28-4-28-82
I-2768
(2)

ornl

MASTER

ORNL/TM-8213

**OAK
RIDGE
NATIONAL
LABORATORY**

**UNION
CARBIDE**

**DO NOT MICROFILM
COVER**

**Development and Evaluation of
Wastewater-Treatment Processes
at the H-Coal Site in
Catlettsburg, Kentucky**

**Volume I: Design Summary and
R&D Task Identification**

G. E. Oswald
J. F. Walker
C. H. Brown
J. A. Klein
R. K. Genung

**OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A03; Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE.
It has been reproduced from the best
available copy to permit the broadest
possible availability.

ORNL/TM-8213

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

DEVELOPMENT AND EVALUATION OF WASTEWATER TREATMENT PROCESSES
AT THE H-COAL SITE IN CATLETTSBURG, KENTUCKY.

VOLUME I: DESIGN SUMMARY AND R&D TASK IDENTIFICATION

G. E. Oswald
J. F. Walker
C. H. Brown
J. A. Klein
R. K. Genung

Date Published - April 1982

ORNL/TM--8213

DE82 013251

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

CONTENTS

ABSTRACT	1
1. INTRODUCTION	2
2. BACKGROUND	3
3. PROJECT OBJECTIVES	4
4. DESIGN SUMMARY	5
4.1 Siting Considerations	5
4.2 General Flowsheet	6
4.3 Unit Process Designs	6
4.3.1 Ozonation	10
4.3.2 Carbon adsorption	10
4.3.3 Reverse osmosis	13
4.3.4 Ozonation and carbon adsorption contactor columns	15
5. OVERVIEW OF PROJECTED R&D PROGRAM	19
5.1 Ozonation	19
5.2 Carbon Adsorption	23
5.3 Reverse Osmosis	28
5.4 Sequence Comparisons	32
6. REFERENCES AND SELECTED BIBLIOGRAPHY	33

DEVELOPMENT AND EVALUATION OF WASTEWATER TREATMENT PROCESSES
AT THE H-COAL SITE IN CATLETTSBURG, KENTUCKY.

VOLUME I: DESIGN SUMMARY AND R&D TASK IDENTIFICATION

G. E. Oswald
J. F. Walker
C. H. Brown
J. A. Klein
R. K. Genung

ABSTRACT

The design of a mobile process development unit (PDU) for coal conversion wastewater treatment and an overview of the associated R&D program for its use are described. The PDU consists of three modular units, which can be arranged in various sequences: carbon adsorption, ozonation, and reverse osmosis. Each of the units has a nominal flow capacity of ~60 mL of wastewater feed per second (1 gpm). The PDU will be operated first at the H-Coal pilot plant at Catlettsburg, Kentucky. The feed to the PDU will be taken as a sidestream from the existing wastewater treatment system at the H-Coal site. It will have been processed through oil-water separation and distillation stripping, and can be taken both before and after bio-oxidation by an activated sludge process.

The ozonation system experimental parameters are ozone contact time, ozone treatment rate, column pressure, and pH. The system will be analyzed as a continuous stirred tank reactor. The calculated results will include ozone reaction, treatment, and absorption rates, contaminant depletion and reaction rates, ozone absorption and contaminant removal efficiencies, and ozone volumetric mass-transfer coefficients.

The carbon adsorption system will be operated to obtain bed-depth-service-time (BDST) data for various carbons and operating conditions. The BDST method will yield the rate of carbon exhaustion as well as the minimum depth of carbon required to remove contaminants.

Reverse osmosis will be studied to measure dissolved solids rejection efficiency, permeate recovery, and fouling characteristics of various commercially available membranes.

Recommended sequences of operating the three modular processes will be determined. Results will be published in subsequent volumes of this report.

1. INTRODUCTION

In the next few decades, the projected major use of coal conversion products will be for boiler fuels, fuel oil, residential heating, and chemical feedstocks. Several methods are presently under intensive technological study, with the goal to provide engineering data suitable for scale-up purposes. Concomitant with these anticipated engineering advances and the emphasis on commercialization is the need to ensure the environmental acceptability of the various processes.

Generally, all effluent streams (gaseous, liquid, and solid releases) need to be investigated when addressing environmental control technology. Considerable past efforts have been concentrated in the area of gaseous streams, and only recently has attention been focused on liquid and solid effluents.¹⁻¹⁶ This project will address the aqueous concerns.

Currently, real deficiencies exist in the application of environmental control to the emerging coal conversion technologies. Because of the developing nature of the coal conversion industry, hard data on the characteristics of the output streams are not available. Unfortunately, this means that the necessary information is lacking for the design of efficient control systems. In addition, the past history of the industry has been one of adding on the minimum amount of control technology necessary to meet permit requirements with little thought to the integration of the process and the controls or to obtaining data for future control development. The lack of consistent effluent guidelines, moreover, presents a moving target to developers of control technologies. Only now are the Environmental Protection Agency (EPA) and the various state agencies coming to grips with the problem of establishing regulations for coal conversion facilities. The present debate is indicative of the various opinions being held in this area. Discharge regulations, equipment recommendations, and zero discharge options are all being considered.

