is breaking new ground with respect to the movement of Eastern coal. This pipeline is projected to have a capacity in the 15-45 million tons per year range. Pipeline length is estimated at 1,500 miles. Coal will be transported from the Illinois and West Virginia areas to use sites in the Florida-Georgia region. The San Marco slurry pipeline will transport coal from southern Colorado to delivery sites in Texas with the terminus of the pipeline located in the Houston area. This pipeline will be about 900 miles long with a capacity of about 10 million tons per year. Coal will be obtained from the Walsenburg coal deposit in Colorado with water obtained from wells. As with the Energy Transportation Systems, Incorporated pipeline project, extensive work has been conducted with respect to obtaining and developing the water resources to be used.

The Northwest Integrated Coal Energy System (NICES) pipeline will deliver coal from Wyoming to use sites in the Oregon-Washington area. Pipeline length will be about 1,100 miles. Annual throughput capacity is expected to be about 25 million tons per year.

The Allen-Warner Valley pipeline is part of a complex coal delivery-power generation-extra high voltage transmission project. Pipeline length is relatively short by current standards since it will be part of an integrated system. The pipeline is expected to deliver about 11.6 million tons of coal per year.

The Texas Eastern Corporation pipeline would move coal from the Powder River Basin to the Houston, Texas area. Pipeline capacity is estimated to be about 22 million tons per year. Pipeline length is expected to be about 1,260 miles (8). Difficulty in obtaining sufficient water rights has inhibited development of this project.

The Virginia Electric Power Company (VEPCO) pipeline will move Eastern coal to market. Pipeline length is anticipated to be about 350 miles. Capacity of the pipeline will be about 5 million tons per year (8).

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The Pacific Bulk pipeline will be about 650 miles in length in the United States. Annual throughput capacity is estimated at 10 million tons per year (8).

Numerous other pipeline corridors have been or are being investigated. Figure 2 provides a graphical summary of these corridors.



Figure 2: Summary Of Existing, Planned And Proposed Coal Slurry Pipelines And Of Corridors Which Have Been Evaluated (Reprinted From STA Data (8))

CONSOLIDATED COAL COMPANY PIPELINE

Annual throughput capacity was about 1.3 million tons per year. As with other slurry pipeline systems, the overall operation consisted of three basic steps. These were slurry preparation, slurry transportation and slurry dewatering.

Slurry preparation essentially consisted of screening, crushing, mixing, and storage facilities. Clean 3/8 inch by 0 coal was initially screened with the screen undersize stored in drag tanks. The screen oversize was either crushed or stored in a storage pond. If crushed, the screen oversize was either sent to drag tanks or to a second storage pond. The destination was determined by the quantity of coal needed for the pipeline at that particular time. The very fine coal carried over with the overflow from the drag tanks was stored in a third pond. Storage in three ponds rather than in a single pond was used to avoid segregation by size fractions. By preventing segregation, the size fractions could be recombined in the proportions required (5).

Slurry movement in the pipeline was accomplished by a series of pumping stations. The gradation of coal used in this pipeline is shown in Table 1.

Dewatering of the coal slurry mixture was accomplished by thickening, vacuum filtration and flash drying. The general dewatering scheme was thickening to about 60 percent solids (by weight), vacuum filtration to about 20 percent, and flash drying to the extent required. Particulates from the drier were collected and either sent to the boiler or flocculated and returned to the vacuum filter. The filtrate from the vacuum filter was flocculated and settled before discharge (5).

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Size Gradation Of Coal Transported In The Consolidated Coal Company Pipeline (After Frey, Jonakin and Caracristi(8))

<u>Screen Mesh</u>	Percent Retained
8	0.7
14	6.9
28	18.2
48	18.9
100	15.1
200	10.4
325	6.3
-325	23.5

BLACK MESA PIPELINE

The Black Mesa pipeline was constructed in the late 1960's for the purpose of delivering coal to the Mohave Power Station. Pipeline capacity is 4.8 million tons per year. Pipeline length is 273 miles with a diameter of eighteen inches for most of its length.

Coal preparation consists of reducing the particle size in a two-step operation. Initially, the crushed coal received at the preparation plant is reduced in size by cage impactors. The 3/8 inch by 0 coal from the cage impactors is sent through rod mills for further size reduction. Water is added in the rod milling step. After rod milling, sufficient water is added to the coal to obtain the desired coal-water mixture (about 50 percent coal by weight). Following slurry formation, the slurry is stored until introduction in the pipeline.

Positive displacement pumps are used to inject the slurry into the pipeline and to move the slurry to the receiving station. Discharge pressures at

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the preparation plant are about 1,600 pounds per square inch. Four pumping stations, including the station at the preparation plant, are used in the Black Mesa system. Flow velocity is within the four to six feet per second range typical of coal slurry pipelines.

Dewatering of the slurry at the Mohave Station is accomplished by sedimentation and centrifugation. Conventional ball mills are used at this station to achieve the size characteristics needed for firing in the boiler (6).

COAL-WATER RELATIONSHIPS IN SLURRIES

Numerous physical, chemical and/or biological activities can occur in coal-water mixtures. These activities are complex with a complete identification of all activities very difficult. Coal contains a variety of contaminants and impurities which may be transferred to the aqueous phase upon mixing with water. Similarly, some of the parameters in the water used to form the slurry may be mitigated in concentration by contact with the coal, may contribute to the concentrations in the aqueous phase. Additionally, some parameters which are initially leached from the coal in significant quantities are returned to the solid phase by absorption, precipitation or other mechanism.

Several investigations have been conducted to determine the interrelationships of coal and water in slurries (1,2,10,11,12,13,14,15,16,17,18,19). Most of these have involved Western coals. With respect to concentration only, the most significant water quality parameters are alkalinity, biochemical oxygen demand, calcium, chemical oxygen demand, dissolved solids, chlo-

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ride, sodium, potassium, silica, sulfate and total hardness. The concentrations of these parameters in the liquid phase of the slurry are dependent on a variety of factors of which coal source, water source, detention time, type of environment (aerobic, anaerobic, sequential aerobic-anaerobic), solids concentration and rate of mixing are known to be important (1,2).

With respect to the parameters of primary interest from the viewpoint of complying with water quality standards, identification of the parameters is necessarily site specific. The water quality standards of the receiving watercourses, parameter concentrations in the liquid phase of the slurry, and the dilution available in the receiving stream are site specific factors which influence the significance of each parameter. However, concerning the slurries prepared with Western coals, generally biochemical oxygen demand and chemical oxygen demand, calcium, chloride, dissolved solids, sulfate and certain trace metals must be evaluated with respect to complying with water quality standards (2).

A variety of relationships have been identified concerning parameter concentrations in slurries prepared with Western coal (1,2,20,21). For some parameters, the concentrations decrease with increasing detention time. For others, the concentrations increase with increasing detention time. Still other parameters show relatively constant concentrations, after a short mixing period, with respect to detention time. For some parameters, the concentrations in the liquid phase of the slurry are relatively unaffected by the quality of the water used to form the slurry. For others, the concentrations in the water used to form the slurry are essentially additive with those which will be leached from the coal. The relationships are clearly parameter specific.

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In essence, definitive data for specific coal and water sources must be developed using those coal and water sources which will be used in a specific pipeline project.

CLEANING OF EASTERN COALS

Because of the lack of data regarding the coal-water relationships in slurries prepared with Eastern coals, a literature review was conducted to determine the information available in the general area of wastewaters resulting from several coal mining activities.

About 80 to 90 percent of the coal cleaned in the United States is washed with water. Most of this coal is Eastern coal. A variety of processes and equipment are used in fine-coal cleaning and in coal-water separation. These include wet tables, jig washing, air cleaning, classifiers, and launders for cleaning; flotation for recovery of fines, and; dewatering screens, thickeners, cyclones, centrifuges, thermal dryers, filtration, flocculation and desliming for dewatering (13,14).

Sulfur

One of the obvious impurities of concern in coal is sulfur both because of the limits on sulfur dioxide emissions from new coal-fired sources under the New Source Performance Standards and because sulfate is one of the parameters ordinarily controlled by surface water quality standards. Sulfur is always present in coal, but varies in quantity and in form as a function of coal source. The sulfur content of coal is divided into organic, inorganic and sulfate sulfur fractions. Organic Sulfur. Organic sulfur may be defined as the sulfur occurring in combination with the coal substance and is distributed throughout the coal as part of the molecular structure (13,14). Because of this distribution, organic sulfur is not usually removed by conventional mechanical cleaning processes. Organic sulfur usually predominates in low sulfur coal, but ordinarily is a relatively small fraction of the sulfur present in high-sulfur coals. Organic sulfur contents of 0.04 to 5.44 percent have been reported in coals in the United States (13,14).

<u>Inorganic Sulfur</u>. Commonly known as pyritic sulfur, inorganic sulfur is ordinarily the predominate form of sulfur in Eastern coals and is present in coals as the minerals pyrite and marcasite. Both pyrite and marcasite have the same chemical formula, FeS2, but possess different physical structures. Pyritic sulfur is distributed in coal in various ways including lenses and bonds, joints or cleats, balls or nodules, and as finely disseminated particles. The variation in distribution contributes to the varying sulfur removal rates for mechanical cleaning operations. The pyritic content of coal can vary widely. Pyritic sulfur contents ranging from 0.01 to 7.9 have been reported in United States coals (13,14).

Crushing of the coal may release the pyrite in the lenses, bonds, cleats and bands for subsequent removal by mechanical cleaning. Finely disseminated pyrite ordinarily cannot be removed unless the coal is crushed and/or ground to a very small size and the pyrite separated from the coal substance by special treatment (13,14).

<u>Sulfate</u> <u>Sulfur</u>. Sulfate sulfur may be defined as sulfur combined with calcium and iron. This form of sulfur is usually less significant than or-

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ganic and pyritic sulfur in freshly crushed coal with respect to sulfur content of the coal. However, since pyrite and marcasite are easily oxidized to sulfate in the presence of moisture, the sulfate content of aged coal may be significant.

<u>Total Sulfur</u>. Total sulfur is the sum of the organic, inorganic and sulfate sulfur contents of coal. Coals are frequently classified according to the sulfur content. One such classification system is as follows:

> Low Sulfur Coal - 1.0 percent or less Medium sulfur coal - 1.01 to 3.0 percent High sulfur coal - 3.01 percent or more

Sulfate Leaching From Coal

The problem of acid mine drainage has been investigated for many years. One of the phenomena involved is the oxidation of sulfur-bearing coal. Leaching of the oxidation products of the metallic sulfides in the coal yields sulfate as well as the metal. Concerning the inorganic (pyritic) sulfur in coal, both the pyrite and marcasite may be oxidized. The marcasite is unstable and degrades to pyrite.

The oxidation of the pyritic materials has been described by the following equations:

> 1) $2\text{FeS}_2 + 70_2 + 2\text{H}_20 \rightarrow 2\text{Fe}^{++} + 4\text{SO}_4^{=} + 4\text{H}^+$ 2) $4\text{Fe}^{++} + 0_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{+++} + 2\text{H}_20$ 3) $\text{Fe}^{+3} + 3\text{H}_20 \rightarrow \text{Fe}(0\text{H})_3 + 3\text{H}^+$

> > - 24 -

4) FeS_2 + 14Fe⁺³ + 8H₂O \rightarrow 15Fe⁺² + 250₄⁻² + 16H⁺

In equation 1, the iron in the metallic sulfide is oxidized to ferrous iron, the sulfur is oxidized to sulfate and hydrogen ions are released. The hydrogen ions released reduce the pH of the solution. In the second equation, the ferrous iron is oxidized to ferric iron. In the third equation, the ferric iron combines with water to form the relatively insoluble ferric hydroxide releasing additional hydrogen ions, thus further reducing the pH. The first three equations are frequently written as one equation as follows:

5) $4\text{FeS}_2 + 150_2 + 14\text{H}_20 \rightarrow 8\text{H}_2\text{SO}_4 + 4\text{Fe(OH)}_2$

The overall equation indicates the end products of the reactions are sulfuric acid and ferric hydroxide. The net results of the reactions are a decrease in pH (frequently severe), increase in the sulfur content of the leaching solution and an increase in the iron concentration in the water. The rates of reaction of the oxidation of the pyrite are increased dramatically by the presence of iron bacteria. The iron bacteria serve as catalysts. Ferrobacillus ferroxidans become increasingly more significant when the pH decreases below 5 and are the primary contributors to the oxidation of ferrous materials.

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Quality Characterization Data For Coal Wastewaters

From a water pollution viewpoint, most of the problems associated with coal mining are associated with drainage and with washing of the coal. Table 2 shows the mineral content of an Illinois basin coal preparation waste (23,24).

TABLE 2

Mineral Content Of An Illinois Basin Coal Preparation Waste (After Williams, et.al. (231))

Mineral	<u>Weight</u> <u>Percent</u>
Illite	11.7
Kaolinite	7.8
Other Clays	19.5
Quartz	19.2
Pyrite	17.2
Marcasite	12.4
Gypsum	1.2

The major inorganic elements in the Illinois Basin coal preparation waste are included in Table 3. Silica, iron and aluminum were present in the largest quanitities in the waste.

The average effluent concentrations in coal pile leachate for three coal regions in the United States are shown in Table 4. The three regions are the Appalachian, Interior Western and the Western. The Appalachian region includes Alabama, Eastern Kentucky, Georgia, Maryland, Ohio, Pennsylvania, Tennessee, Virginia and West Virginia. The Interior Western region includes Ar-

Major Inorganic Elements In An Illinois Basin Coal Preparation Wastes (After Williams, et.al. (231))

Element	Weight Percent		
Silicon	13.6		
Iron	11.0		
Aluminum	5.1		
Potassium	1.1		
Titanium	0.35		
Magnesium	0.23		
Sodium	0.16		
Calcium	0.09		

kansas, Iowa, Kansas, Missouri, Nebraska, Oklahoma and Texas. The Western region includes Arizona, Colorado, Idaho, New Mexico, Utah, Washington and Wyoming. The data reflected in the table were obtained using simulation studies.

Table 5 includes additional data reported for four mine drainage sources (25). The concentrations of several parameters vary considerably among the four sources. For example, the four sulfate concentrations were 5,150, 640, 1,080 and 385 milligrams per liter.

Quality characterization data for drainage water from a tailings pile near Elliot Lake, Ontario are shown in Table 6. These data clearly represent acid mine drainage.

Table 7 shows acid mine drainage quality characteristics from a mine near Kellogg, Idaho. Very high sulfate, iron, zinc, manganese, aluminum, and magnesium concentrations are indicated by the table. The nickel, copper, aluminum and cadmium concentrations were also high.

