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STUDY OF THE TREATABILITY OF WASTEWATER FROM A COAL GASIFICATION PLANT

Final Report for Period July 15, 1978—July 14, 1980

By
Albert F. Iglar

Work Performed Under Contract No. AS22-78ET00234

East Tennessee State University
School of Public and Allied Health
Department of Environmental Health
Johnson City, Tennessee

U. S. DEPARTMENT OF ENERGY

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FINAL REPORT

Study of the Treatability of Wastewater From a Coal Gasification Plant

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East Tennessee State University
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Under
Special Research Agreement
AS22-78-ET00234

With

U.S. Department of Energy
Pittsburgh Energy Technology Center

By

Albert F. Iglar, Ph.D., P.E., Principal Investigator,
and Other Project Personnel

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Abstract

This study focused on the coal gasification facility serving the Holston Army Ammunition Plant in Kingsport, Tennessee. Objectives were to characterize the wastewater produced by the gasification facility, and to evaluate technology for treating the waste in preparation for discharge to the environment.

Most wastewater was recycled for scrubbing and cooling the product gas, with the excess requiring disposal found to be an average of only 1,170 gallons per day (53 gallons per ton of coal, as received, and 366 gallons per million cubic feet of product gas). Chemical characterization of the untreated wastewater was based on approximately 40 samples. Analysis indicated that the waste was warm, high in alkaline material, especially ammonia, high in organic material, especially phenols, and also contaminated with other substances. Sulfides and thiocyanates were especially high in concentration.

It was found that pretreatment could be accomplished by stripping (air injection) at high pH, removal of grease and oil (by pH suppression and light aeration) and neutralization. Equations were developed to describe the first two steps.

Biological treatment through activated sludge was found to be successful, but effected only a moderate degree of treatment, and was troubled with frequent process upset. Attempts to improve treatment efficiency and stability included stabilized influent concentration of biochemical oxygen demand (little improvement), chemical precipitation in the aeration tank (apparently beneficial), and chemical precipitation of the biological effluent (very effective in removing high suspended solids). The data indicated the need to study aerated waste stabilization ponds as an alternative to activated sludge. Joint treatment of small amounts of coal gasification wastewater mixed with settled municipal sewage also was successful. Biological reaction kinetics were studied for activated sludge.

Evaluation of the application of granular activated carbon suggested that this could be an effective practical means of tertiary treatment.

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Chapter 1

Introduction

On July 24, 1978, the United States Department of Energy, through the Pittsburgh Energy Technology Center, entered into Special Research Agreement AS2278ET-00234 with East Tennessee State University. Appendix A includes a copy of the most pertinent provisions of the contract.

Generally, the contract provided for a study of wastewater from the coal gasification plant serving the Holston Army Ammunition Plant, Holston Defense Corporation, Kingsport, Tennessee. Specific objectives included:

1. Characterization of the wastewater flow, physical characteristics, and, especially, chemical characteristics.
2. Evaluation of control technology for processing the wastewater preparatory to discharge to the environment, including:
   a. pretreatment
   b. by-product recovery
   c. emphasis on biological treatment, especially by the activated sludge process, and considering several treatment alternatives, levels of pollutant parameters before and after treatment, loading and design parameters, and investigation of treatment kinetics.

The Holston Coal Gasification Plant

Figure 1 is a schematic diagram of the Holston Coal Gasification Plant. The Annual Report for this study, dated July, 1979 (89) provides a thorough description of the plant. For the present, only basic data on the Gasification Plant and its operation will be noted:

Year of construction: 1942

Number of Gasifiers: 12

Plant nominal capacity: 132 tons per day of coal; 19 million standard cubic feet per day of product gas.

Plant Operation: 2 gasifiers, 22 tons per day of coal, 3.2 million standard cubic feet per day of product gas.