The PDU for coal conversion wastewater treatment will address and help resolve technical and operational questions which could limit commercial acceptance of the technologies involved. These areas of concern could include the following tasks:

1. detailed characterization of wastes and wastewaters to be processed,
2. selection of appropriate processes based on previous knowledge and basic process development work,
3. effluent characterizations, with analyses of each process in each sequence as well as the final effluent; conventional pollutants, toxicity, mutagenicity, etc. will be considered,
4. development of material balances, including the fate of trace heavy metals,
5. development of optimum operating conditions for treatment processes,
6. development of design criteria for modified conventional processes and for innovative processes,
7. selection of process equipment and control and monitoring instrumentation, and
8. economic evaluations and comparisons of flowsheets for viable treatment technologies.

2. BACKGROUND

During the mid-1970s, the Department of Energy (DOE) as well as EPA, academia, and industry became deeply involved in the assessment of both available and advanced control technology for the treatment of aqueous discharges. These efforts at the Oak Ridge National Laboratory (ORNL) and other places highlighted a number of unit operations that appeared to hold promise for application to future coal conversion facilities. For various reasons, including the reluctance to test advanced control technology as well as the advanced coal conversion processes, only limited amounts of control technology were included in the process development units and pilot plants that were being constructed. In 1980 it was determined that larger-scale tests would be needed to assess the viability of the various identified control technologies.¹⁷ Concurrently,

actual coal conversion pilot plants were being constructed that would produce considerable amounts of water that would be available for testing purposes.

At this time, ORNL was requested by the Assistant Secretary for Environment (ASEV), DOE, to develop for consideration comprehensive environmental and health plans to study the H-Coal Direct Liquefaction Pilot Plant being constructed at Catlettsburg, Kentucky. Emphasis was to be placed on those aspects of the operation that are applicable to a commercial-size facility. As part of this program, it was deemed appropriate to construct and test a 60-mL/s (1-gpm) process development unit (PDU) to assess various control technologies.

3. PROJECT OBJECTIVES

The 60-mL/s (1-gpm) process development unit consists of three transportable continuous unit operations: carbon adsorption, reverse osmosis, and ozonation. These units will be operated first at the H-Coal pilot plant site in Catlettsburg, Kentucky. The initial objectives of the study are twofold:

1. To evaluate the effectiveness of ozonation, carbon adsorption, and reverse osmosis to produce water of suitable quality for reuse within the conversion process (most probably cooling tower makeup) while minimizing brine disposal requirements. A simultaneous objective is to treat water to quality levels capable of meeting future legal regulations for stream discharge.
2. To provide scale-up data for larger plants.

Carbon adsorption and ozonation will be evaluated as both primary steps in the removal of dissolved organics and as ultimate polishing operations. For the former, the units will process the feed stream to the existing activated sludge process; for the latter, the units will process the existing activated sludge clarifier overflow, which is the present river discharge. The reverse osmosis unit will typically process the effluent from the ozonation and carbon adsorption units to remove

dissolved solids. Reverse osmosis or ultrafiltration may also be evaluated as a primary roughing step prior to biological oxidation for the removal of high-molecular-weight organics, suspended solids, and oil droplets.

The design of the transportable units and the proposed methods for data analysis are the subjects of the remainder of this report. The methods for data analysis are fundamental in the design of a plausible experimental program in that the necessary measured variables are elucidated.

4. DESIGN SUMMARY

The process development unit (PDU) for coal conversion wastewater treatment [60 mL/s (1-gpm) nominal throughput] consists of three transportable continuous processing units — ozonation, granular carbon adsorption, and reverse osmosis (hyperfiltration). These units will be operated initially on selected wastewater streams at the H-Coal pilot plant site in Catlettsburg, Kentucky, to evaluate their effectiveness toward achieving zero stream discharge (i.e., producing an effluent of suitable quality for reuse in the conversion process while minimizing brine disposal requirements) or in producing an effluent capable of meeting future, more stringent stream discharge regulations. These three polishing operations were selected based on (1) reviews of proposed treatment schemes for future large-scale processes, (2) discussions of mutual interest with the personnel of Ashland Synthetic Fuels, Inc., and (3) discussions with the Assistant Secretary for Environment, currently called DOE Assistant Secretary for Environmental Protection, Safety, and Emergency Preparedness.

4.1 Siting Considerations

Coal conversion wastewaters are coal type and process specific and therefore cannot be easily preserved and transported for later processing. Onsite, onstream operations are thus required (1) to produce reliable design data for large-scale processes, and (2) to evaluate the effectiveness of these polishing operations in handling the variations in wastewater composition that result from process upsets and changes in operating conditions.

A schematic of the PDU as sited at the H-Coal pilot plant is given in Fig. 1. The PDU trailers are situated on a paved road between the H-Coal wastewater treatment plant and the coal preparation and storage areas for the H-Coal pilot plant. Wastewater is supplied to the PDU from the existing water treatment plant (from both before and after the aeration basin) through 3/4-in.-diam steel pipe at ~ 0.3 MPa (45 psig). After processing through the PDU, the wastewater is returned to the H-Coal water treatment plant.