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Average Effluent Drainage Concentrations By Coal Region (After Wachter (25))

Region

Effluent Parameters Interior Western Appalachian Western Total Suspended Solids 1521 1853 2486 Total Dissolved Solids 259 5539 1900 Sulfate 66 4860 240 3.1 8.2 1131 Iron 0.4 Manganese 0.03 17.9 Free Silica 12.3 86.3 BDL BDL** BDL. Cyanide <0.001 **<**1.2 Biochemical Oxygen Demand **<**5.0 2.5 Chemical Oxygen Demand 1407 1053 1826 1.8 Nitrate 0.12 0.09 Total Phosphate BDI. BDL BDL 10.1 5.6 Arsenic 23 BDL BDL BDL Beryllium Cadmium BDL 0.05 0.005 0.03 0.04 Chromium BDL 0.02 2.2 BDL Copper 0.07 Lead 0.05 0.33 Mercury 0.001 0.004 0.005 Nickel 0.06 10.2 0.05 15.0 Selenium 23.8 25.2 Silver BDL BDL BDL Zinc **\$0.008** 25.0 0.15 ъH 6.28 2.81 7.24 Chloride 0.33 2.3 BDL Total Organic Carbon 251.7 90.5 318.4

*All Concentrations (except pH) are in milligrams per liter. **BDL - below detectable limit

Effluent Data For Mine Drainage From Four Sources (After Doyle (26))

Source

Parameter	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Volume, mgd	0.025	0.119	0.199	30
pH	3.05	3.35	3.05	3.43
Acidity, mg/1	6,700	330	780	278
Total Iron, mg/1	2,090	27	134	53
Ferrous Iron, mg/1	1,780	26	133	53
Aluminum, mg/1	725	100	141	30
Calcium, mg/1	150	77	102	40
Magnesium, mg/1	80	83	80	42
Sulfate, mg/l	5,150	640	1,080	385
Temperature, C	19	16	15	18
Specific Gravity	1.11	1.09	1.10	1.10

Effect Of Environment On Acid Mine Drainage Formation

Several experiments have been conducted for the purpose of establishing the relationship between acid mine drainage formation and the type of gaseous environment to which the pyritic material is exposed (27,28). Generally, the results indicated that the rate of acid production is proportional to the partial pressure of oxygen available. Environments investigated were air, nitrogen, methane and carbon dioxide. The results indicated that acid production from pyrite in a nitrogen environment was less than one percent of that produced in an air environment (27,28). Several conclusions drawn from this study have potential application in the development of coal slurry pipelining water quality data. These conclusions were:

1. The acid drainage from coal mine pyrite, in terms of iron, sulfate, acidity, and conductivity, is proportional to the partial pressure of oxygen in the gas phase.

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Mine Drainage Characteristics (After Doyle (26))

Parameter	Concentration
рН	2.0
Sulfate	7,440
Acidity	14,600
Ferric Iron	1,450
Ferrous Iron	1,750
Uranium	7.2
Zinc	11.4
Nickel	3.2
Cobalt	3.8
Copper	3.6
Manganese	5.6
Aluminum	588
Lead	0.67
Cadmium	0.05
Lithium	0.07
Vanadium	20.0
Silver	0.05
Titanium	15.0
Magnesium	106.0
Calcium	416
Potassium	69.5
Sodium	920
Arsenic	0.74
Phosphorous	5.0
Chemical Oxygen Demand	270
	•

All data (except pH) expressed in parts per million.

- 2. Acid production by pyrite under an inert gas atmosphere is affected by the dissolved oxygen content of the feed water.
- 3. The amount of water available does not influence the rate of oxidation of the pyrite.

Quality Characterization Data For Coal Mine Drainage (After Doyle (26))

Constituent	Concentration
рН	2.2
Sulfate	63,000
Total Iron	16,250
Zinc	14,560
Nickel	4.8
Copper	13.4
Manganese	2,625
Aluminum	347
Lead	0.8
Cadmium	22.5
Magnesium	1,500
Calcium	31.6
Potassium	0.7
Sodium	0.5
Chromium	0.3
Chloride	38
Nitrate	77.5
Conductivity	48,000

All values expressed in milligrams per liter except pH and conductivity.

4. Inert gas blanketing of coal mine pyrites is an effective method of reducing pyrite oxidation and thus acid production.

Chapter 4

EXPERIMENTAL PROCEDURES AND EQUIPMENT

EXPERIMENTAL APPARATUS

Twenty-four batch reactors were used in two twelve-gang stirring units. The reactors were designed to allow aerobic, anaerobic or sequential aerobicanaerobic investigations. Nitrogen gas was used to provide the anaerobic environment.

Eight-inch diameter polyvinyl chloride pipe was used as the cylinders for the reactors. Ten-inch square plexiglass plates were used for the top and bottom of each reactor. O-rings were used to seal the top plates to the cylinders and to seal the opening in the top plate through which the mixing shaft protruded. The bottom plates were attached to the cylinders using solvent.

Stainless steel mixing shafts, driven by a common motor on each twelvegang unit, were used. Pulleys and V-belts were used to drive the individual mixers. Figure 3 shows a general view of each reactor.

Inlet and outlet ports were installed in each reactor to allow introduction of the nitrogen gas for purging the air from each reactor and for maintaining a bleed stream throughout the mixing period. The bleed stream was maintained to provide a positive pressure inside the reactors to insure the anaerobic environment. With the positive pressure, minor gaseous leaks at the O-ring sealing the shaft entrance would not allow introduction of air into the reactor environment. Additional details are shown on Figure 4.



Figure 3: Schematic of Batch Reactors



Figure 4: Cross-sectional View of Batch Reactors

EXPERIMENTAL PROCEDURES

Coal Sources

The coals used in the water quality characterization studies were obtained from Freeman United Coal Company and from Pittsburg Mining Company. Specifically, the Illinois coal was obtained from Freeman United Coal Company's Orient No. 3 mine located near Waltonville, Illinois. The Kansas coal was obtained from Pittsburg Mining Company's mine located near LaCygne, Kansas. Both are high-sulfur bituminous coal deposits.

The coal used in the biological treatability study involving Western coal was obtained from the Cordero Mining Company at Gillette, Wyoming, and will be identified in this report as Wyoming coal. The Eastern coal biological treatability study was conducted using the Kansas coal obtained from the LaCygne mine.

Coal Preparation

The coal samples were initially air-dried to reduce the surface moisture content. After air-drying, the coal was reduced in size with a burr grinder followed by additional size reduction with a Brown pulverizer. Following size reduction, the coal was separated into several size fractions using Ro-Tap sieve shakers. The sieved coal was then recombined in the desired size gradation. The particle size gradation used in the analyses is shown in Table 8.

Water Sources

To determine the effects of the slurry media water quality on the characteristics of the slurry wastewater, three water sources were used. These in-

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Particle Size Distribution Of Coal

Screen, mesn	Percent Retained	
8	2.5	
14	6.5	
28	14.3	
48	23.4	
100	8.3	
200	17.0	
325	6.0	
-325	22.0	

cluded distilled water, surface water and wastewater treatment plant effluent. The surface water used was tap water from the Fayetteville, Arkansas water distribution system. The tap water was derived from Beaver Lake, a large Corps of Engineers impoundment located in northwestern Arkansas. Treatment bf the water for public consumption includes coagulation, flocculation, sedimentation, and chlorination. The mineral water quality of the surface impoundment is good.

The wastewater used in the water quality characterization studies was obtained from the final clarifier of the Fayetteville, Arkansas wastewater treatment plant. The tap water derived from Beaver Lake is the carriage water for the Fayetteville wastewater.

The slurry was formed by combining equal amounts of coal and water (by weight) to yield a fifty percent solids slurry. In a formula format, the solids concentrations can be expressed as follows: Solids Concentration (%) = (Wc)/(Wc + Ww))(100)

where: Wc = weight of coal, grams Ww = weight of water, grams

The slurry samples were mixed for periods ranging from one hour to fifteen days in the two twelve-gang stirring units. The mixing speed used was 250 revolutions per minute. This mixing speed just maintains the coal in suspension. After the desired time had elapsed for a particular sample, the slurry was extracted from the stirring unit. The sample was then separated into the solid and liquid components by vacuum filtration. Whatman No. 14 filter paper was mounted in a Buchner funnel for this purpose. The vacuum applied was approximately 24 inches of mercury. The filtrate from the dewatering step was filtered through a 0.45 micron glass fiber filter. The liquid passing through the glass fiber filter is termed "slurry wastewater" in this report.

Biological Treatment Studies

Acclimation of the microorganisms was necessary for successful biological treatment studies. Two approaches were used for accomplishing the acclimation. One was basically the procedure used for determining the treatability of industrial wastewaters. This procedure is described in A Procedure For Determination Of The Biological Treatability Of Industrial Wastes (29). Activated sludge from the aeration basin of the Fayetteville Water Pollution Control Plant was used as the source of the microorganisms. The activated sludge was placed in the laboratory-scale activated sludge units and aerated. Each twenty-four hour cycle involved aeration of the units for twenty-three hours, settling of the mixed liquor for one hour, withdrawal of one liter of superna-

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tant and the addition of one liter of wastewater. The wastewater added was initially 100 percent primary clarifier effluent. At each twenty-four hour interval, the constituency of the wastewater fed was modified. That is, the proportion of primary clarifier effluent was decreased by 10 percent. Thus, the wastewater added consisted of 90 percent primary clarifier effluent and 10 percent coal slurry wastewater the second day. This procedure was continued Thereafter, only slurry until 100 percent coal slurry wastewater was added. wastewater was added until the biological treatability studies were initiated. Adequate nutrients were added to the activated sludge units to insure that growth was not inhibited by insufficient nutrients. The pH of the mixed liquor was checked and adjusted daily to within the range of 6.5 to 7.5. Potassium phosphate was used for adjusting the pH. The mixed liquor suspended solids concentrations were monitored to determine the stability of the acclimation.

The second approach was to collect soil/coal samples from a coal mine and to use the microorganisms in this material as the organisms for determining biological treatability of the slurry wastewaters. Both procedures were successful.

Two batch-fed, fill and draw aeration units were operated at food-to-microorganism (F:M) ratios of 0.2 and 0.6 for the treatability studies. Figure 5 shows a sketch of the laboratory activated sludge units used in the investigations. Calcium chloride, ferric chloride, magnesium sulfate and phosphate were added in accordance with the procedures outlined in Part 507 of <u>Standard</u> <u>Methods For The Examination Of Water And Wastewater</u> for dilution water (30). Air was supplied at a rate of two liters per minute to each unit through porous stone diffusers.

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Figure 5: Laboratory Activated Sludge Units (after Symons, et.al, (29))

ANALYTICAL PROCEDURES

Tests performed on the slurry wastewaters for the characterization studies included alkalinity, boron, calcium, soluble biochemical oxygen demand, soluble chemical oxygen demand, chloride, chromium, copper, dissolved solids, fluoride, iron, lead, magnesium, manganese, nickel, nitrate, pH, phosphate, potassium, silica, specific conductance, sodium, sulfate, titanium, total hardness and zinc. For the biological treatability study the following parameters were measured: soluble and total five-day biochemical oxygen demand, soluble and total chemical oxygen demand, soluble total organic carbon, soluble inorganic carbon, volatile suspended solids, total suspended solids and pH.

Alkalinity

Total alkalinity concentrations were determined in accordance with the procedures described in Part 403 of <u>Standard Methods For The Examination Of</u> <u>Water And Wastewater</u> (30). Since the pH values of all samples were below 8.3 no phenolphthalein alkalinity was present in any of the samples.

Aluminum

The aluminum concentrations were measured using a Perkin-Elmer Model 305B atomic absorption spectrophotometer using a Cathodeon hollow cathode lamp. Solutions with aluminum concentrations of 0.5, 1.0, 1.5 and 2.0 milligrams per liter were used to develop the standard curves. The procedures described in <u>Analytical Methods For Atomic Absorption Spectrophotometry</u> were used as the test method (31).

Biochemical Oxygen Demand

The five-day biochemical oxygen demand concentrations were determined in accordance with the procedures described in Part 507 of <u>Standard Methods For</u> <u>The Examination Of Water And Wastewater</u>. Acclimated seeds were used in the biochemical oxygen demand determinations. The seeds were developed in accordance with the procedures outlined by Symons, et. al. (29) and are described as follows:

- One and one-half liters of activated sludge were collected from the aeration basin of the Fayetteville Water Pollution Control Plant, and were poured into the laboratory activated sludge unit.
- 2. The sample was aerated for a period of 23 hours at a rate of two liters of air per minute through a porous stone diffuser.
- 3. At the completion of the aeration period, the sample was allowed to settle for one hour. One liter was then decanted from the unit followed by the addition of one liter of wastewater.
- 4. The wastewater added to the activated sludge units daily was varied from 100 percent municipal wastewater and 0 percent slurry wastewater on the first day to 0 percent municipal wastewater and 100 percent slurry wastewater on the tenth day.
- 5. After the ten day period the microorganisms in the activated sludge unit were acclimated and only slurry wastewater was added thereafter. This served as the seed for the biochemical oxygen demand determination.

Boron

Boron measurements were made using the circumin turbidimetric method as described in Part 405A of <u>Standard Methods</u> For <u>The Examination Of</u> <u>Water And</u> <u>Wastewater</u> (30). Sample turbidity was measured using a Coleman Hitachi 101 spectrophotometer.

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Cadmium

Cadmium measurements were conducted using a Perkin-Elmer Model 305B atomic absorption spectrophotometer in accordance with the procedures described in Analytical Methods For Atomic Absorption Spectrophotometry (31).

Calcium

Calcium concentrations were measured using the procedures described in Part 306C of <u>Standard Methods For The Examination Of Water And Wastewater</u> (30). Twenty-five milliliter samples were used in these measurements.

Carbon

The inorganic carbon concentrations were determined with a Beckman Model 915 Total Organic Carbon Analyzer in accordance with the procedures described in <u>Standard Methods For The Examination Of Water And Wastewater</u> (30).

Total organic carbon concentrations were determined by measuring the total carbon content and deducting the inorganic carbon concentrations. The total carbon measurements were made using the Beckman carbon analyzer in accordance with the procedures described in <u>Standard Methods For The Examination Of</u> <u>Water And Wastewater</u> (30).

Chemical Oxygen Demand

Chemical oxygen demand concentrations were measured using the procedures described in Part 509 of <u>Standard Methods For The Examination Of Water And</u> <u>Wastewater</u> (30). Chemical oxygen demand measurements in the water quality characterization studies were conducted on samples filtered through 0.45 micron glass fiber filters yielding soluble chemical oxygen demand concentrations. The sample size used was 20 milliliters.

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Chloride

The concentration of chloride in each sample was measured by titration in accordance with the procedure described in Part 408B of <u>Standard Methods For</u> The Examination Of Water And Wastewater (30).