Operation of the Coal Gasification Plant was reported to be nearly constant

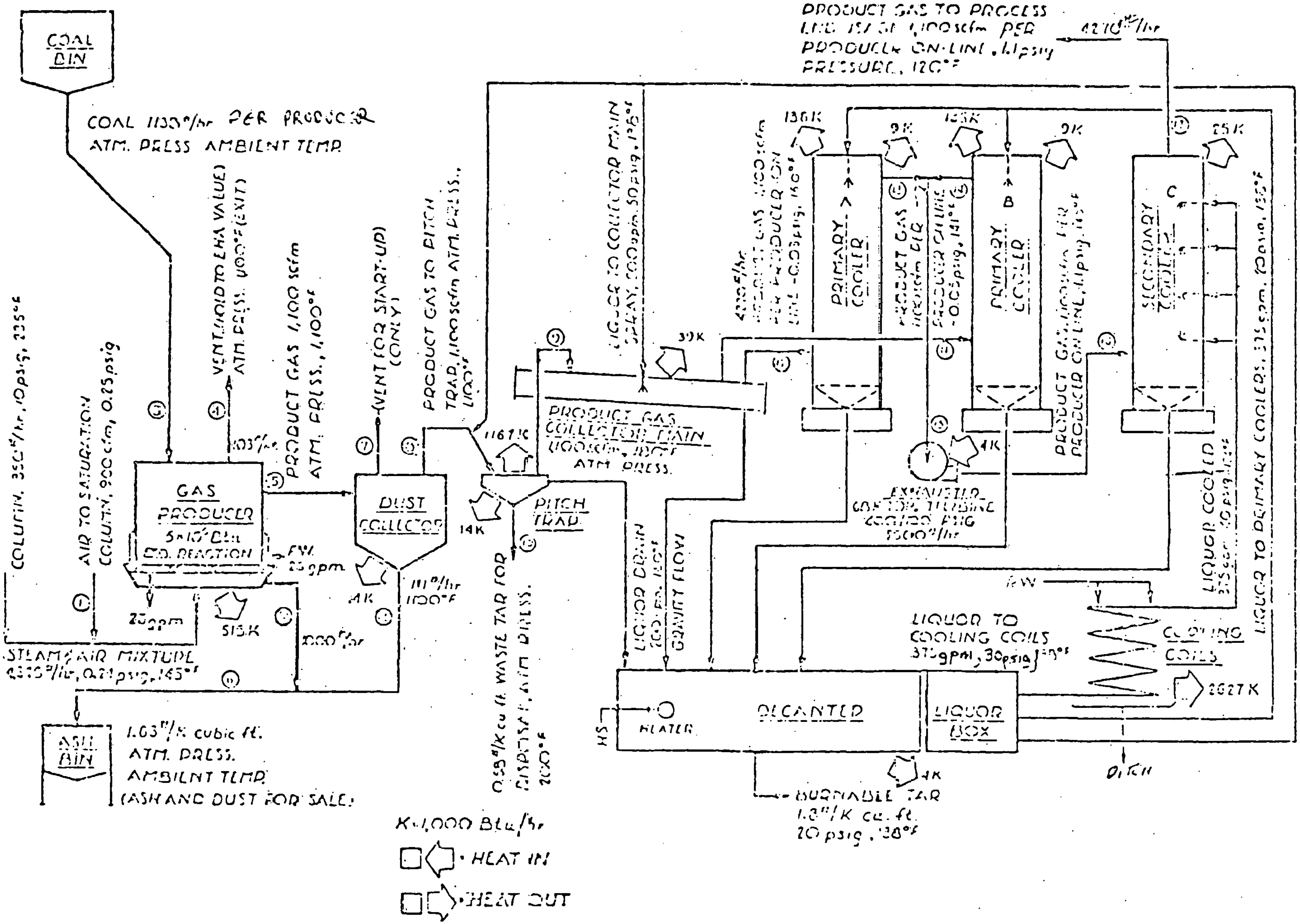


Figure 1

Schematic Diagram of the Holston Coal Gasification Plant over the course of time. However, routine operation involves placing individual gasifiers in service and out of service, as necessary to keep two units in operation at any given time, as well as subjecting gasifiers to "burn-out" in order to remove accumulations of combustible material. Table 1 gives the history of these activities during the period of this study, as taken from plant operation records.

Table 1

History of Operation of Gasifiers at Holston Army Ammunition Plant For Period of Study

Gasifier Number	Date	Activity
1	4/8/80	Placed in service
2	4/9/80	Placed in service
7	5/12/78	Burn-out
	9/1/78	Taken out of service
	10/5/78	Placed in service
	12/13/78	Burn-out
	4/13/79	Taken out of service, burn-out
	6/6/79	Placed in service
	9/5/79	Burn-out, returned to service
	12/11/79	Burn-out, returned to service
	4/9/80	Taken out of service, burn-out
8	1/27/78	Taken out of service, burn-out
	12/11/78	Placed in service
	4/11/79	Burn-out, returned to service
	6/7/79	Taken out of service, burn-out
	9/13/79	Placed in service
	12/13/79	Burn-out, returned to service
	4/9/80	Taken out of service, burn-out
9	8/25/78	Burn-out, returned to service
	10/3/78	Taken from service, burn-out
	4/9/79	Placed in service
	6/15/79	Taken from service, burn-out
10	4/7/78	Taken from service, burn-out
	9/1/78	Placed in service
	12/15/78	Taken from service, burn-out
	6/14/79	Placed in service
	9/7/79	Burn-out, returned to service
	9/13/79	Taken from service

Coal for the plant is obtained under long-term contract. It is a metallurgical grade fuel, used in pieces about 2 to 4 inches in size. Beginning about May 1, 1979, coal began to be received from a new source, and, though similar to coal previously used in many characteristics, was thought by plant personnel to yield increased grease and oil in the wastewater. Table 2 provides four analyses of the coal, considered by plant staff to be typical of the numerous analyses actually performed.