4.2 General Flowsheet

The existing wastewater treatment facility at the H-Coal pilot plant (see Fig. 2) consists of gravity separation and induced air flotation for oils and suspended solids removal, distillation stripping for ammonia and sulfide removal, and activated sludge bio-oxidation. The three polishing units will be operated on two streams in the existing facility: the feed stream to the activated sludge unit (see Fig. 2, marker 1), and the overflow stream from the activated sludge clarifier (see Fig. 2, marker 2), which is the present discharge stream. The polishing units can be interconnected as desired to produce various series processing schemes (see Sect. 5.4 for discussion) or they can be operated individually. Each unit includes a 2.65-m^3 (700-gal) mix/surge tank at the front end to permit mixing of any necessary reagents with the process water and to provide surge capacity between the units during series operation.

4.3 Unit Process Designs

Each of the units is designed for a nominal throughput of 60 mL/s (1-gpm). The units are constructed as skid-mounted, self-contained modules that include the vessels, piping, pumps, and instrumentation for each unit. A mixed-media roughing filter is used to prefilter the incoming wastewater stream before it enters the 2.65-m^3 (700-gal) mix/surge tanks associated with each unit. The assemblies will be installed in two 12.4-m (40-ft)-long van trailers for use at the Catlettsburg site. As shown in Fig. 3, the three processing units will be placed in one trailer, while the tanks,

Fig. 2. A schematic of the H-Coal Pilot Plant Wastewater Treatment Facility as operated by Ashland Synthetic Fuels, Inc.

Fig. 3. Layout of polishing train in two 12.4-m (40-ft)-long van trailers as designed by ORNL.

roughing filter, and reagent storage vessels will be placed in the other. Detailed descriptions of the three polishing units are given in the following three sections.

4.3.1 Ozonation

A diagram of the piping and instrumentation for the ozonation system is shown in Fig. 4. Ozone is contacted in counterflow with influent water in a vertical column (26.5 cm in diameter by 1.5 m high). The liquid level in the column is controlled by LIC 202 such that the liquid residence time in the column can be varied independently of the liquid flow rate through the column. The column volume is open, but packing or static mixing elements can be inserted. Four sample ports are positioned along the length of the column and also on the inlet and outlet streams. The maximum ozone delivery rate is 2.7 kg/d when the generator is operated on oxygen; the rate decreases to 1.4 kg/d when operated on air. Maximum gas flow is 1.4 mm³/s (3.0 scfm). The gas phase is dispersed into the column by a 20-cm-diam porous ceramic disk located in the conical section; the nominal bubble size is 3 mm. Column pressure can be controlled at up to 0.3 MPa (30 psig) to improve ozone dissolution. Prior to entering the column, the influent stream is filtered via F-201 to 25 μ m to remove suspended solids that could exert a high ozone demand; the filter can be bypassed if desired. The liquid flow rate to the column is regulated by flow control loop FRC-201. The feed tank circulation pump, P-202, recirculates the tank charge at 600 mL/s ($\sim$ 10 gpm) to mix added reagents and provide pressure head for the feed stream to the contactor column. A pH monitoring and control system can be used to adjust the pH of the feed tank charge by reagent addition. Overpressure protection is provided by a rupture disk on the column head.

4.3.2 Carbon adsorption

A diagram of the piping and instrumentation for the carbon adsorption system is shown in Fig. 5. The configuration consists of three equi-sized columns (26.5 cm in diam by 1.5 m high) filled with granular activated carbon. Typically, only two of the columns are operated in series at one time, while the third is being emptied of spent carbon and refilled with

a fresh carbon charge. Thus the first bed in the series becomes completely contaminant-saturated before it is taken out of service for reloading. The piping network will allow any one of the columns to be first in the treatment sequence. This arrangement provides for the continuous processing of water without interruption of flow during the column unloading-reloading operation. Each column has four sample ports along its length as well as inlet and outlet sample ports. The column samples are withdrawn from the center of the bed. The influent stream is filtered via F-301 to remove suspended solids larger than 25 μm in diam, which (if allowed) could blind the carbon bed; the filter can be bypassed if desired. The liquid flow rate to the column is regulated by flow control loop FRC-301. The feed tank circulation pump, P-302, recirculates the tank charge at 600 mL/s (~ 10 gpm) to mix added reagents and provide pressure head for the feed stream to the system. A pH monitoring and control system can be used to adjust the pH of the feed tank charge by reagent addition. Carbon slurry is transported to and from the columns by pneumatic overpressure. Water flush lines function both in cleaning the carbon slurry transport lines and in back flushing the column underdrains. Overpressure protection is provided by rupture disks on each column.

4.3.3 Reverse osmosis

Figure 6 is a diagram of the piping and instrumentation for the reverse osmosis system. The major components in this system are the high-pressure positive displacement feed pump, P-403 [440 mL/s at 7.0 MPa (7 gpm at 1000 psi)], the pressure control system, PRC-402, for maintaining the desired differential pressure across the membrane, and the membrane assembly, M-401. A concentrate recycle loop is included for high-recovery studies. In this mode of operation, HV-100 is open, and FRC-403 sets the recycle flow rate while FRC-402 sets the rate at which the concentrate leaves the system. With recirculation of the concentrate stream, high liquid velocities across the membrane can be maintained concurrently with high permeate recovery. The system can also be operated in the one-pass mode by closing HV-100. This procedure eliminates the concentrate recycle; thus the concentrate stream makes one pass through the membrane and then exits the system via