Dissolved Solids

Dissolved solids concentrations were determined in accordance with the method described in Part 407B of <u>Standard Methods</u> For The <u>Examination Of Water</u> And Wastewater (30).

Fluoride

Fluoride measurements were made using the SPADNS Method in accordance with the procedures described in Part 414C of <u>Standard Methods For The Exami-</u> <u>nation Of Water And Wastewater</u> (30). The sample turbidity was measured using a Coleman Hitachi 101 spectrophotometer.

Iron

Iron concentrations were determined with a Perkin-Elmer Model 305B atomic absorption spectrophotometer in accordance with the method described in <u>Ana-</u> lytical Methods For Atomic Absorption Spectrophotometry (31).

Lead

The lead data were developed using a Perkin-Elmer Model 305B atomic absorption spectrophotometer in accordance with the procedures described in <u>Ana-</u> <u>lytical Methods For Atomic Absorption Spectrophotometry</u> (31). Solutions of 0.1, 0.2, 0.3 and 0.4 milligrams per liter were used to develop the standard curves.

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Magnesium

The magnesium data were developed using a Perkin-Elmer Model 305B atomic absorption spectrophotometer with a Cathodeon hollow cathode lamp. The solutions used to develop the curves contained 0.1, 0.2, 0.4 and 0.5 milligrams per liter. The method described in <u>Analytical Methods For Atomic Absorption</u> Spectrophotometry was used (31).

Manganese

Manganese concentrations were determined using a Perkin-Elmer Model 305B atomic absorption spectrophotometer with the procedures described in <u>Analyti</u>cal Methods For Atomic Absorption Spectrophotometry (31).

Nickel

Nickel concentrations were measured with a Perkin-Elmer Model 305B atomic absorption spectrophotometer. The procedures described in <u>Analytical Methods</u> For Atomic Absorption Spectrophotometry were used (31).

Nitrate

The nitrate concentrations were measured by the cadmium reduction method. Hach Nitraver V Nitrate Reagent was used in the analyses. A Coleman Hitachi 101 spectrophotometer was used to measure the light transmittance. The procedures described in <u>Hach Water And Wastewater Analysis</u> <u>Procedures Manual</u> were used (32). The pH of each sample was measured with a Beckman Zeromatic pH meter. The meter was standardized at pH values of 4, 7 and 10.

Phosphate

The phosphate concentrations were determined using the single reagent method for phosphorous and orthophosphate as described in <u>Standard Methods For</u> <u>The Examination Of Water And Wastewater</u> (30). Turbidity measurements were conducted with a Coleman Hitachi 101 spectrophotometer.

Potassium

Potassium concentrations were determined with the Perkin-Elmer Model 305B atomic absorption spectrophotometer using a Jarrell Ash hollow cathode lamp. The standard curves were developed using solutions containing 0.5, 0.75, 1.0, 1.5 and 2.0 milligrams per liter. The procedures used are described in <u>Ana-</u> lytical Methods For Atomic Absorption Spectrophotometry (31).

Silica

Silica was determined in accordance with the procedures described in Part 426C of <u>Standard Methods</u> For <u>The Examination</u> <u>Of Water And</u> <u>Wastewater</u> (30). The results are reported in milligrams per liter as SiO2.

Sodium

The sodium concentrations were measured using the Perkin-Elmer Model 305B atomic absorption spectrophotometer. A Cathodeon hollow cathode lamp was used for the test. Standard curves were developed using solutions of 0.2, 0.5, 0.8

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and 1.0 milligrams per liter. The tests were conducted in accordance with the procedures described in <u>Analytical Methods</u> For <u>Atomic Absorption Spectrophoto-</u><u>metry</u> (31).

Suspended Solids

The suspended solids determinations were made in accordance with the procedures described in Part 208C of <u>Standard Methods</u> For The <u>Examination Of</u> <u>Water And Wastewater</u> (30).

Titanium

The titanium concentrations were measured using the Perkin-Elmer Model 305B atomic absorption spectrophotometer with a Cathodeon hollow cathode lamp. The standard curves were developed using solutions containing 0.5, 0.75, 1.0 and 1.25 milligrams per liter. The test procedures described in <u>Analytical</u> Methods For Atomic Absorption Spectrophotometry were used (31).

Total Hardness

Total hardness concentrations were measured using the procedures listed in Part 309B of <u>Standard Methods For The Examination Of</u> <u>Water And Wastewater</u> (31). Twenty-five milliliter samples were used in the tests.

Zinc

Zinc concentrations were measured with the Perkin-Elmer Model 305B atomic absorption spectrophotometer in accordance with the procedures outlined in <u>Analytical Methods For Atomic Absorption Spectrophotometry</u> (31).

Chapter 5

RESULTS AND DISCUSSION

Nine objectives were identified in the research program. These were: 1) to determine the type and extent of water quality changes which will occur as a result of slurry pipelining of high-sulfur Eastern coal; 2) to determine the treatment procedures applicable for restoration of the wastewater resulting from the slurry pipelining of high-sulfur Eastern coal; 3) to develop the ultimate biochemical oxygen demand curves for coal samples from several sources to determine their similarities and differences, and to determine if the curves are predictable; 4) to identify and assess the significance of the factor inhibiting biological treatment of the slurry wastewater; 5) to identify the type and extent of organic materials present in the slurry wastewa-6) to assess the significance of these organic materials; 7) to deterter: mine the treatment measures suitable for removal of the organic materials, if 8) to develop a procedure whereby the chemical parameter concennecessary; trations can be predicted for a given coal and water quality, and; 9) to investigate the feasibility of using saline water as the slurry medium. The research program was divided into nine phases corresponding with the nine objectives.

PHASE I RESULTS

The objective of this phase was to determine the type and extent of water quality changes which will result from the slurry pipelining of high-sulfur Eastern coal. Kansas and Illinois coals were used to develop these data.

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Alkalinity

Alkalinity in water consists of some combination of carbonate, bicarbonate and hydroxide ions depending on pH. Alkalinity serves as a buffer which resists changes in pH to either higher or lower values, as do other weak bases The buffering capacity in a solution is a function of the and weak acids. concentration of alkalinity present and is a direct function of the concentration. That is, the greater the alkalinity concentration the larger is the buffering capacity. When no buffering capacity is present, the pH can fluctuate radically when only small amounts of acids or bases are added. Conversely, a water with a large buffering capacity will reflect only small increases or decreases in pH even when relatively large amounts of bases or acids are added. Large concentrations of alkalinity in water are ordinarily objectionable. However, the alkalinity concentrations measured during the experimental work were all low.

The endpoints of the titrations for phenolphthalein and total alkalinities are 8.3 and 4.3. Because the pH of all samples titrated was below 8.3, no phenolphthalein alkalinity was present in any of the samples. Figure 6 shows the alkalinity concentrations in slurry wastewaters prepared with Kansas coal and two water sources - distilled water and surface water. As shown by the figure, the total alkalinity concentrations in the slurry wastewaters prepared with the surface water generally exceeded those in the wastewater prepared with the distilled water. Although the data were somewhat variable, a general trend of decreasing alkalinity as a function of detention time was apparent. The decreasing trend is consistent with data developed using Western coals (1,2). The variation in the data probably reflects leaching of a fraction of the calcium carbonate present in the coal with a simultaneous destruction of some of the alkalinity.

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Figure 6: Total Alkalinity As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

Figure 7 provides a comparison of the alkalinity concentrations in slurry wastewaters prepared with distilled water and wastewater treatment plant effluent. These data also indicated a generally decreasing trend as a function of detention time. The average concentrations for the distilled water and final effluent runs were 19 and 34 milligrams per liter, respectively. The background concentration in the final effluent was 20 milligrams per liter and did not change during the experimental run. The alkalinity in the slurry wastewaters prepared with the final effluent ranged from 15 to 45 milligrams per liter. Kansas coal was used to form the slurries.

Figure 8 shows a comparison of the alkalinity concentrations in slurry wastewaters prepared with distilled water using Kansas and washed Illinois coals. The average alkalinity concentrations were 18 and 10 milligrams per liter, respectively, for the slurries prepared with the Kansas and Illinois coals.



Figure 7: Total Alkalinity As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

Figure 9 provides a graphical comparison of the alkalinity concentrations in slurry wastewaters prepared with distilled water and final effluent using Illinois coal. The background concentration in the final effluent was 17 milligrams per liter and remained constant throughout the experimental run.

A comparison of the total alkalinity concentrations in slurry wastewaters prepared with distilled water and treated surface water using Illinois coal is shown on Figure 10. The average concentrations were 10 and 8 milligrams per liter, respectively, for the slurries prepared with the distilled and surface waters.



Figure 8: Total Alkalinity As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water Using Kansas And Illinois Coals At 50 Percent Solids In An Anaerobic Environment.



Figure 9: Total Alkalinity As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled And Final Effluent Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.



Figure 10: Total Alkalinity As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled And Surface Water Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.

Biochemical Oxygen Demand

Biochemical oxygen demand can be defined as the quantity of molecular oxygen required to stabilize the biodegradable fraction of a waste by aerobic biochemical action. The two biochemical oxygen demand values ordinarily used are the five-day biochemical oxygen demand (BOD5) and the ultimate biochemical oxygen demand (BODu). The five-day biochemical oxygen demand refers to the quantity of oxygen required to stabilize a waste in a five-day incubation period at twenty degrees Celsius. The ultimate biochemical oxygen demand refers to the maximum quantity of oxygen required to biologically stabilize a waste aerobically with an incubation temperature of 20 degrees Celcius. The ultimate biochemical oxygen demand is usually exerted in 25 to 30 days for "typical" domestic wastewater and is usually about 1.5 times the five-day biochemical oxygen demand. These relationships do not necessarily hold true for
industrial wastewaters. Industrial wastewaters may range from non-biodegradable to readily biodegradable depending on the type of industrial waste involved.

In general, the five-day biochemical oxygen demand concentrations in the slurry wastewaters prepared with the two Eastern coals were relatively low, both with respect to municipal wastewater and with slurry wastewaters prepared with Western coals. Figure 11 shows the five-day biochemical oxygen demand concentrations as a function of time for slurry wastewaters prepared with distilled water and surface water using Kansas coal. The biochemical oxygen demand concentrations in the slurry wastewaters prepared with the distilled water tended to remain more constant than those representing the surface The latter exhibited a decreasing trend as a function of increasing water. detention time. The average concentrations were 58 and 37 milligrams per liter, respectively, for the distilled water and surface water slurry wastewaters. The surface water average is somewhat misleading because of the significant decrease in concentration observed in the later stages of the experimen-No five-day biochemical oxygen demand was present in the surface tal run. water prior to mixing with coal.

Chemical Oxygen Demand

The chemical oxygen demand test also provides a measure of the organic materials present in a slurry wastewater. The test uses a strong oxidant (potassium dichromate) in the presence of a strong acid (sulfuric) and heat to oxidize organic materials present in a sample. Since the chemical oxygen demand test measures both non-biodegradable and biodegradable organic material,

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Figure 11: Five-Day Biochemical Oxygen Demand Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

the chemical oxygen demand in a wastewater sample is larger than the biochemical oxygen demand, except in those instances when certain specific chemicals which interfere with the test are present.

A graphical comparison of the chemical oxygen demand concentrations in slurry wastewaters prepared with distilled water and surface water using Kansas coal is shown on Figure 12. As shown by the figure, the chemical oxygen demand concentrations in the slurry wastewaters prepared with distilled water were generally greater than those representing the surface water slurry wastewaters. The average chemical oxygen demand concentrations were 92 and 55 milligrams per liter for the distilled water and surface water slurries, respectively.

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Figure 12: Chemical Oxygen Demand Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

A similar comparison of chemical oxygen demand concentrations in slurry wastewaters prepared with distilled water and wastewater treatment plant effluent is shown on Figure 13. The average concentrations were 92 and 101 milligrams per liter, respectively, for the distilled water and final effluent slurries. The average concentration in the final effluent during the run was 25 milligrams per liter. Kansas coal was used to form the slurries.

Figure 14 provides a graphical comparison of the chemical oxygen demand concentrations in slurry wastewaters prepared with distilled water and final effluent using Illinois coal. The average concentrations were 23 and 104 milligrams per liter for distilled water and final effluent slurry wastewaters, respectively. The average final effluent chemical oxygen demand concentrations is somewhat misleading because of the high initial concentration.



Figure 13: Chemical Oxygen Demand Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

A similar comparison of chemical oxygen demand concentrations in slurry wastewaters prepared with distilled water and treated surface water is shown on Figure 15. The average concentrations were 23 and 18 milligrams per liter for the distilled and surface water slurries, respectively.

An indication of the effect of coal source on the chemical oxygen demand concentrations in slurry wastewaters prepared with distilled water and the two coals is shown on Figure 16. The average concentrations were 23 and 87 milligrams per liter, respectively, for the Illinois and Kansas coal slurries. Although the concentrations were significantly different, they were relatively low in both sets of data.



Figure 14: Chemical Oxygen Demand Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.



Figure 15: Chemical Oxygen Demand Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.



Figure 16: Chemical Oxygen Demand Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water Using Kansas And Illinois Coals At 50 Percent Solids In An Anaerobic Environment.

Five-Day Biochemical Oxygen Demand/Chemical Oxygen Demand

A comparison of the five-day biochemical oxygen demand and chemical oxygen demand concentrations in slurry wastewaters prepared with distilled water and Kansas coal is shown on Figure 17. The average five-day biochemical oxygen demand to chemical oxygen demand ratio was 0.67 which indicated a readily biodegradable wastewater.

Figure 18 shows graphically the five-day biochemical oxygen demand and chemical oxygen demand concentrations in slurry wastewaters prepared with final effluent and Kansas coal. The average five-day biochemical oxygen demand to chemical oxygen demand concentration was 0.46 which indicates a biodegradable wastewater.



Time, days

Figure 17: Comparison Of Five-Day Biochemical Oxygen Demand And Chemical Oxygen Demand Concentrations In Slurry Wastewaters Prepared With Distilled Water And Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

Boron

Concentrations of boron in the slurry wastewaters prepared with the Kansas coal were all below the detection limits of the test procedure used. No boron measurements were made on slurry wastewaters prepared with the Illinois coal.

Calcium And Total Hardness

The term hardness usually refers to the sum of the calcium and magnesium concentrations in a water sample, expressed on a common basis. Technically, the term may refer to the sum of the divalent metal cations or it may refer to the sum of the multivalent metal cations in a sample. Because calcium and magnesium are the predominate metal cations in most waters, all three definitions yield about the same value. The term, as used in this report, refers to the sum of the calcium and magnesium both expressed as calcium carbonate.