FRC-403 and FRC-402. In either mode of operation, liquid throughput is set by controlling the rate at which concentrate exits the system; feed stream and permeate flow rates are continuously recorded by FRC-401 and FR-404. Since most membranes are temperature sensitive, a heat exchanger, E-401, is included for temperature control. At high recycle rates, the heat exchanger can be used to remove the excess heat generated by pump power dissipation, or it can be used to supply heating for elevated temperature tests. The connections to the membrane assembly are by flexible hoses, so assemblies (membrane and pressure vessel) from various manufacturers can be piped in without modification. The feed tank circulation pump, P-402, recirculates the tank charge at 600 mL/s (~ 10 gpm) to mix added reagents and provide pressure head for the feed stream to the system. The influent stream is filtered to 5 μm to remove suspended solids that could possibly blind the membrane surface; the filter can be bypassed if desired. A pH monitoring and control system can be used to adjust the pH of the feed tank charge by reagent addition. The conductivities of the feed, concentrate, and permeate streams are continuously monitored to provide an on-line measurement of separation effectiveness; sample ports are also included on these three streams. Overpressure protection is provided by an adjustable relief valve at the high-pressure pump discharge. All wetted metals in the system are composed of 304 or 316 stainless steel.

4.3.4 Ozonation and carbon adsorption contactor columns

Figures 7, 8, and 9 are the detailed design drawings for the ozonation and carbon adsorption contactor columns. These drawings also contain information on the placement of the porous ceramic diffuser for the ozone flow, the underdrain system for the carbon adsorption columns, and the liquid samplers for the columns. The columns, all interconnecting piping, and the mix/surge tanks are constructed of 304 stainless steel.

Fig. 7. Carbon adsorption and ozonation piping assembly.

5. OVERVIEW OF PROJECTED R&D PROGRAM

5.1 Ozonation

The experimental parameters for ozonation are contact time, ozone treatment rate, column pressure, and pH. The influent and effluent streams will be analyzed for phenols, total organic carbon (TOC), and chemical oxygen demand (COD).

The nominal liquid residence time in the contactor column is 15 min at ~60 mL/s (1 gpm) flow rate and liquid level at 75% of column height. At maximum output, the ozone generator (OREC model 03B6-AR/O) can supply 2.7 kg/d ozone when operated on oxygen and half this amount when operated on air; this value is equivalent to 1.9 or 0.95 g ozone (dependent on parent gas) per gallon of water at 60 mL/s (1 gpm) feed rate. The nominal gas flow rate from the generator is 1.4 mm³/s (3 scfm); maximum ozone concentration on the gas phase at this flow rate is 1 or 2 wt% dependent on parent gas. Concentrations up to 4% can be achieved at lower flow rates. The amount of ozone introduced into the column can be reduced to any value less than maximum by decreasing the power supplied to the ozone generator. Contact time in the column can be varied by either changing the liquid level in the column or by changing the water feed rate to the column. Maximum liquid feed rate is 190 mL/s (3 gpm). Controlled column pressure can be increased to a maximum of 0.3 MPa (30 psig) to enhance dissolution of ozone into the aqueous phase.

The contactor column will approximate a continuous stirred tank reactor. Experimental runs will be conducted at room temperature (~25°C). Figure 10 is a diagram of the contactor column, identifying each of the column streams. Table 1 lists the independent variables, the measured variables, and the parameters that will be calculated from this information. Reaction rate data will be correlated in the form

$$r_x = k[\chi]^f [O_3]^g ,$$

where $[\chi]$ is the contaminant concentration (phenol, COD, TOC) and $[O_3]$ is the dissolved ozone concentration. Investigators (Hewes and Davidson,¹⁸ Gould and Weber,¹⁹ and Li and Kuo²⁰ have shown that the reaction rate of

ORNL DWG 82-160

Fig. 10. Schematic of ozonation column.

Table 1. Ozonation system analysis; independent and measured variables, and calculated parameters

Independent variables → maximum value

Water influent rate → 190 mL/s (3 gpm)

Liquid holdup in contactor column → 75 L (20 gal)

Ozone treatment rate → 2.7 kg/d (6 lb/d)

Pressure → 0.3 MPa (30 psig)

pH of influent water → 11

Measured variables

Water influent rate - $Q_1 \left[\frac{m}{t} \right]$

Gas influent rate - $Q_3 \left[\frac{m}{t} \right]$

Water influent contaminant concentration - $X_1 \left[\frac{m}{m} \right]$

Water effluent contaminant concentration - $X_2 \left[\frac{m}{m} \right]$

Gas influent O_3 concentration - $Y_3 \left[\frac{m}{m} \right]$

Gas effluent O_3 concentration - $Y_4 \left[\frac{m}{m} \right]$

Dissolved O_3 concentration in reactor liquid phase - $Y_2 \left[\frac{m}{m} \right]$

pH of reactor liquid phase

Calculated parameters

Ozone treatment rate $\left[\frac{m}{t} \right]$

$$\dot{m}_{O_3} = Y_3 Q_3$$

Table 1. (continued)

Ozone absorption rate $\left[\frac{m}{t}\right]$

$$\dot{m}_{O_3, ABS} = Y_3 Q_3 - Y_4 Q_4$$

Contaminant depletion $\left[\frac{m}{t}\right]$

$$\dot{m}_x = X_1 Q_1 - X_2 Q_2$$

Contaminant reaction rate $\left[\frac{m}{L^3 t}\right]$

$$r_x = \frac{Q_1(X_1 - X_2)}{V}$$

V — contactor column liquid holdup $[L^3]$

Ozone absorption efficiency

$$\eta_{O_3, ABS} = \frac{\dot{m}_{O_3, ABS}}{\dot{m}_{O_3, IN}}$$

Contaminant removal efficiency

$$\eta_{x, O_3, ABS} = \frac{\dot{m}_x}{\dot{m}_{O_3, ABS}}$$

or

$$\eta_{x, O_3, IN} = \frac{\dot{m}_x}{\dot{m}_{O_3, IN}}$$

Volumetric mass-transfer coefficient $[t^{-1}]$

$$k_L a = \frac{\dot{m}_{O_3, ABS}}{V \rho (Y^* - Y_2)_{lm}}$$

Y^* — dissolved O_3 concentration in equilibrium with the gas phase

Table 1. (continued)

ρ - density of water $\left[\frac{\text{m}}{\text{L}^3}\right]$

$$(Y^* - Y_2)_{lm} = \frac{(Y^*_{IN} - Y_2) - (Y^*_{OUT} - Y_2)}{\ln \left[\frac{Y^*_{IN} - Y_2}{Y^*_{OUT} - Y_2} \right]}$$

ozone with dissolved organic compounds depends on the quantity of dissolved ozone decomposing rather than directly on the concentration of dissolved ozone, and that the rate of ozone decomposition increases with increasing pH. Therefore, the rate constant in the kinetic expression is pH dependent.

Experimental runs will be conducted at different operating conditions (pH, contact time, ozone treatment rate, and column pressure) to generate data for correlation of the kinetic parameters.

5.2 Carbon Adsorption

The carbon adsorption unit is designed to permit bed-depth-service-time studies (BDST)²¹⁻²³ using carbons from various manufacturers; these tests will provide the information required for optimal design of an adsorption system for a specific wastewater. Experimental parameters are carbon type, pH, and flow rate to the columns — up to 190 mL/s (3 gpm). The columns will be operated isothermally at room temperature (~25°C). Water pH may have an appreciable effect on adsorption characteristics because phenolics, which are weak organic acids, adsorb more easily in the undissociated state than in the dissociated state. The nominal flow rate to the columns is 60 mL/s (1 gpm); this represents a hydraulic

loading of 1360 mL/s-m² (2 gpm/ft²) based on column cross-sectional area. Sample ports are located on the feed and discharge streams for each column and at 30-cm intervals within the columns. Figure 11 is a diagram of an adsorber column which illustrates the flow configuration and sample port placement. Typically, two columns will be operated in series. When the lead column becomes contaminant saturated, it is taken off-line and the column that was second in the series becomes the new lead column. The remaining column is brought on-line as the second column in the treatment sequence. This procedure is cycled to allow the adsorption wave front to become fully established.

The BDST analysis is based on work by Bohart and Adams,²¹ Klotz,²² and Dole and Klotz.²³ Simultaneous material balances are performed on both the liquid flowing through the carbon bed and on the stationary carbon bed. It is assumed that the rate of solute adsorption is proportional to the product of the fraction of adsorptive capacity remaining in the carbon and the concentration of adsorbate in the liquid phase. This results in the following equation:

$$t = \frac{a_o^2 \rho A}{C_o^2 Q} x - \frac{1}{k C_o} \ln \left(\frac{C_o}{C} - 1 \right) \quad (1)$$

where

- a_o = adsorptive capacity of carbon in $\left[\frac{m}{m} \right]$ equilibrium with feedstream concentration,
- A = cross-sectional area of adsorber column, L²;
- C_o = feedstream concentration, $\frac{m}{m}$;
- C = liquid-phase breakthrough concentration, $\frac{m}{m}$;
- k = adsorption rate constant, t⁻¹;
- t = service time at breakthrough, t;
- x = bed depth, L;
- ρ = carbon bulk density, $\frac{m}{L^3}$;
- Q = feed rate, $\frac{m}{t}$.

ORNL DWG 82-159

Fig. 11. Schematic of carbon adsorption column.

For a given carbon-wastewater system with a specified discharge quality, α , A , C , k , and ρ are constant. At constant flow rate, Q and influent concentration, C_0 , Eq. (1) reduces to a straight-line form:

$$t = mx + b \quad , \quad (2)$$

where

$$m = \text{slope, } \frac{t}{L}; \text{ and}$$

$$b = \text{intercept, } t.$$

The slope, m , is proportional to the inverse of the rate of movement of the adsorption wave-front and the t intercept, b , is inversely proportional to the adsorption rate constant, k .

For the BDST studies, the flow rate to the columns is held steady, and samples of the feed and the liquid in the columns at all intermediate bed sample points are taken and analyzed at regular intervals for phenols, COD, and TOC. To produce breakthrough curves, these data are plotted as percent impurity remaining vs service time (or equivalently, flow) for each sample point. A sample plot is presented in Fig. 12. Once the adsorption wave is established as indicated by invariant shape of successive breakthrough curves, breakthrough points, the height of the mass transfer zone (HMTZ) and the rate of carbon exhaustion or rate of movement of the mass transfer zone (RMTZ) can be determined. The HMTZ is defined as the bed height required for liquid concentration to decrease from influent to an arbitrary specification concentration. The HMTZ is the length of carbon bed between the specification concentration and influent concentration. This length is indicated by the vertical line on Fig. 12. The RMTZ is determined by measuring the time required for the effluent specification concentration to progress through a known bed depth. This rate is indicated by the horizontal line on Fig. 12; the RMTZ represents the time (cumulative flow) required for the adsorption wave-front to progress the distance between the two sample points in the carbon bed. The BDST equation [Eq. (1)] can be used to extrapolate breakthrough curve data to operating conditions other than those