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Figure 18: Comparison Of Five-Day Biochemical Oxygen Demand And Chemical Oxygen Demand Concentrations In Slurry Wastewaters Prepared With Final Effluent And Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

Figure 19 shows the relationships between calcium and total hardness in slurry wastewaters prepared with distilled water and Kansas coal. The average calcium to total hardness ratio was 0.73 and was relatively consistent throughout the experimental run. The average ratio ranged from 0.71 to 0.76.

A similar comparison of calcium and total hardness concentrations in slurry wastewaters prepared with surface water and Kansas coal is shown on Figure 20. As indicated by the figure, calcium was the predominate hardness constituent. The average calcium and total hardness concentrations were 1,650 and 2,160 milligrams per liter, respectively. The average calcium to total hardness ratio was 0.77.

A comparison of calcium concentrations in slurry wastewaters prepared with distilled water and surface water is shown on Figure 21. As shown by the



Figure 19: Calcium And Total Hardness Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

figure, the calcium hardness in the slurry wastewaters prepared with the surface water exhibited higher concentrations than those prepared with distilled water, as would be expected. The average calcium concentrations were 1,520 and 1,660 milligrams per liter, respectively, for the slurry wastewaters prepared with distilled water and surface waters.

A similar comparison of total hardness concentrations in slurry wastewaters prepared with distilled water and surface water is shown on Figure 22. The average concentrations were 2,200 and 2,160 milligrams per liter for slurry wastewaters prepared with distilled water and surface water, respectively. The very high concentrations of hardness blanked out the background concentration in the surface water.



Figure 20: Calcium And Total Hardness Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Surface Water And Kansas Coal At 50 Percent Solids In An Anaerobic Environment.



Figure 21: Calcium Hardness Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.



Figure 22: Total Hardness Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

Figure 23 shows a graphical comparison of the calcium concentrations in slurry wastewaters prepared with distilled water and surface water using Kansas coal. The average calcium concentrations were 1,520 and 1,590 milligrams per liter, respectively, for slurry wastewaters prepared with distilled water and wastewater treatment plant effluent.

A similar comparison of total hardness concentrations is shown on Figure 24. The average concentrations were 2,200 and 2,230 milligrams per liter for the slurry wastewaters prepared with distilled water and final effluent, respectively. The background total hardness concentration in the final effluent was 120 milligrams per liter. The average calcium to total hardness ratio was 0.71 for the final effluent experimental run.

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Figure 23: Calcium Hardness Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

Figure 25 portrays graphically the calcium and total hardness concentrations in slurry wastewaters prepared with Illinois coal. The average concentrations were 1,980 and 2,140 milligrams per liter for slurry wastewaters prepared with distilled water and the Illinois coal. The average calcium to total hardness ratio was 0.94. As indicated by the figure, the hardness clearly tended to increase with increasing detention time.

A similar comparison of calcium and total hardness concentrations is shown on Figure 26. These data represent slurry wastewaters prepared with treated surface water and Illinois coal. The average concentrations were 2,070 and 2,170 milligrams per liter, respectively, for the calcium and total hardness. As shown by the figure, the predominate hardness constituent was calcium with only relatively small quantities of magnesium present. The average calcium to total hardness ratio of 0.95 also reflects the high percentage



Figure 24: Total Hardness Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic



Figure 25: Calcium And Total Hardness Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.

of calcium. These data also indicated a tendency for increasing concentrations with increasing detention time.



Figure 26: Calcium And Total Hardness Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Surface Water And Illinois Coal At 50 Percent Solids In An Anaerobic Environment.

Figure 27 shows the calcium and total hardness concentrations in slurry wastewaters prepared with final effluent and Illinois coal. The average calcium and total hardness concentrations were 2,370 and 2,510 milligrams per liter, respectively.

The effect of coal source on the calcium hardness concentrations in slurry wastewaters prepared with distilled water is shown on Figure 28. As shown by the figure, the calcium concentrations in the slurry wastewater prepared with the Kansas coal were significantly lower than in slurry wastewaters prepared with Illinois coal. The average concentrations were 1,520 and 1,980



Figure 27: Calcium And Total Hardness Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Final Effluent And Illinois Coal At 50 Percent Solids In An Anaerobic Environment.

milligrams per liter, respectively, for the Kansas and Illinois coal wastewaters.

A similar comparison of total hardness concentrations is shown on Figure 29. The average total hardness concentrations were 2,200 and 2,140 milligrams per liter for the Kansas and Illinois coals, respectively. These curves show the different tendencies as a function of detention time previously noted.

The calcium to total hardness concentrations were substantially different for slurry wastewaters prepared with the two coals. Figure 30 shows these ratios. The average ratios were 0.73 and 0.94, respectively, for the Kansas and Illinois coals.

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Figure 28: Calcium Hardness Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water Using Kansas And Illinois Coals At 50 Percent Solids In An Anaerobic Environment.



Figure 29: Total Hardness Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water Using Kansas And Illinois Coals At 50 Percent Solids In An Anaerobic Environment.



Figure 30: Calcium To Total Hardness Ratios As A Function Of Time For Slurry Wastewaters Prepared With Distilled Water Using Illinois And Kansas Coals At 50 Percent Solids In An Anaerobic Environment.

Chloride

The chloride concentrations in slurry wastewaters prepared with the two coals were substantially different. The average concentrations were 90 and 1,500 milligrams per liter for slurry wastewaters prepared with the Illinois and Kansas coals, respectively. Figure 31 shows the data for the two experimental runs conducted with distilled water used as the slurry media.

Dissolved Solids

Dissolved solids represents the residue remaining following passage of a sample through a 0.45 micron glass fiber filter and subsequent evaporation to dryness. Surface water quality standards contain limits on the amount of dissolved solids which may be discharged to surface watercourses. For this reason, this parameter is particularly important with respect to the water quality aspects of coal slurry pipelining.

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Figure 31: Chloride Concentrations As A Function Of Detention Time For Slurry Wastewater Prepared With Distilled Water Using Kansas And Illinois Coals At 50 Percent Solids In An Anaerobic Environment.

The dissolved solids concentrations in the slurry wastewaters prepared with the two coals were significantly different for the two coals. Figure 32 shows the dissolved solids concentrations in slurry wastewaters prepared with distilled water and final effluent using the Kansas coal. As shown by the figure, the general tendency was for increasing dissolved solids concentrations as a function of detention time. Little difference in the dissolved solids concentrations of the slurry wastewaters prepared with distilled water and final effluent was observed. The average concentrations were 3,610 and 3,540 milligrams per liter, respectively, for the slurry wastewaters prepared with the distilled water and wastewater treatment plant effluent. The average total dissolved solids concentration in the wastewater treatment plant effluent was 450 milligrams per liter.



Time, days

Figure 32: Dissolved Solids Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

Similar results were observed for the experimental runs conducted with distilled water and surface water with the Kansas coal. The average dissolved solids concentrations were 3,610 and 3,420 milligrams per liter for the distilled water and surface water slurry wastewaters, respectively. Figure 33 shows the comparison of these data.

Dissolved solids concentrations in slurry wastewaters prepared with surface water and the two coals are shown on Figure 34. As shown by the figure, the dissolved solids in the slurry wastewaters prepared with the Illinois coal were substantially greater than with the Kansas coal. The average concentrations were 3,420 and 5,600 milligrams per liter, respectively, for the Kansas and Illinois coals.



Figure 33: Dissolved Solids Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

Fluoride.

Figure 35 shows the fluoride concentrations in slurry wastewaters prepared with distilled water and surface water using Kansas coal. The average concentrations were 1.54 and 1.76 milligrams per liter for the slurry wastewaters prepared with the distilled water and surface water, respectively. The background concentration in the surface water was 0.60 milligrams per liter. Thus, the concentrations were not additive.

Figure 36 portrays graphically the comparison of fluoride concentrations in slurry wastewaters prepared with distilled water and surface water using Kansas coal. The average concentrations were 1.54 and 1.94 milligrams per liter, respectively, for slurry wastewaters prepared with distilled water and wastewater treatment plant effluent. The background concentration was 1.27 milligrams per liter in the final effluent. The fluoride concentrations in

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Figure 34: Dissolved Solids Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Surface Water Using Kansas And Illinois Coals At 50 Percent Solids In An Anaerobic Environment.



Figure 35: Fluoride Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

the distilled water data were not additive with the background concentrations in the final effluent.



Figure 36: Fluoride Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

A comparison of fluoride concentrations in slurry wastewaters prepared with Illinois coal is shown on Figure 37. The average concentrations were 1.60 milligrams per liter for slurry wastewaters prepared with both the distilled water and surface water.

Figure 38 provides a comparison of the fluoride concentrations in slurry wastewaters prepared with distilled water using the two coals. There was very little difference in the data with respect to coal source. The average concentrations were 1.54 and 1.60 milligrams per liter, respectively, for slurry wastewaters prepared with the Kansas and Illinois coals.

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Figure 37: Fluoride Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.

Iron

The iron concentrations in the slurry wastewaters prepared with both coals were very low. Consequently, the iron concentrations were not measured routinely in the study. However, after the coal was exposed to ambient atmospheric conditions for an extended length of time, the iron concentrations in slurry wastewaters were very high. Thus, aging of the coal with respect to exposure to atmospheric conditions may result in significant iron concentrations in the liquid phase of the coal-water mixture.

Lead

Lead was measurable in slurry wastewaters prepared with both coals. Figure 39 shows the lead concentrations in slurry wastewaters prepared with distilled water and surface water using Kansas coal. A general tendency for de-



Figure 38: Fluoride Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water Using Kansas And Illinois Coals At 50 Percent Solids In An Anaerobic Environment.

creasing lead concentrations as a function of detention time was observed. The average concentrations were 0.10 and 0.12 milligrams per liter for the distilled water and surface water slurry wastewaters, respectively.

The concentrations of lead in slurry wastewaters prepared with the Illinois coal were below the detectable limits of the test procedure used.

Manganese

Manganese concentratons in the slurry wastewaters prepared with distilled water and surface water using Kansas coal were variable although a general decreasing trend was observed as a function of detention time. The average concentrations were 3.5 and 3.4 milligrams per liter, respectively, for slurry wastewaters prepared with distilled water and surface water. No significance should be attached to the difference in the average concentrations as the 0.1

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Time, days

Figure 39: Lead Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

milligrams per liter difference is within the experimental error. Figure 40 shows the data obtained during these two experimental runs.

The manganese concentrations in slurry wastewaters prepared with final effluent from the wastewater treatment plant were also variable and indicated a generally decreasing trend as a function of detention time. Figure 41 graphically portrays these data. The average concentrations were 3.5 and 4.3 milligrams per liter for the slurry wastewaters prepared with distilled water and final effluent, respectively.

Manganese concentrations in slurry wastewaters prepared with the Illinois coal were lower than in wastewaters prepared with the Kansas coal. Figure 42 shows the data for the wastewaters prepared with surface water and final ef-

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Figure 40: Manganese Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.



Figure 41: Manganese Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

fluent. The average concentrations were 1.1 and 0.7 milligrams per liter for the slurry wastewaters prepared with the surface water and final effluent, respectively.



Figure 42: Manganese Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.

Nickel

Nickel concentrations in slurry wastewaters prepared with the Kansas coal and distilled and surface waters were clearly a function of detention time. The concentrations decreased with increasing detention time. The average concentrations were 0.7 milligrams per liter for both runs reflecting removal of much of the nickel from the aqueous phase. The data are displayed graphically on Figure 43.

The clear tendency for reduced nickel concentrations with increasing detention time also was observed in the experimental run conducted with wastewa-

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Time, days

Figure 43: Nickel Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

ter treatment plant effluent. A comparison of data measured on slurry wastewaters prepared with distilled water and final effluent is shown on Figure 44. The average concentrations were 0.7 and 0.8 milligrams per liter, respectively, for slurry wastewaters prepared with distilled water and final effluent using Kansas coal. The background concentration in the wastewater treatment plant effluent was below the detectable limits of the test procedure used.

Similar results were obtained in the experimental runs conducted with distilled water and Illinois coal. Figure 45 shows a comparison of the nickel concentrations in slurry wastewaters prepared with distilled water and Illinois and Kansas coals. The average concentrations were 0.4 and 0.7 milligrams per liter for the Illinois and Kansas coals, respectively. Significant differences in the initial concentrations were evident. The nickel concentra-

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Figure 44: Nickel Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

tions after one hour of mixing were 3.9 and 0.8 milligrams per liter, respectively, for the slurry wastewaters prepared with the Kansas and Illinois coals.

рH

The pH values in slurry wastewaters prepared with distilled water and surface water using Kansas coal are shown on Figure 46. As indicated by the figure, there was a general tendency for increasing pH as a function of detention time. The average pH values were 7.6 and 7.7, respectively, for the distilled water and surface water slurries. All pH values were well within a satisfactory range.



Time, days

Figure 45: Nickel Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Surface Water Using Kansas And Illinois Coals At 50 Percent Solids In An Anaerobic Environment.

The pH values for slurry wastewaters prepared with distilled water and wastewater treatment plant effluent using Kansas coal are shown on Figure 47. Greater fluctuations in the pH values of the slurry wastewaters prepared with the final effluent were observed than in the wastewater prepared with the distilled water. However, all pH values were well within an acceptable range. The average pH values for both runs were 7.6.

The pH values of slurry wastewaters prepared with distilled water and surface water using Illinois coal are shown on Figure 48. The average pH values were 7.2 for both experimental runs.

A similar comparison of pH values for slurry wastewaters prepared with distilled water and wastewater treatment plant effluent using Illinois coal is shown on Figure 49. As indicated by the figure, the pH values of the slurry



Time, days

Figure 46: pH As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.



Figure 47: pH As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.



Figure 48: pH As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.

wastewaters prepared with the final effluent were lower than for the wastewaters prepared with the distilled water. The average pH values were 7.2 and 6.7, respectively, for slurry wastewaters prepared with distilled water and final effluent.

Phosphate

Phosphate concentrations in the slurry wastewaters prepared with both the Kansas and Illinois coals were below the detectable limit for the single reagent method used in the analysis.



Figure 49: pH As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.

Potassium

Potassium concentrations in the slurry wastewaters prepared with distilled water and surface water were relatively low and would not be significant. A general tendency for increasing potassium concentrations as a function of detention time was indicated by the data. The average concentrations were 11.1 and 11.5 milligrams per liter, respectively, for slurry wastewaters prepared with distilled water and surface water using Kansas coal. The data are shown on Figure 50.

The potassium concentrations in slurry wastewaters prepared with distilled water and final effluent using Kansas coal are shown on Figure 51. These data also indicated a general tendency for increasing concentrations as a function of detention time. The average concentrations for the distilled water and final effluent runs were 11.1 and 13.4 milligrams per liter, respectively.