Fig. 12. Simulated breakthrough curves for carbon adsorption experiments.

at which the column tests were performed. Sample BDST plots are presented in Fig. 13. Each line represents a different breakthrough specification. As noted previously, the slope, m , of the BDST equation is proportional to the inverse of the RMTZ and is given by

$$m = \frac{a_o^2 \rho A}{C_o^2 Q} \quad (3)$$

The slope can be adjusted for changes in any of the operating parameters in this expression. Also, the intercept, b , can be adjusted for changes in feed concentration and effluent specification, since

$$b = - \frac{1}{kC_o} \ln \left(\frac{C_o}{C} - 1 \right)$$

For adsorption of phenolics from petroleum refinery wastewater, Hutchins²⁴ used a similar method to verify extrapolations of BDST results for 50% changes in flow rate and concentration.

5.3 Reverse Osmosis

Commercially available reverse osmosis membranes will be evaluated for dissolved solids rejection, permeate recovery, and fouling characteristics. The three major classes of membrane materials will be investigated — cellulose acetate, polyamide, and hydrous zirconium oxide. The cellulose acetate membrane provides very high salt rejection, but usage is restricted to pH ranges 2 to 8 to prevent hydrolysis of the membrane. Polyamide membranes provide salt rejections as high as cellulose acetate, and they can be used over a broader pH range; however, they are very sensitive to oxidation. The hydrous zirconium oxide membranes are very stable chemically but do not reject salt as well as cellulose acetate or polyamide. The amount of pH adjustment, degree of prefiltering, and antifoulant additives required for stable operation of each membrane type will be determined.

ORNL DWG 82-161

Fig. 13. Bed-depth-service-time plot for a simulated carbon adsorption experiment.

Rejection, γ , is defined as the fractional concentration distribution across the membrane and is shown as

$$\gamma = 1 - \frac{\text{Permeate concentration}}{\text{Brine concentration}} \quad (4)$$

Permeate recovery, R , is the fraction of feed to the membrane that is recovered as permeate and is expressed as

$$R = \frac{\text{Permeate rate}}{\text{Feed rate}} \quad (5)$$

Within the normal concentration operating range of most membranes, rejection is not a function of brine side concentration; that is, rejection is independent of recovery. With this assumption, a differential material balance along the length of a membrane can be performed. This material balance results in the following expression for membrane rejection as a function of recovery, R , feed concentration, χ , and permeate concentration, Y :

$$\gamma = 1 - \frac{\ln \left[1 - \frac{RY}{\chi} \right]}{\ln[1 - R]} \quad (6)$$

This equation will be used to calculate rejections for the various membranes tested.

Figure 14 is a simple flow diagram for the reverse osmosis system. The concentrate circulation loop on the unit will permit variation of concentrate flow rate through the membrane assembly independent of feed rate. This recirculation will allow high permeate recovery to be achieved while maintaining sufficient velocity for turbulent flow on the concentrate (high pressure) side of the membrane.

The primary measurements of permeate quality will be conductivity and total dissolved solids. Samples will also be collected for specific ion and COD analyses. Results will be presented in time-history form for rejection and recovery (flux) so that long-term performance can be evaluated. In addition to reverse osmosis studies, this system can be used to evaluate ultrafiltration membranes for organics removal.

Fig. 14. Reverse osmosis unit schematic diagram.

5.4 Sequence Comparisons

For polishing studies, the carbon adsorption, ozonation, and reverse osmosis units will be operated in series on the activated sludge clarifier overflow stream. The control elements for the feed stream to each module are arranged so that the three processing units can be operated in series by feeding the first unit on flow control while feeding the second and third units on level control from their associated mix/surge tanks. The treatment sequence can be varied as desired since each processing unit has both control modes for the feed stream. When the units are operated singularly, the feed stream rate will be flow controlled. The order of carbon adsorption and ozonation will be interchanged to determine the most effective sequence. Also, ozonation and carbon adsorption will be evaluated as singular treatments prior to reverse osmosis. These same treatment sequences will be evaluated on the activated sludge feed stream for the use of carbon adsorption and ozonation in lieu of biological oxidation.

Another treatment option on the activated sludge feed stream is the use of reverse osmosis or ultrafiltration to remove high-molecular-weight organics and suspended matter.