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Figure 50: Potassium Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

Figure 52 shows the potassium concentrations as a function of detention time for slurry wastewaters prepared with the Illinois coal. Very little difference in the average concentrations was observed for the two experimental runs. The average concentrations were 26 and 29 milligrams per liter, respectively, for the surface water and final effluent runs.

The difference in potassium concentrations between slurry wastewaters prepared with the two coals was significant. However, the concentrations were not high for either set of data and, except for a relatively minor contribution to dissolved solids, would not be significant. Figure 53 shows a comparison of the potassium concentrations in slurry wastewaters prepared with surface water and the two coals. The average concentrations were 11.5 and 26.0 millgrams per liter for slurry wastewaters prepared with Kansas and Illinois coals, respectively.

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Figure 51: Potassium Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.



Figure 52: Potassium Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Surface Water And Final Effluent Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.



Time, days

Figure 53: Potassium Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Surface Water Using Kansas And Illinois Coals At 50 Percent Solids In An Anaerobic Environment.

Silica

Silica concentrations in all experimental runs conducted with the Kansas coal were erratic with no clearly discernible trends. The concentrations were relatively low and represent only a minor contribution to dissolved solids. The primary concern with silica is that it will precipitate on heat exchanger surfaces if the temperature is elevated sufficiently. Reduction in heat transfer rates results from the silica scale. This phenomenom is widely known and, where necessary, remedial measures are taken to avoid the problem. Consequently, the silica concentrations measured in the experimental runs have relatively little significance. Figure 54 shows a comparison of the silica concentrations as a function of detention time for slurry wastewaters prepared with distilled water and surface water using Kansas coal. The average concentrations were 5.6 and 6.7 milligrams per liter (as SiO2). respectively, for
slurry wastewaters prepared with distilled water and surface water. The background concentration in the surface water was 2.0 milligrams per liter.



Figure 54: Silica Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

A similar comparison of silica concentrations in distilled water and wastewater treatment plant effluent slurry wastewaters using Kansas coal is shown on Figure 55. As shown by the figure, the silica concentrations were also erratic in the slurry wastewaters prepared with the final effluent. The average concentrations were 5.6 and 7.3 milligrams per liter, respectively, for slurry wastewaters prepared with distilled water and final effluent. The average silica concentration of 7.3 milligrams per liter for the final effluent experimental run was less than the background silica concentration of 12 milligrams per liter. Consequently, this factor combined with a tendency for decreasing silica concentrations with increasing detention time during the

last one-half of the run indicated that silica was being removed from the aqueous phase.



Figure 55: Silica Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Final Effluent Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

A comparison of the silica concentrations in slurry wastewaters prepared with the Illinois and Kansas coals is shown on Figure 56. As indicated by the figure, the silica concentrations in the slurry wastewaters prepared with the Illinois coal were less than those prepared with the Kansas coal. The average concentrations were 3.9 and 5.6 milligrams per liter (as SiO2), respectively, for the slurry wastewaters prepared with Illinois and Kansas coals. Distilled water was used as the slurry media for these experimental runs. Although the difference in concentrations was clearly apparent, the concentrations of silica were low in both sets of data.



Figure 56: Silica Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water Using Kansas And Illinois Coals At 50 Percent Solids In An Anaerobic Environment.

Figure 57 shows a comparison of silica concentrations in slurry wastewaters prepared with distilled water and surface water using Illinois coal. Although the data were erratic, an apparent tendency for decreasing concentrations with increasing detention time was observed near the end of the surface water experimental run. The average concentrations were 3.9 and 5.1 milligrams per liter (as SiO2) for the slurry wastewaters prepared with distilled water and surface water, respectively.

Sodium

The sodium concentrations in slurry wastewaters prepared with distilled water and surface water using Kansas coal are shown on Figure 58. The average concentrations were 48 and 50 milligrams per liter, respectively, for the slurry wastewaters prepared with distilled water and surface water. No clearly definable trends were evident from these data.

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Figure 57: Silica Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.

Figure 59 shows the sodium concentrations in slurry wastewaters prepared with surface water and final effluent using Illinois coal. The average concentrations were 405 and 375 milligrams per liter, respectively, for slurry wastewaters prepared with the surface water and final effluent.

As shown by Figure 60, the sodium concentrations in slurry wastewaters prepared with the Illinois coal were substantially greater than those in the slurry wastewaters prepared with the Kansas coal. The average concentrations were 50 and 405 milligrams per liter for slurry wastewaters prepared with the Kansas and Illinois coals, respectively. Surface water was used as the slurry media for these experimental runs.

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Figure 58: Sodium Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Surface Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.



Time, days

Figure 59: Sodium Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Surface Water And Final Effluent Using Illinois Coal At 50 Percent Solids In An Anaerobic Environment.



Time, days

Figure 60: Sodium Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Surface Water Using Kansas And Illinois Coals At 50 Percent Solids In An Anaerobic Environment.

Sulfate

The sulfate concentrations in slurry wastewaters prepared with both coals were high and were clearly a function of coal source. The average concentrations were 1,400 and 2,250 milligrams per liter, respectively, for slurry wastewaters prepared with Illinois and Kansas coals. Distilled water was used as the slurry media. Figure 61 illustrates the sulfate concentrations with respect to detention time for slurry wastewaters prepared with Kansas coal and distilled water.



Figure 61: Sulfate Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water Using Kansas Coal At 50 Percent Solids In An Anaerobic Environment.

PHASE II RESULTS

The purpose of this phase of the overall research program was to determine the treatment procedures applicable for restoration of the slurry wastewater resulting from the slurry pipelining of high-sulfur coal to acceptable levels. An examination of the water quality characterization data presented in the Phase I results indicates that potential treatment needs can be divided into three categories. These categories include reduction of the organic content of the water, reduction in dissolved solids and constituent ions, and reduction in certain trace metal concentrations.

Although the biochemical oxygen demand and chemical oxygen demand concentrations in the slurry wastewaters prepared using the two Eastern coals were substantially less than for the Western coals previously investigated, the organic content of the slurry wastewater was sufficiently high to require reduc-

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tion in concentration in most cases. Consequently, biological treatment studies were conducted to determine the acceptability of biological treatment processes for reduction of the biochemical and chemical oxygen demand of the slurry wastewater. These studies were conducted using laboratory-scale activated sludge units. The results of the studies indicated that biological treatment of the slurry wastewater is a viable treatment method. Acclimation of the microorganisms will probably be required in the initial start-up of treatment plant operations. However, several acclimation procedures have been used successfully in the laboratory. Consequently, little if any, difficulty is expected with this aspect of the overall treatment plant operations.

Dissolved Solids

The total dissolved solids concentrations in the slurry wastewaters prepared with both coals were high and would ordinarily require reduction in concentration prior to discharge to surface watercourses or before reuse of the wastewater. However, the constituency of the dissolved solids was clearly coal source specific.

Both coals produced high hardness concentrations in their respective slurry wastewaters. However, the relative relationships of calcium and magnesium varied with the coal source. Nearly all of the hardness in slurry wastewaters prepared with the Illinois coal was attributable to calcium whereas about seventy-five percent of the hardness in slurry wastewaters prepared with the Kansas coal was calcium. Both calcium and magnesium can be removed with lime or lime-soda ash softening, as appropriate. However, it is ordinarily less expensive to remove calcium. Consequently, the greater the ratio of calcium to total hardness the less expensive the softening process will be.

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Reduction in dissolved solids concentrations beyond that achievable by reducing the hardness will be relatively expensive. The predominate ions in the slurry wastewater, in addition to the calcium and magnesium, were sodium, chloride and sulfate in the slurry wastewaters prepared with the Illinois coal. Sodium and chloride are monovalent ions and are relatively expensive to remove from water. Although sulfate is a divalent anion it also is relatively expensive to remove. If significant reductions in dissolved solids beyond that achievable by hardness reduction are required, the more expensive treatment processes, such as ion exchange and reverse osmosis must be used.

The predominate ions in the slurry wastewaters prepared with the Kansas coal were calcium, magnesium and sulfate. Although the sodium and chloride concentrations were relatively low compared with the Illinois coal slurry wastewater, the chloride concentration may be significant. The significance of the chloride concentration would be dependent on the water quality standard for the receiving stream and on the relative rates of flow of the slurry wastewater and the receiving stream (the dilution available). Consequently, broad-scale conclusions concerning the significance of the chloride in slurry wastewaters prepared with the Eastern coals cannot be safely drawn. However, reduction in the sulfate concentration may be required to meet the sulfate provision in water quality standards.

Trace Metals

The concentrations of several metals in the slurry wastewaters prepared with the Eastern coals were sufficiently high to require attention in defining the overall treatment requirements in a particular situation. The nickel concentrations, for example, were much higher than would be allowable in most

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cases. However, the concentrations of several of the heavy metals decreased with increasing residence times. The heavy metals can be reduced in concentration by several treatment methods, such as, precipitation, ion exchange and other processes. The determining factor in selecting a treatment process will likely be the level to which the metal concentration must be reduced. Since this level is dependent on the water quality standard in the receiving stream and on the dilution available in the receiving stream, the viability of the several potential treatment processes are site specific. That is, the reduction in concentration of a particular metal by hydroxide precipitation may be adequate at one site but may be inadequate at another.

PHASE III RESULTS

The purpose of this phase was to develop ultimate biochemical oxygen demand curves for slurry wastewaters prepared with coal from various sources to determine their similarities and differences and to determine if the curves are predictable. The results of these investigations indicated that ultimate biochemical oxygen demand concentrations were clearly a function of coal source. With acclimation of the microorganisms, the ultimate demands were exerted within about a twelve-day period. This is a more rapid development of ultimate biochemical oxygen demand than for "typical" domestic wastewater. As would be expected from these results, the five-day biochemical oxygen demand to ultimate biochemical oxygen demand ratios were high with ratios exceeding 0.86 in all investigations. The ratios ranged as high as 0.96 and indicate that the biochemical oxygen demand in the slurry wastewater is readily biodegradable once the microorganisms are acclimated. Figure 62 shows the ultimate biochemical oxygen demand curve developed using Kansas coal. The slurry wastewater used for this analysis was developed using distilled water and the Kansas coal with a forty-eight hour mixing period. The five-day biochemical oxygen demand to ultimate biochemical oxygen demand ratio was 0.86. Acclimation of the microorganisms was accomplished by utilizing municipal wastewater with increasing fractions of coal.slurry wastewater during the acclimation period. The ultimate biochemical oxygen demand for this slurry wastewater was about 175 milligrams per liter.



Figure 62: Ultimate Biochemical Oxygen Demand Curve For Slurry Wastewater Prepared With Distilled Water Using Kansas Coal At 50 Percent Solids With A Forty-Eight Hour Mixing Period.

Figure 63 provides a comparison of the five-day biochemical oxygen demand concentrations in slurry wastewaters mixed for forty-eight hours using Kansas and Wyoming coals. As shown by the figure, the biochemical oxygen demand concentrations in the slurry wastewater prepared with the Wyoming coal were substantially greater than those representing the Kansas coal. The ultimate biochemical oxygen demand concentration was 370 milligrams per liter with a five-day biochemical oxygen demand concentration of 320 milligrams per liter. The five-day biochemical oxygen demand to ultimate biochemical oxygen demand ratio was 0.86. This ratio was equivalent to the ratio for the Kansas coal for the same mixing period.



Time, days

Figure 63: Ultimate Biochemical Oxygen Demand Curve For Slurry Wastewater Prepared With Distilled Water Using Kansas and Wyoming Coals At 50 Percent Solids With A Forty-Eight Hour Mixing Period.

Figure 64 shows the ultimate biochemical oxygen demand curves for slurry wastewaters prepared with the Kansas coal using a 120-hour mixing period. This curve was developed over a ninety day period to assess any long-term phenomena which might develop. The five-day and ultimate biochemical oxygen demand concentrations were 230 and 240 milligrams per liter, respectively, yielding a five-day biochemical oxygen demand to ultimate biochemical oxygen demand ratio of about 0.96.



Figure 64: Ultimate Biochemical Oxygen Demand Curve For Slurry Wastewater Prepared With Distilled Water Using Kansas Coal At 50 Percent Solids With A 120-Hour Mixing Period.

A comparison of the ultimate biochemical oxygen demand curves for the slurry wastewaters prepared with distilled water and Kansas coal with the two mixing periods is shown on Figure 65.

The ultimate biochemical oxygen demand curve for a slurry wastewater mixed in a sequential aerobic-anaerobic environment for thirteen days is shown on Figure 66. The five-day and ultimate biochemical oxygen demand concentrations were 95 and 105 milligrams per liter, respectively. The five-day biochemical oxygen demand to ultimate biochemical oxygen demand ratio was 0.90.



Figure 65: Ultimate Biochemical Oxygen Demand Curve For Slurry Wastewater Prepared With Distilled Water Using Kansas Coal At 50 Percent Solids With 48- and 120-Hour Mixing Periods.



Figure 66: Ultimate Biochemical Oxygen Demand Curve For Slurry Wastewater Prepared With Distilled Water Using Kansas Coal At 50 Percent Solids Mixed In A Sequential Aerobic-Anaerobic Environment For 13 Days.

PHASE IV RESULTS

The primary purpose of this objective was to determine if biological treatment of the slurry wastewater was a viable alternative for reducing the biochemical oxygen demand of the slurry wastewater. Consequently, this objective was addressed to both the biological treatment of slurry wastewaters prepared with both Eastern and Western coals. Several treatability studies were conducted in laboratory activated sludge units using slurry wastewaters pre-The results of these treatability pared with both Eastern and Western coals. studies indicated that biological treatment is a viable alternative, and will probably be the preferred alternative, for reducing the biochemical oxygen demand and chemical oxygen demand of the slurry wastewater. For the coals investigated, acclimation of microorganisms was required before either reliable biochemical oxygen demand concentrations could be determined, or successful activated sludge studies could be conducted. Acclimation of the microorganisms using a synthetic substrate, sodium benzoate, was not successful. However. the use of microorganisms obtained from soil at a coal mine resulted in a successful acclimation. Successful acclimation was also attained using mixed liquor from the aeration basin of an activated sludge wastewater treatment plant used for the treatment of domestic and industrial wastewater.

Some instability seemed to occur during some of the acclimation attempts using the mixed liquor. It was later learned that the municipal treatment plant was experiencing operational problems during this period because of the periodic discharge of heavy metals into the wastewater collection system. Consequently, the apparent instability of the acclimation was probably caused by the heavy metal content of the wastewater.

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The results of the treatability investigations and the laboratory activated sludge treatment studies indicated that biological treatment of the slurry wastewater is a viable alternative. Based on the coals investigated, the requirement for acclimation of microorganisms should be expected.