6. REFERENCES AND SELECTED BIBLIOGRAPHY

1. J. S. Zogorski and S. D. Faust, "Operational Parameters for Optimum Removal of Phenolic Compounds from Polluted Waters by Columns of Activated Carbon," *AIChE Symp. Ser. — Water*, No. 166, 73:59 (1976).
2. G. M. Lukchis, "Adsorption Systems — Design by Mass-transfer Zone Concept," *Chem. Eng.* 80(6):111 (1973).
3. K. B. Hird, W. R. Kube, and H. H. Schobert, *Activated Carbon Absorption from a High TOC Wastewater*, DOE/GFETC/RI-80/6.
4. B. M. Vliet and W. J. Weber, Jr., "Comparative Performance of Synthetic Absorbents and Activated Carbon for Specific Compound Removal from Wastewaters," *J. Water Pollut. Control Fed.* 53(11):1585 (1981).
5. D. M. Giusti, R. A. Conway, and G. T. Lawson, "Activated Carbon Adsorption of Petrochemicals," *J. Water Pollut. Control Fed.* 46(5):947 (1974).
6. R. G. Luthy, "Treatment and Reuse of Coal Conversion Wastewaters," presented at the Symposium on Environmental Aspects of Fuel Conversion Technology, V, St. Louis, Mo., September 1980.
7. Y. Argaman and W. W. Eckenfelder, Jr., "Factors Affecting the Design of Multistage Carbon Columns for Industrial Waste Treatment," *AIChE Symp. Ser. — Water*, No. 166 73:36-42 (1976).
8. R. K. Chakravorti and T. W. Weber, "A Comprehensive Study of the Adsorption of Phenol in a Packed Bed of Activated Carbon," *AIChE Symp. Ser. — Water*, No. 151, 11:392 (1975).
9. D. A. Dzombak and R. G. Luthy, *Water Management and Wastewater Reuse in SRC Coal Liquefaction Facilities*, DOE/PC/30262-1 (1981).
10. *Processing Needs and Methodology for Wastewaters from the Conversion of Coal, Oil Shale, and Biomass to Synfuels*, DOE/EV-0081 (1980).
11. C. A. Brandon and G. Spencer, *Assessment of Hyperfiltration and Ultrafiltration for Treatment of Oil Shale Wastewater*, prepared for Monsanto Research Co. by Carre, Inc., Seneca, S.C. (1981).
12. R. A. Knight, "Separation of Coal Conversion Wastewater Components by Reverse Osmosis," presented at the Division of Environmental Chemistry, American Chemical Society, New York, August 1981.
13. S. L. Klemetson, "Treatment of Phenolic Waste," p. 447 in *Proceedings of the Environmental Aspects of Fuel Conversion Technology, III*, EPA-600/7-78-063 (April 1978).

14. A. G. Hill, J. B. Howell, and H. K. Huckabay, "Reaction of Ozone with Trace Organics in a Pressurized Bubble Column," *AIChE Symp. Ser.*, No. 197, 76:150 (1980).
15. K. Y. Li and C. H. Kuo, "Absorption and Reactions of Ozone in Phenolic Solutions," *AIChE Symp. Ser.*, No. 197, 76:161 (1980).
16. J. A. Roth, W. L. Moench, and K. A. Debelak, "Kinetic Modeling of the Ozonation of Phenol in Water," Vanderbilt University, Nashville, Tennessee, 1981, unpublished data.
17. T. W. Barrs et al., *Assessment of Coal Gasification Wastewater Treatment Technology*, prepared for U.S. DOE METC, Morgantown, W. Va., by the Mittelhauser Corporation, Downers Grove, Ill., November 1980.
18. C. G. Hewes and R. R. Davidson, "Kinetics of Ozone Decomposition and Reaction with Organics in Water," *AIChE J.* 17:141 (1971).
19. J. P. Gould and W. J. Weber, "Oxidation of Phenols by Ozone," *J. Water Pollut. Control Fed.* 48:27 (1976).
20. K. Y. Li, C. H. Kuo, and J. L. Weeks, "A Kinetic Study of Ozone-Phenol Reaction in Aqueous Solutions," *AIChE J.* 25:583 (1979).
21. G. S. Bohart and E. Q. Adams, "Some Aspects of the Behavior of Charcoal with Respect to Chlorine," *J. Am. Chem. Soc.* 42:523 (1920).
22. I. M. Klotz, "The Adsorption Wave," *Chem. Rev.* 39:241 (1946).
23. M. Dole and J. M. Klotz, "Sorption of Chloropicrin and Phosgene on Charcoal from a Flowing Gas Stream," *Ind. Eng. Chem.* 38:1289 (1946).
24. R. A. Hutchins, "Activated Carbon Systems," *Chem. Eng.* 80(19):133 (1973).

INTERNAL DISTRIBUTION

1. C. R. Boston	31. H. R. Meyer
2-6. C. H. Brown	32-36. G. E. Oswald
7. C. K. Brown	37. L. W. Rickert
8. G. F. Cada	38. J. W. Roddy
9. H. D. Cochran	39. J. C. Rose
10. K. E. Cowser	40. C. D. Scott
11. J. L. Epler	41-42. C. H. Shappert
12. R. B. Gammage	43. R. H. Strand
13. C. W. Gehrs	44. S. D. Van Hoesen
14-18. R. K. Genung	45. V. C. A. Vaughan
19. M. R. Guerin	46-50. J. F. Walker
20. M. T. Harris	51. S. K. Whatley
21. A. R. Hawthorne	52. A. M. Squires (Consultant)
22. J. R. Hightower	53-54. Laboratory Records
23. J. K. Huffstetler	55. Laboratory Records - RC
24. C. R. Kirkpatrick	56. ORNL Patent Section
25-29. J. A. Klein	57-58. Central Research Library
30. L. E. McNeese	59. ORNL-Y-12 Technical Library
Document Reference Section

EXTERNAL DISTRIBUTION

Argonne National Laboratory, 3700 South Cass Avenue, Argonne, IL 60439

- 60. C. Reilly
- 61. J. Stetter
- 62. K. E. Wilzbach

Ashland Synthetic Fuels, Inc., P. O. Box 391, Ashland, KY 41101

63. B. Cherton	67. R. H. Hill
64. J. H. Gray	68. S. W. Kuhner
65. R. Gross	69. J. Padula
66. J. Hill	70. T. H. Wigglesworth

Battelle Pacific Northwest Laboratories, P. O. Box 999, Richland, WA 99352

71. H. Drucker	73. J. Strand
72. R. Gray	74. B. Vaughan

DOE-Environmental Protection, Washington, D. C. 20545

75. J. A. Coleman	79. D. Lillian
76. C. Grua	80. R. D. Shull
77. H. Hollister	81. R. J. Stern
78. P. House	82. F. E. Witmer

DOE-Fossil Energy, Washington, C. C. 20545

83. J. H. Abraham	92. J. C. Johnson
84. J. D. Batchelor	93. E. J. Lievens
85. D. Bauer	94. S. Matovich
86. P. H. Buhl	95. L. Miller
87. G. F. Dick	96. J. Morris
88. J. K. Farley	97. P. Musser
89. W. E. Fernald	98. J. A. Nardella
90. R. M. Hamilton	99. M. Rogowsky
91. A. Hartstein	100. R. Von Saunder
	101. R. Weinraub

DOE Morgantown Energy Technology Center, P. O. Box 880, Morgantown, WV 26505

102. L. Headley	104. A. Pituito
103. J. D. Pearson	105. R. E. Schafer

DOE-Oak Ridge Operations

106. Office of Assistant Manager for Energy Research and Development	107. C. W. DiBella
	108. J. A. Reafsnyder
	109. R. R. Santore

DOE-OHER/ER, Washington, D. C. 20545

110. N. F. Barr	125. H. McGammon
111. J. R. Blair	126. M. L. Minthorn
112-121. A. P. Duhamel	127. D. A. Smith
122. C. W. Edington	128. G. Stapleton
123. R. Franklin	129. J. Thiessen
124. G. Goldstein	130. F. Wobber
	131. R. W. Wood

DOE Pittsburgh Energy Technology Center, 4800 Forbes Avenue, Pittsburgh, PA 15213

132. S. W. Chun	134. H. Retcofsky
133. C. Drummond	135. A. G. Sharkey

Electric Power Research Institute, 3412 Hillview Avenue, Palo Alto, CA 94303

- 136. R. M. Perhac
- 137. W. C. Rovesti

Exxon R&D, Slorham Park, NJ 07932

- 138. S. Blum
- 139. D. Thomas
- 140. J. Vic

Gulf Mineral Resources Company, 1720 South Bellaire, Denver, CO 80222

- 141. D. Schmalzer
- 142. W. Hubis

Kentucky Center for Energy Research, Kentucky Department of Energy,
P. O. Box 11888, Lexington, KY 40578

- 143. H. Enoch
- 144. J. Mitchell

U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

145. D. L. Coffin	151. J. Javanovich
146. R. Hangebrauk	152. D. Kirchgassnar
147-148. D. B. Henschel	153. A. Moghissi
149-150. T. K. Janes	154-155. W. J. Rhodes
	156. E. Tucker

- 157. Paul Boron, Calgon Corporation, Calgon Center, P. O. Box 1346, Pittsburgh, PA 15230.
- 158. Lee Comb, Osmonics, Inc., 5951 Clearwater Drive, Minnetonka, MN 55343.
- 159. Kenneth A. Debelak, Chemical Engineering, Vanderbilt University, Nashville, TN 37235.
- 160. M. S. Denton, Chemical Separations Corporation, One Technology Drive, Pellissippi Parkway, Concord, TN.
- 161. W. W. Eckenfelter, Jr., Vanderbilt University, Nashville, TN 37235.
- 162. M. Fuchs, Radian Corporation, 8501 Mo-Pac Boulevard, P. O. Box 9948, Austin, TX 78166.
- 163. W. Goldman, Hydrocarbon Research Inc., N.Y. and Puritan Avenue, P. O. Box 6047, Lawrenceville, NJ 08648.
- 164. Peter A. Krenkel, University of Nevada, P. O. Box 60220, Reno, NV.
- 165. M. J. Massey, Environmental Research and Technology, 700 Fifth Avenue, Pittsburgh, PA 15219.

166. R. E. Maurer, Black, Sivalls, and Bryson, Inc., Coal Gasification Systems, 8303 Southwest Freeway, Houston, TX 77074.
167. F. O. Mixon, P. O. Box 12194, Research Triangle Park, NC 27709.
168. R. D. Neufeld, Environmental Engineering Program, 949 Benedum Hall, University of Pittsburgh, Pittsburgh, PA 15261.
169. R. E. Poulson, Laramie Energy Technology Center, P. O. Box 3395, University Station, Laramie, WY 82071.
170. R. Steele, SRI International, Building 110, 333 Ravenswood Avenue, Menlow Park, CA 94025.
171. J. Tao, International Coal Refining Company, P. O. Box 2752, Allentown, PA 18001.
- 172-198. Technical Information Center, Oak Ridge, TN 37830.
199. C. W. Zielke, Conoco Coal Development Company, Research Division, Library, PA 15129.