PHASE V RESULTS

The purpose of this phase was to identify the type and extent of the organic materials present in the slurry wastewater. This phase was included in the research program because of the current concern with respect to the presence of trace organic compounds in some municipal water supplies and in certain municipal and industrial wastewaters. Because of this concern, it was deemed appropriate to examine wastewater which would result from the slurry pipelining of coal to determine if trace organics of concern were present.

Several approaches were used with respect to this objective. These included gas chromatograph-mass spectrometer studies of the wastewater for the priority pollutants and gas chromatographic analyses of the slurry wastewater for aromatic hydrocarbons such as phenols and cresols. All tests exhibited negative results with respect to the organic priority pollutants and with respect to the presence of aromatic hydrocarbons. Consequently, concerns with respect to trace organics should not apply to slurry wastewaters.

PHASE VI RESULTS

The presence of significant concentrations of biochemical and chemical oxygen demands in the slurry wastewaters resulting from the mixing of Western coal and water caused some concern as to the nature of these materials. As indicated in the PHASE V RESULTS section, it was deemed appropriate to examine the slurry wastewaters for the priority pollutants to determine the presence or absence of any of these materials. Gas chromatographic - mass spectrometer studies were used in these evaluations. None of the priority pollutants were found. Consequently, since the organic content of the slurry wastewater can be reduced by either biological treatment or by activated carbon, only the usual significance should be attached to the organic content of the slurry wastewater. That is, assessment of the need for reduction of the biochemical oxygen demand and chemical oxygen demand concentrations needs to be conducted using specific coal and water sources and detention times of the coal slurry in the pipeline for each pipeline project. Such treatment may or may not be required depending on the specific circumstances.

PHASE VII RESULTS

The purpose of this phase of the investigation was to determine the treatment measures suitable for removal of any organic priority pollutants present in the slurry wastewater, should any be found. Of specific interest was the ability of activated carbon columns to reduce the concentrations of any organic priority pollutants to the required level, given the nature of the coal slurry wastewater. Loading rates and other design data suitable for coal slurry wastewater were also of interest. However, since none of the organic priority pollutants were found, these treatment studies were neither required or applicable.

PHASE VIII RESULTS

The purpose of this phase of the investigation was to develop a procedure whereby the chemical parameter concentrations could be predicted for a given coal source and water quality. The major thrust used in the investigation was to statistically examine slurry wastewater quality data to determine the relationship between parameter concentrations and detention time, and to determine the relationship between parameter concentrations and the other variables as a function of detention time. Variables used include coal source, influent water quality, mixing speed, type of environment (aerobic, anaerobic, sequential aerobic-anaerobic) and solids concentration. Linear and multiple regression analyses were used in the statistical analyses.

Since the coal slurry pumped into the pipeline will initially be aerobic because of the dissolved oxygen contained in the coal-water mixture, slurry wastewater quality data developed in an aerobic environment were used to develop the initial tendencies or trends. After an interval of time, the dissolved oxygen in the slurry will be depleted and an anaerobic environment will exist. Consequently, sequential aerobic-anaerobic environment plots were developed.

The parameter concentrations in slurry wastewaters are usually a function of the type of environment to which the slurry is exposed during mixing. For a limited number of parameters the concentrations are relatively independent of the type of environment used. These will be identified in subsequent sections.

Alkalinity

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All of the linear regression analyses conducted on alkalinity data representing slurry wastewaters prepared with Western coals under aerobic environments showed a general decrease in alkalinity as a function of detention time.

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The alkalinity concentrations were clearly a function of water source and coal source. Figure 67 shows the results as a function of detention time for slurry wastewaters prepared with distilled water and municipal wastewater treatment plant effluent using Wyodak coal. The mean concentrations were 40 and 14 milligrams per liter, respectively, for slurry wastewaters extracted from slurries prepared with distilled water and municipal effluent. The slopes of the curves were -15 and -11 milligrams per liter per day for the distilled water and municipal effluent slurries, respectively.



Time, days

Figure 67: Comparison Of Total Alkalinity Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.

A similar comparison of total alkalinity concentrations as a function of detention time is shown on Figure 68. These data represent slurry wastewaters prepared with South Bel Air coal. As indicated by the figure, although the tendency for decreasing concentrations as a function of detention time was evident, the rates of decrease were clearly different. The slopes of the curves were -8.8 and -51 milligrams per liter per day for slurry wastewaters representing the distilled water and municipal effluent slurries, respectively. The mean concentrations were 65 and 72 milligrams per liter for slurry wastewaters extracted from slurries prepared with distilled water and municipal effluent, respectively.



Figure 68: Comparison Of Total Alkalinity Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using South Bel Air At 50 Percent Solids In An Aerobic Environment.

Figure 69 shows a comparison of the linear regression analyses on alkalinity data for slurry wastewaters prepared with Wyodak coal using 40 and 50 percent solids slurries. As shown by the figure, the total alkalinity concentrations were clearly a function of the solids concentration used in preparing the slurry wastewaters. The linear regression analyses also indicated decreasing alkalinity concentrations with increasing detention time. The mean

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concentrations were 43 and 65 milligrams per liter, respectively, for slurries prepared with 40 and 50 percent solids concentrations. The slopes of the curves were -14 and 8.8 milligrams per liter per day for slurry wastewaters prepared with distilled water and Wyodak coal at 40 and 50 percent solids concentrations, respectively.



Time, days

Figure 69: Comparison Of Total Alkalinity Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 and 50 Percent Solids In An Aerobic Environment.

The effects of the environment used on the alkalinity concentrations in slurry wastewaters prepared with Cordero coal and distilled water in aerobic and anaerobic environments are shown on Figure 70. As shown by the figure, the alkalinity concentrations in slurry wastewaters prepared from slurries mixed in an anaerobic environment exhibited a tendency to increase whereas those representing slurries mixed in an aerobic environment decreased. The slopes of the curves were -7.8 and 1.5 milligrams per liter per day for slurry

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wastewaters extracted from slurries mixed in aerobic and anaerobic environments, respectively. The mean concentrations were 34 and 140 milligrams per liter, respectively, for slurry wastewaters representing the aerobic and anaerobic slurries.



Figure 70: Comparison Of Total Alkalinity Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Cordero Coal At 40 Percent Solids In Aerobic And Anaerobic Environments.

The alkalinity data representing slurry wastewaters prepared with the Kansas coal showed a slight tendency to decrease as a function of detention time. However, the linear regression analyses of the alkalinity data did not exhibit any clear trends. The alkalinity concentrations in the slurry wastewaters prepared with the Illinois coal were very low and may have reflected the influence of other buffers in addition to the carbonate-bicarbonate-hydroxide relationships. Figure 71 shows the combined curve respresenting aerobic and anaerobic data for slurry wastewaters prepared with Cordero coal and distilled water at 40 percent solids. A two-day aerobic mixing period was used to develop the curve.



Figure 71: Combination Of Aerobic And Anaerobic Curves Representing Total Alkalinity Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Cordero Coal At 40 Percent Solids.

In all slurries prepared with both Eastern and Western coals the total alkalinity concentrations were low. Despite the low alkalinity concentrations, the pH values of the slurries were all well within the acceptable range. Consequently, unless unusual circumstances exist, alkalinity is not expected to be an important factor in slurry wastewater processing and disposal.

Aluminum

The aluminum concentrations in the slurry wastewaters prepared with the Western coals in aerobic environments all showed a tendency to increase with increasing detention time. The concentrations in the slurry wastewaters were all low. Although the rate of increases would be significant from a theoretical point of view, the aluminum data indicate that the parameter is not significant from a practical viewpoint for most applications. Thus, the inital concentrations were generally representative of the concentrations measured throughout the sixty-hour mixing period. Figure 72 can be used to illustrate this point. The aluminum concentrations for the slurry wastewaters prepared with distilled water and Wyodak coal increased at a rate of 0.04 milligrams per liter per day based on the results of the linear regression analysis. The aluminum concentrations in the slurry wastewaters prepared with the municipal wastewater treatment plant effluent and Wyodak coal increased at a rate of 0.02 milligrams per liter per day.

Similar results were obtained with slurry wastewaters prepared with distilled water and municipal effluent using South Bel Air coal at 50 percent solids in an aerobic environment. The rates of increase in aluminum concentrations were 0.04 and 0.02 milligrams per liter per day, respectively, for slurry wastewaters prepared with distilled water and municipal effluent. Figure 73 is a graphical illustration of these results.

Figure 74 shows the effect of solids concentration on aluminum concentrations in slurry wastewaters prepared using 40 and 50 percent solids slurries. As expected, the 50 percent solids slurries yielded higher aluminum concentrations than the 40 percent solids slurries.

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Figure 73: Comparison Of Aluminum Concentrations In Slurry Wastewaters Prepared With Distilled Water Using South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.



Figure 74: Comparison Of Aluminum Concentrations In Slurry Wastewaters Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 and 50 Percent Solids In An Aerobic Environment.

As indicated by the data, very low aluminum concentrations were measured in slurry wastewaters prepared with the Western coals. Aluminum concentrations in slurry wastewaters prepared with the Eastern coals were all below the detectable limits of the test procedure used. Although substantial quantities of aluminum are present in coal, only a very small fraction of the aluminum is leached from the coal into the aqueous phase of the coal-water mixture.

Calcium Hardness

Figure 75 shows a comparison of the results of the linear regression analyses conducted on calcium hardness data for slurry wastewaters prepared with distilled water and municipal effluent. Wyodak coal was used to form the slurry. As shown by the figure, the rates of change in concentrations were

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substantially different for the two water sources. The increase in concentration in the slurry wastewater prepared with the distilled water was 2.1 milligrams per liter per day. Conversely, the calcium hardness decreased at a rate of 37 milligrams per liter per day in the slurry wastewaters prepared with the municipal wastewater. The mean concentrations were 170 and 230 milligrams per liter, respectively, for the slurry wastewaters representing the distilled water and municipal effluent slurries.



Figure 75: Comparison Of Calcium Hardness Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.

A similar comparison with South Bel Air coal is shown on Figure 76. For the South Bel Air coal, the calcium hardness curves diverged with increasing detention time rather than converging as indicated for the Wyodak coal data. The rates of change in concentrations were -19 and 54 milligrams per liter per day, respectively, for slurry wastewaters prepared from slurries formed with distilled water and municipal effluent.



Figure 76: Comparison Of Calcium Hardness Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.

Figure 77 shows the results of the linear regression analyses conducted on the calcium hardness data developed from slurry wastewaters prepared with slurries formed with 40 and 50 percent solids concentrations. The mean concentrations were 120 and 170 milligrams per liter for slurry wastewaters prepared with 40 and 50 percent solids slurries, respectively. The slopes of the curves were -11 and 2.1 milligrams per liter per day, respectively, for slurries formed with 40 and 50 percent solids.

As shown by Figure 78, the calcium hardness concentrations in slurries mixed in an anaerobic environment were significantly greater than in slurries mixed in an aerobic environment. The mean concentrations were 150 and 240 milligrams per liter. The slopes of the curves were -14 and -6.5 milligrams per liter per day, respectively, for slurry wastewaters representing the aerobic and anaerobic slurries. Cordero coal was used to develop these data.

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Figure 77: Comparison Of Calcium Hardness Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 And 50 Percent Solids In An Aerobic Environment.

Figure 79 shows the combination of the aerobic and anaerobic curves for the Cordero coal. A two-day aerobic mixing period was used.

Chemical Oxygen Demand

Figure 80 shows a comparison of the results of the linear regression analyses conducted on chemical oxygen demand data from slurry wastewaters prepared with the Wyodak coal. As shown by the figure, the chemical oxygen demand in the slurry wastewaters prepared with the municipal effluent decreased rapidly relative to the chemical oxygen demand in slurry wastewaters prepared with distilled water. The rates of change in concentrations were -4.8 and 97 milligrams per liter per day, respectively, for slurry wastewaters prepared with distilled water and municipal effluent. The mean concentration were 160 milligrams per liter for the distilled water slurries and 230 milligrams per liter for the municipal effluent slurries.



Figure 78: Comparison Of Calcium Hardness Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Cordero Coal At 40 Percent Solids In Aerobic And Anaerobic Environments.







Figure 80: Comparison Of Chemical Oxygen Demand Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.

A similar comparison of the results of the linear regression analyses on chemical oxygen demand data from slurry wastewaters prepared with South Bel Air coal is shown on Figure 81. The mean concentrations were 74 and 120 milligrams per liter, respectively, for slurry wastewaters prepared with distilled water and municipal effluent. The rates of change in concentrations were -37 and -30 milligrams per liter per day for slurry wastewaters prepared with slurries formed with distilled water and municipal effluent, respectively.

The mean concentrations in slurry wastewaters prepared with distilled water and Wyodak coal at 40 and 50 percent solids were 110 and 160 milligrams per liter, respectively. The rates of change in concentration were -23 and -4.8 milligrams per liter per day for the 40 and 50 percent solids slurries, respectively. Figure 82 shows a graphical comparison of the results of the linear regression analyses for the 40 and 50 percent solids slurries.

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Figure 81: Comparison Of Chemical Oxygen Demand Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.

Figure 83 provides a comparison of the results of the linear regression analyses conducted on chemical oxygen demand data developed from slurry wastewaters prepared from slurries mixed in aerobic and anaerobic environments. The mean concentrations were 85 and 160 milligrams per liter, respectively, for slurries mixed in aerobic and anaerobic environments. The rates of change in concentration for the slurry wastewaters representing the aerobic and anaerobic slurries were -12 and -5.2 milligrams per liter per day, respectively. Cordero coal was used for forming the slurries.

Figure 84 shows the combination of the aerobic and anaerobic curves with a two-day aerobic mixing period. As shown by the figure, the chemical oxygen demand concentrations would be expected to decrease at a slower rate once the free dissolved oxygen in the slurry becomes depleted.



Figure 82: Comparison Of Chemical Oxygen Demand Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 And 50 Percent Solids In An Aerobic Environment.



Figure 83: Comparison Of Chemical Oxygen Demand Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Cordero Coal At 40 Percent Solids In Aerobic And Anaerobic Environments.



Figure 84: Combination Of Aerobic And Anaerobic Curves Representing Chemical Oxygen Demand Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Cordero Coal At 40 Percent Solids.

Chloride

The results of the linear regression analyses on chloride data obtained from slurry wastewaters prepared with the Wyodak and South Bel Air coals in an aerobic environment indicated a tendency for increasing concentrations as a function of detention time. However, these increases were nominal in all cases. Thus, for practical purposes, the initial concentrations can be taken to be representative of those measured throughout the sixty-hour aerobic mixing period.

Figure 85 shows a comparison of the results of the linear regression analyses on chloride data in slurry wastewaters prepared with distilled water and municipal effluent using Wyodak coal at 50 percent solids in an aerobic environment. The mean concentrations were 11 and 51 milligrams per liter, respectively, for slurry wastewaters prepared with distilled water and municipal effluent. The rates of change in concentration were 0.93 and 0.31 milligrams per liter per day for slurry wastewaters prepared with distilled water and municipal effluent, respectively.

A similar comparison of the results of the linear regression analyses performed on chloride data obtained from slurry wastewaters prepared with distilled water and municipal effluent using South Bel Air coal at 50 percent solids in an aerobic environment is shown on Figure 86. The rates of increase in concentration were 0.77 and 0.73 milligrams per liter per day, respectively, for slurry wastewaters prepared with distilled water and municipal effluent. The mean concentrations were 6.1 and 47 milligrams per liter, respectively, for slurries prepared with distilled water and municipal effluent. The mean concentrations were 6.1 and 47 milligrams per liter, respectively, for slurries prepared with distilled water and municipal effluent. These data clearly indicated that chloride concentrations in slurry wastewaters prepared with Western coal were a function of the influent water quality.

The chloride concentrations in slurry wastewaters were a function of the solids concentrations used in preparing the slurries, as shown on Figure 87. The mean concentrations were 7.8 and 11 milligrams per liter respectively, for slurry wastewaters prepared with the 40 and 50 percent solids slurries. The rates of increase in concentrations were 0.10 and 0.93 per day for the 40 and 50 percent solids slurries, respectively.

Multiple regression analyses of the chloride data obtained from slurry wastewaters prepared with distilled water and Illinois coal also indicated the tendency for increasing concentrations with increasing detention time. These concentrations were very large compared with the chloride data obtained from slurry wastewaters prepared with Western coals. The rates of increase in concentration were also relatively large compared with similar data for Western coal.

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Figure 85: Comparison Of Chloride Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.



Time,-days-




Figure 87: Comparison Of Chloride Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 And 50 Percent Solids In An Aerobic Environment.

Figure 88 shows the results of the combination of the aerobic and anaerobic curves for chloride data obtained with Cordero coal. This figure indicates that the chloride concentrations were in the same general range regardless of the type of environment used.

Lead

The lead concentrations in slurry wastewaters prepared with the Western coals were all less than 1 milligram per liter. However, since surface water quality standards frequently contain very low limits on the discharge of lead into surface waters, lead may be a significant water quality parameter in the slurry wastewaters. In general, the lead concentrations remained relatively constant throughout the sixty-hour aerobic mixing period. For some circumstances, the linear regression analyses indicated no change in lead concentra-



Figure 88: Combination Of Aerobic And Anaerobic Curves Representing Chloride Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Cordero Coal At 40 Percent Solids.

tion as a function of detention time. The linear regression analyses indicated decreasing lead concentrations with increasing detention time in other circumstances. However, the rates of change in concentrations were small in all cases.

Figure 89 shows the results of the linear regression analyses conducted on data obtained from slurry wastewaters prepared with distilled water and municipal effluent using Wyodak coal at 50 percent solids in an aerobic environment. The linear regression analyses indicated no change in lead concentrations as a function of detention time. The average concentrations were 0.29 and 0.13 milligrams per liter for slurry wastewaters prepared with distilled water and municipal effluent, respectively.



Figure 89: Comparison Of Lead Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.

Figure 90 shows the results of the linear regression analyses of lead data for slurry wastewaters prepared with distilled water and South Bel Air coal at 50 percent solids in an aerobic environment. The regression analysis indicated no change in lead concentrations as a function of detention time. The mean concentration was 0.15 milligram per liter.

A comparison of the lead concentrations in slurry wastewaters prepared with 40 and 50 percent solids slurries in an aerobic environment is shown on Figure 91. As shown by the figure, the linear regression analyses indicated no change in concentration as a function of detention time. The mean concentrations were 0.25 milligrams per liter for both the 40 and 50 percent solids slurries. Distilled water and Wyodak coal were used to develop the data.



Figure 90: Comparison Of Lead Concentrations In Slurry Wastewaters Prepared With Distilled Water And South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.

As indicated by the results of the linear regression analyses, the initial lead concentrations were representative of the concentrations measured throughout the sixty-hour aerobic mixing periods. The lead concentrations in slurry wastewaters prepared with the Kansas and Illinois coals were below the detectable limit of the test procedure used.

Magnesium

Results of the linear regression analyses of the magnesium data were inconsistent with respect to both the magnitude and direction of the rate of change in concentration as a function of detention time. In some instances, these rates were significant and would require evaluation in estimating the relationship of detention time and magnesium concentrations.



Figure 91: Comparison Of Lead Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 And 50 Percent Solids In An Aerobic Environment.

Figure 92 shows the results of the linear regression analyses on the magnesium data obtained from slurry wastewaters prepared with distilled water and municipal effluent using Wyodak coal at 50 percent solids in an aerobic environment. The mean concentrations were 34 and 57 milligrams per liter, respectively, for slurries prepared with distilled water and municipal effluent. The rates of change in concentration were 0.39 and -7.2 milligrams per liter per day for slurry wastewaters prepared with distilled water and municipal effluent.

A similar comparison of data developed using South Bel Air coal to prepare the slurry wastewaters is shown on Figure 93. As shown by the figure, the magnesium concentrations increased with increasing detention time in slurry wastewaters prepared with municipal effluent whereas the concentrations decreased as a function of detention time for slurry wastewaters prepared with

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Figure 92: Comparison Of Magnesium Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.

distilled water. The rates of change in concentrations were -4.8 and 5.0 milligrams per liter per day for slurry wastewaters prepared with distilled water and municipal effluent, respectively. The mean concentrations were 32 and 45 milligrams per liter, respectively, for the distilled water and municipal effluent slurries.

Figure 94 shows a comparison of the results of the linear regression analyses on magnesium data measured in slurry wastewaters mixed in aerobic and anaerobic environments using Cordero coal and distilled water to prepare the slurries. As shown by the figure, the magnesium concentrations were larger in slurry wastewaters prepared from slurries mixed in an anaerobic environment than in those from slurries mixed in an aerobic environment. The mean concentrations were 27 and 36 milligrams per liter, respectively, for slurries mixed in aerobic and anaerobic environments. The rates of change in concentration



Figure 93: Comparison Of Magnesium Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.

were 0.62 and -1.3 milligrams per liter per day, for slurry wastewaters prepared with slurries mixed in aerobic and anaerobic environments, respectively.

Figure 95 shows the results of the combination of the aerobic and anaerobic curves for magnesium data obtained using the Cordero coal and distilled water. A two-day aerobic mixing period was used for this set of data. As shown by the figure, the magnesium concentrations would be lower than if an aerobic environment was used solely.

The magnesium concentrations were clearly a function of coal source, influent water quality, the type of environment used during the mixing phase, and detention time. Thus, magnesium data needs to be developed using the detention time(s) appropriate for a specific pipeline situation.



Figure 94: Comparison Of Magnesium Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Cordero Coal At 40 Percent Solids In Aerobic And Anaerobic Environments.

Nitrate

The results of the linear regression analyses yielded inconsistent results with respect to the rate of change in concentration as a function of detention time. Figure 96 shows a comparison of the curves for nitrate data developed from slurry wastewaters prepared with distilled water and municipal effluent. The mean concentrations were 3.3 and 4.4 milligrams per liter, respectively, for slurry wastewaters prepared with distilled water and municipal effluent. The rates of change in concentrations were 0.03 and 0.21 milligrams per liter per day for slurries prepared with distilled water and municipal ef-

A similar comparison of the linear regression analyses results in slurry wastewaters prepared with South Bel Air coal is shown on Figure 97. The rates of increase in concentration were 0.0 and 0.59 milligrams per liter per day



Figure 95: Combination Of Aerobic And Anaerobic Curves Representing Magnesium Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Cordero Coal At 40 Percent Solids.

for slurry wastewaters prepared with distilled water and municipal effluent, respectively. The mean concentrations were 3.9 and 4.9 milligrams per liter respectively, for slurries prepared with distilled water and municipal effluent.

Figure 98 shows the results of the linear regression analyses for the nitrate data developed from slurry wastewaters prepared with distilled water and Wyodak coal in an aerobic environment. The mean concentrations were 2.0 and 3.3 milligrams per liter, respectively, for slurry wastewaters prepared from slurries formed with 40 and 50 percent solids. The rates of change in concentration were 0.03 and 0.16 milligrams per liter per day for the slurries prepared with 40 and 50 percent solids, respectively.





Figure 96: Comparison Of Nitrate Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.

pН

Figure 99 shows a comparison of the results of the linear regression analyses conducted on the pH data developed with Wyodak coal, and distilled water and municipal effluent. The mean pH values were 6.7 for both the distilled water and municipal effluent slurries. The slopes of the curves were 0.31 and .45 pH units per day for the slurries formed with distilled water and municipal effluent, respectively. Wyodak coal was used to develop these data.

A similar comparison of pH data developed using South Bel Air coal is shown on Figure 100. The rates of change of pH values were 0.32 and 0.16 pH units per day, respectively, for slurries formed with distilled water and municipal effluent. The mean values were 6.6 and 6.8 for slurry wastewaters extracted from slurries formed with distilled water and municipal effluent, respectively.



Figure 97: Comparison Of Nitrate Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.



Figure 98: Comparison Of Nitrate Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 and 50 Percent Solids In An Aerobic Environment.



Figure 99: Comparison Of pH Values In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.

Figure 101 shows a comparison of the pH values in slurry wastewaters prepared with 40 and 50 percent solids slurries. Wyodak coal was used to develop these data.

Figures 102 shows a comparison of pH values in slurry wastewaters extracted from slurries mixed in aerobic and anaerobic environments for a nineday period. Cordero coal was used to form the slurries. The mean pH values were 6.9 and 7.5, respectively, for slurry wastewaters developed with aerobic and anaerobic environments. The slopes of the curves were 0.06 and 0.21 pH units per day for the slurry wastewaters representing the aerobic and anaerobic slurries, respectively.

Figure 103 shows the curve produced by combining the aerobic and anaerobic curves for the Cordero coal and distilled water slurries. As indicated by



Figure 100: Comparison Of pH Values In Slurry Wastewaters Prepared With Distilled Water Using South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.

the combined curve, the pH would be expected to rise significantly following depletion of the free dissolved oxygen in the slurry. A two-day aerobic mixing period was used to develop the curve.

Potassium

The results of the linear regression analyses on potassium concentrations in slurry wastewaters prepared with distilled water and municipal effluent using Wyodak coal at 50 percent solids in an aerobic environment are shown on Figure 104. The potassium concentrations in the slurry wastewaters prepared with distilled water averaged 8.3 milligrams per liter and increased at the rate of 0.24 milligrams per liter per day. The potassium concentrations in the slurry wastewaters prepared with municipal effluent averaged 9.5 milli-



Figure 101: Comparison Of pH Values In Slurry Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 And 50 Percent Solids In An Aerobic Environment.



Time, days Figure 102: Comparison Of pH Values In Slurry Wastewaters Prepared With Distilled Water Using Cordero Coal At 50 Percent Solids In Aerobic And Anaerobic Environments.



Time, days

Figure 103: Combination Of Aerobic And Anaerobic Curves Representing pH Values As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water Using Cordero Coal At 40 Percent Solids.

grams per liter and decreased at the rate of 0.67 milligrams per liter per day.

A similar comparison involving South Bel Air coal is shown on Figure 105. The rates of change in concentration were 0.31 and 0.46 milligrams per liter per day for slurry wastewaters prepared with distilled water and municipal effluent, respectively. The mean concentrations were 6.8 milligrams per liter for the slurry wastewater prepared with the distilled water and 8.3 milligrams per liter for the slurry wastewater prepared with municipal effluent.

As would be expected, the potassium concentrations in slurry wastewaters prepared with 50 percent solids slurries were larger than those prepared with 40 percent solids slurries. The results of the linear regression analyses are



Figure 104: Comparison Of Potassium Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.

shown on Figure 106. The rate of change in concentration and the mean concentration were -0.11 milligrams per liter per day and 7.1 milligrams per liter for the 40 percent solids slurries. Comparable values for the 50 percent solids slurries were 0.24 milligrams per liter per day and 8.0 milligrams per liter for the 50 percent solids slurries.

Figure 107 shows a comparison of the results of the linear regression analyses on potassium data obtained using aerobic and anaerobic environments. The rates of change in concentration were -0.38 and -0.06 milligrams per liter per day for slurry wastewaters prepared using aerobic and anaerobic environments, respectively. The mean concentration for slurries mixed in the aerobic environment was 11.0 milligrams per liter which was slightly less than the mean concentration of 13.6 milligrams per liter for slurries mixed in an anaerobic environment.



Figure 105: Comparison Of Potassium Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.

Although the tendencies for the rates and directions of changes in potassium concentrations were not consistent, the inital concentrations can be used as generally representative of the concentrations expected for longer detention periods for three reasons. First, the potassium concentrations were low. Secondly, potassium is not a directly regulated parameter in water quality standards and, except for a nominal contribution to dissolved solids, is not significant. Finally, the rates of change were small.

Silica

Figure 108 shows the results of the linear regression analyses conducted on silica data developed using Wyodak coal. Distilled water and municipal effluent were used as the slurry media. As shown by the figure, the silica concentrations in the slurry wastewaters converged with increasing detention



Figure 106: Comparison Of Potassium Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 and 50 Percent Solids In An Aerobic Environment.



Figure 107: Comparison Of Potassium Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Cordero Coal At 40 Solids In Aerobic And Anaerobic Environments.

time. The rates of change in concentration were 3.7 and -1.95 milligrams per liter per day, respectively, for slurry wastewaters prepared from slurries developed with distilled water and municipal effluent. The average concentrations were 9.3 and 25 milligrams per liter for the distilled water slurry and 25 milligrams per liter for the municipal effluent slurry.

A similar comparison of the results of the linear regression analyses for slurry wastewaters prepared with South Bel Air coal is shown on Figure 109. As shown by the figure, these data also converged with increasing detention time. The mean concentrations were 12 milligrams per liter for the distilled water slurries and 16 milligrams per liter for the slurries prepared with municipal effluent. The rates of change in concentration were 1.8 milligrams per liter per day for the distilled water slurries and -0.5 milligrams per liter per day for slurry wastewaters prepared with municipal effluent.

Figure 110 shows a comparison of the results of the linear regression analyses conducted on silica data developed from slurry wastewaters prepared with 40 and 50 percent solids slurries. The mean concentrations were 8.4 and 9.3 milligrams per liter, respectively, for slurry wastewaters prepared with 40 and 50 percent solids slurries. The rates of change in concentration were 5.1 and 3.7 milligrams per liter per day for slurry wastewaters prepared from slurries formed with distilled water and Wyodak coal at 40 and 50 percent solids.

A comparison of the results of the linear regression analyses conducted on silica data developed using aerobic and anaerobic environments is shown on Figure 111. As shown by the figure, silica concentrations in slurries mixed in an anaerobic environment increased significantly. The rate of increase in

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Figure 108: Comparison Of Silica Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.



Time, days

Figure 109: Comparison Of Nitrate Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.



Figure 110: Comparison Of Silica Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 and 50 Percent Solids In An Aerobic Environment.

concentration was 1.0 milligram per liter. The rate of change in concentration for the silica in slurries mixed in an aerobic environment was -0.32 milligram per liter. The mean concentrations were 11 and 16 milligrams per liter, respectively, for slurry wastewaters prepared from slurries mixed in aerobic and anaerobic environments.

Figure 112 shows the curve produced by combining the aerobic and anaerobic curves for the Cordero coal and distilled water slurries with a aerobic mixing period of two days. The combined curve indicates that silica concentrations should increase after the dissolved oxygen in the slurry is depleted.

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Figure 111: Comparison Of Silica Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Cordero Coal At 40 Percent Solids In Aerobic And Anaerobic Environments.

Sodium

The results of the linear regression analyses on sodium data obtained from slurry wastewaters prepared with Wyodak and South Bel Air coal were inconsistent. Figure 113 shows the results of these analyses on sodium data measured in slurry wastewaters prepared with distilled water and municipal effluent using Wyodak coal at 50 percent solids in an aerobic environment. The rates of change in concentrations were 0.57 and -1.6 milligrams per liter per day, respectively, for slurry wastewaters prepared with distilled water and municipal effluent. The mean concentrations were 38 and 41 milligrams per liter for slurries prepared with distilled water and municipal effluent.

A similar comparison of sodium data in slurries prepared with South Bel Air coal is shown on Figure 114. As indicated by the figure, the tendency for the municipal effluent data was for increasing concentrations with increasing



Figure 112: Combination Of Aerobic And Anaerobic Curves Representing Silica Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Cordero Coal At 40 Percent Solids.

detention time. This tendency was opposite that for data developed using distilled water. The latter decreased with increasing detention time. The rates of change in concentrations were -1.9 and 3.3 milligrams per liter per day, respectively, for slurry wastewaters prepared with distilled water and municipal effluent. The mean concentrations were 45 and 60 milligrams per liter for slurries prepared with distilled water and municipal effluent.

Figure 115 shows the results of the linear regression analyses of sodium data for slurry wastewaters prepared with 40 and 50 percent solids slurries. Wyodak coal and distilled water were used to prepare the slurries. As shown by the figure, the sodium concentrations were clearly a function of the percent solids used in preparing the slurries. The rates of change in concentration were 0.57 and -0.71 milligrams per liter per day for slurry wastewaters prepared with 40 and 50 percent solids, respectively. The mean concentrations were 31 and 38 milligrams per liter.

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Time, days

Figure 113: Comparison Of Sodium Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.



Figure 114: Comparison Of Sodium Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.



Figure 115: Comparison Of Sodium Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 and 50 Percent Solids In An Aerobic Environment.

Figure 116 shows the results of the linear regression analyses conducted on sodium data developed over a longer mixing period. The rates of change in concentration were greater than for the data developed with the Wyodak and South Bel Air coals. The data shown on Figure 116 reflect slurry wastewaters prepared with distilled water and Cordero coal. The sodium concentrations in slurry wastewaters mixed in an aerobic environment averaged 160 milligrams per liter and decreased at the rate of 6.7 milligrams per liter per day. The mean concentration was 200 milligrams per liter for the slurries mixed in an anaerobic environment. Sodium in these slurries decreased at the rate of 2.3 milligrams per liter per day.



Figure 116: Comparison Of Sodium Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Cordero Coal At 40 Percent Solids In Aerobic And Anaerobic Environments.

Sulfate

Figure 117 shows the results of the linear regression analyses conducted on slurry wastewaters prepared with Wyodak coal. The mean concentrations were 480 and 600 milligrams per liter, respectively, for slurry wastewaters prepared with distilled water and municipal effluent. The rates of increase in concentrations were 8.1 and 26 milligrams per liter per day for slurry wastewaters prepared from slurries formed with distilled water and municipal effluent, respectively. As indicated by the figure, the initial concentrations were generally representative of those measured during the remainder of the sixty-hour aerobic mixing period.

A similar comparison of the results of the linear regression analyses conducted on sulfate data for slurry wastewaters prepared with South Bel Air coal is shown on Figure 118. As shown by the figure, the sulfate concentra-



Figure 117: Comparison Of Sulfate Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.

tions increased rapidly in the slurry wastewaters prepared with the municipal effluent with increasing detention time. The rate of increase was 160 milligrams per liter per day. The rate of increase for the slurry wastewaters prepared with distilled water was low at 0.1 milligrams per liter per day. The mean concentrations were 520 and 790 milligrams per liter, respectively, for slurry wastewaters prepared from slurries formed with distilled water and municipal effluent.

Figure 119 shows the effect of the solids concentrations used in forming the slurries on sulfate in the slurry wastewaters. The mean concentrations were 360 and 480 milligrams per liter, respectively, for slurries formed with 40 and 50 percent solids concentrations. Wyodak coal and distilled water were used to form the slurries. The rates of change in sulfate concentrations were 8.1 and 12.9 milligrams per liter per day for the 40 and 50 percent solids



Figure 118: Comparison Of Sulfate Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.

slurries, respectively. As with the previous illustration of the Wyodak slurry data, the initial concentrations were essentially representative of the concentrations measured throughout the remainder of the study.

Figure 120 shows a comparison of the results of the linear regression analyses conducted on sulfate data developed from slurry wastewaters formed with distilled water and Cordero coal. As shown by the figure, the slopes of the curves were substantially different. The rates of change in concentrations were 1.9 and 37 milligrams per liter per day, respectively, for slurry wastewaters prepared from slurries mixed in aerobic and anaerobic environments. The mean concentrations are misleading because of the relatively large increase in concentration with increasing detention time for the anaerobic data.



Aerobic Environment.

Combination of the aerobic and anaerobic curves with a two-day aerobic mixing period is shown on Figure 121. As shown by the figure, the sulfate concentrations would be expected to increase rapidly following depletion of dissolved oxygen in the slurry.

Titanium

The results of the linear regression analyses indicated no change in totanium concentrations as a function of detention time for slurry wastewaters prepared with 50 percent solids slurries. Similar analyses on the slurry wastewater data for 40 percent solids slurries indicated a rate of change of 0.1 milligram per liter per day. Consequently, the initial titanium concentrations in slurry wastewaters prepared with the Wyodak and South Bel Air coals in aerobic environments were essentially representative of those measured throughout the sixty-hour mixing periods.



Figure 120: Comparison Of Sulfate Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Cordero Coal At 40 Percent Solids In Aerobic And Anaerobic Environments.

Figure 122 shows a comparison of the results of the linear regression analyses on titanium data developed from slurry wastewaters prepared with distilled water and municipal effluent using Wyodak coal at 50 percent solids in an aerobic environment. The mean concentrations were 0.78 and 0.97 milligrams per liter for slurry wastewaters prepared with distilled water and municipal effluent, respectively.

A similar comparison for slurry wastewaters prepared with distilled water and municipal effluent using South Bel Air coal is shown on Figure 123. The mean concentrations were 0.83 and 0.95 milligrams per liter, respectively, for slurry wastewaters prepared with distilled water and municipal effluent. The raw data indicated a peak concentration occurred at a detention time of between one and two days wilh a decreasing concentration for the remainder of the sixty-hour aerobic mixing period.



Figure 121: Combination Of Aerobic And Anaerobic Curves Representing Sulfate Concentrations As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Cordero Coal At 40 Percent Solids.

Figure 124 shows the results of the linear regression analyses on titanium data developed from slurry wastewaters prepared with distilled water and Wyodak coal using 40 and 50 percent solids slurries. As would be expected, the titanium concentrations in slurry wastewaters prepared with the 50 percent solids slurries exceeded those in slurry wastewaters prepared with the 40 percent solids slurries. The mean concentrations were 0.55 and 0.78 milligrams per liter. The results of the linear regression analyses indicated rates of increase in titanium concentrations of 0.1 and 0.0 milligrams per liter per day for the 40 and 50 percent solids slurries, respectively.

Total Hardness

Figure 125 shows the results of the linear regression analyses conducted on total hardness data developed using Wyodak coal with distilled water and



Figure 122: Comparison Of Titanium Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.

municipal effluent. The mean concentrations were 330 and 434 milligrams per liter, respectively, for slurry wastewaters prepared from slurries formed with distilled water and municipal effluent. The slopes of the curves were 1.9 and -73 milligrams per liter for the slurry wastewaters representing the distilled water and municipal effluent slurries, respectively.

A similar comparison of total hardness data developed with South Bel Air coal is shown on Figure 126. The rates of change in concentrations were -31 and 80 milligrams per liter per day, respectively, for slurry wastewaters prepared from slurries formed with distilled water and municipal effluent. The mean concentrations were 300 and 419 milligrams per liter for slurry wastewaters representing the distilled water and municipal effluent, respectively.



Figure 123: Comparison Of Titanium Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using South Bel Air Coal At 50 Percent Solids In An Aerobic Environment.



Time, days

Figure 124: Comparison Of Titanium Concentrations In Slurry Wastewaters Prepared With Distilled Water Using Wyodak Coal At 40 and 50 Percent Solids In An Aerobic Environment.



Figure 125: Comparison Of Total Hardness Concentrations In Slurry Wastewaters Prepared With Distilled Water And Municipal Effluent Using Wyodak Coal At 50 Percent Solids In An Aerobic Environment.

Figure 127 shows a comparison of the results of the linear regression analyses conducted on total hardness data developed from slurries formed with 40 and 50 percent solids. The mean concentrations were 230 and 330 milligrams per liter, respectively, for slurry wastewaters representing the distilled water and municipal effluent slurries. The slopes of the curves were -21 and 1.9 milligrams per liter per day for the slurry wastewaters prepared from slurries mixed in aerobic and anaerobic environments.

The results of the linear regression analyses conducted on total hardness data developed using aerobic and anaerobic environments are shown on Figure 128. The total hardness concentrations in slurry wastewaters prepared from slurries mixed in an anaerobic environment exceeded those in slurries mixed in an aerobic environment. The mean concentrations were 230 and 380 milligrams per liter. The rates of change in concentrations were -22 and -10 milligrams



Figure 127: Comparison Of Total Hardness Concentrations In Slurry Waste waters Prepared With Distilled Water Using Wyodak Coal At 40 And 50 Percent Solids In An Aerobic Environment.

per liter per day for slurry wastewaters extracted from slurries mixed in aerobic and anaerobic environments, respectively. Cordero coal was used to develop these data.



Figure 128: Comparison Of Total Hardness Concentrations In Slurry Waste waters Prepared With Distilled Water Using Cordero Coal At 40 Percent Solids In Aerobic And Anaerobic Environments.

Figure 129 shows the combination of the aerobic and anaerobic curves for slurry wastewaters prepared using Cordero coal and distilled water. The tendency for larger concentrations when an anaerobic environment was used noted in the calcium hardness data was also evident from the total hardness curves.


Figure 129: Combination Of Aerobic And Anaerobic Curves Representing Total Hardness As A Function Of Detention Time For Slurry Wastewaters Prepared With Distilled Water And Cordero Coal At 40 Percent Solids.

PHASE IX RESULTS

The purpose of this phase of the overall research program was to investigate the feasibility of using saline water as the slurry media. Because of limited water resources in the western United States, the use of either saline water or poor quality water would be more acceptable.

The approach used to satisfy this objective was to conduct mass balances of chloride following mixing of the coal and saline water for various periods of time. The quantity of chloride in the saline water used as the slurry media plus that contributed by the coal was then compared with the quantity of chloride in the slurry wastewater produced by liquid-solids separation and the quantity of chloride washed from the coal by distilled water after the liquidsolids step. That is, two sinks exist for the chloride after the liquid-solids step. The chloride must be either in the slurry wastewater or retained with the coal. In equation form, the equation would be as follows:

Ws = Wsc + Wsw - We

Where: Ws = weight of chloride in the saline water Wsc = weight of chloride retained with the coal following liquid-solids separation Wsw = weight of chloride in the slurry wastewater Wc = weight of chloride contributed by the coal

The specific procedure used was to determine the quantity of chloride which would be leached from the coal during mixing of the coal and water. Slurries prepared with Wyodak coal and distilled water were mixed for the desired length of time in the batch reactors. Fifty-percent slurries were used in these analyses. Upon extraction of the slurry from the reactors, the slurry was dewatered by vacuum filtration and the quantity of slurry wastewater measured. The concentration of the chloride in the slurry wastewater was determined. Multiplication of the concentration by the volume yielded a measure of the quantity of chloride which would be leached from the coal.

The chloride concentration of the saline water was determined by the procedures identified in Part 408B of <u>Standard Methods For The Examination Of</u>

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Water And Wastewater (31). Two thousand milliliters of the saline water were combined with 2,000 grams of coal to form the slurry to be evaluated. The slurry was mixed for the desired length of time in the batch reactors, ex-The volume of the slurry wastewater tracted from the reactor and dewatered. and the concentration of the chloride in the slurry wastewater were then de-The coal remaining following the liquid-solids separation step was termined. then rinsed with distilled water. The volume of rinse water and the chloride concentration in the rinse water were measured. These data were used to determine the mass balance. Excellent comparisons of the weights of chloride in the saline water combined with chloride contributed by the coal with the amounts of chloride in the slurry wastewater and in the rinse water were obtained.

The results of the laboratory analyses indicated that substantial quantities of chloride are retained with the coal. The quantity of chloride retained is basically equal to the quantity of water retained by the coal multiplied by the concentration of chloride in the saline water used to form the slurry.

Because of the amount of chloride retained with the coal, the use of saline water as the slurry media should only be adopted after very careful analyses of the potential adverse effects of the chloride on downstream processes and equipment and of the chloride on the pipeline and associated equipment have been conducted.

Several potential adverse effects exist for the use of high chloride coal. For example, firing of chloride-laden coal in the furnace of an electric power generating station has the potential for accelerated chloride corrosion of boiler components and of corrosion of scrubber internals in flue gas desulfurization systems. Since flue gas desulfurization is currently required for all new and modified electric power generation stations, potential adverse effects on these processes and equipment must be evaluated. Flue gas desulfurization systems have been particularly susceptible to chloride corrosion because of the hot, wet environment inside the scrubbers. Water containing chloride evaporates leaving a more highly concentrated solution eventually resulting in a very corrosive situation in many cases.

The use of saline water also contributes to the difficulty of slurry wastewater quality restoration, reuse and/or disposal because of the highly mineralized nature of the saline water. Although the use of saline water need not be ruled out, very careful analyses of the benefits and shortcomings of such usage should be evaluated before this alternative is adopted in a particular situation.

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