Two decanters, each serving a side of six gasifiers, receive all process waters from the coal gasification plant, but not cooling water. One decanter is used to serve the two gasifiers in operation at any given time, and functions essentially as a settling tank, removing excess grease and oil from the wastewater as preparation for recycling the wastewater for scrubbing and cooling the product gas. Data on the system are as follows:

Decanter dimensions: 47 feet long by 8 feet wide by 11 feet liquid depth (each).

Decanter capacity: 31,000 gallons (each).

Decanter heating: steam heater used to maintain 60°C.

Table 2

Analyses of Coal Used at Holston Coal Gasification Plant

	Date of Delivery of Coal			
	8/14-8/26, 1978	9/18-10/2, 1978	3/19-4/1, 1980	4/3-4/14, 1980
As Received:				
Moisture, %	2.9	2.9	4.4	3.7
BTV/lb.	13,910	14,290	13,640	13,830
Dry Basis:				
Volatile Matter, %	40.1	40.0	38.5	38.2
Fixed Carbon, %	55.6	57.6	56.4	57.1
Ash, %	4.3	2.4	5.1	4.7
Sulfur, %	0.8	0.6	1.0	0.7
BTU/lb.	14,330	14,720	14,260	14,360

Recycle pumps: Three, having rated capacities of 200 gpm, 375 gpm, and 375 gpm. Present capacity not known.

Decanter detention: 0.68 hour, based on pumps operating at 80% of rated capacity.

Evaporators: Two units, each horizontal cylinders, 9 feet in diameter by 20 feet long.

Evaporator operation: Excess wastewater overflows the decanter into the evaporator sump. Wastewater is evaporated, typically three times per week in winter, one time per week in summer, with the evaporator concentrate (about 2/3 of original volume) returned to evaporator sump. From sump, wastewater is pumped back to the decanter as necessary to make up for water loss when accumulated tar is pumped from the decanter, about once every two days.

Amount of wastewater actually evaporated: Estimated at 7,200 gallons per week in winter, 2,400 gallons per week in summer, and an annual average of 4,800 gallons per week (685 gallons per day).

Additionally, some water is removed with the grease and oil accumulations pumped from the decanter. Table 3 records the amounts pumped during most of the period of study. Plant personnel estimated that the material contained 10% of water, and had a density of 9.5 pounds per gallon. This would mean an increase of approximately 485 gallons per day in the annual average amount of wastewater produced, for a total of 1,170 gallons per day. It is to be noted that this compares well with the 1,100 to 1,200 gallons per day which typically would be added in the form of steam and as moisture in the coal.

Table 3

Amount of Grease and Oil Pumped From Decanter

Month	Amount Pumped (lb.)
July, 1978	136,999
August, 1978	119,030
September, 1978	137,328
October, 1978	137,872
November, 1978	146,435
December, 1978	145,475
January, 1979	158,301
February, 1979	127,905
March, 1979	147,712
April, 1979	152,939
May, 1979	153,920
June, 1979	137,503
July, 1979	155,552
August, 1979	119,048
September, 1979	128,713
October, 1979	149,783
November, 1979	144,131
December, 1979	124,869
January, 1980	114,261
February, 1980	133,956
March, 1980	119,257
April, 1980	155,446
May, 1980	126,764
Range	114,261 - 158,301
Mean	137,965
S.D.	13,548
n	23

CHAPTER 2

Review of the Literature

A number of gasification techniques are among the various coal conversion processes that are at various stages of development (35). Though it has been suggested that water pollution from gasification plants may be manageable (2), there also are indications that problems with water pollution could occur unless adequate precautions are taken. This chapter notes the general characteristics of coal gasification wastewater, and concentrates on a survey of possibilities for its management.

The Wastewater

Wastewater arising from coal gasification processes has several general sources, including water formed by condensation of steam, water formed by chemical reaction, water from the quenching of slag and residue and their removal as slurry, water used for cooling, water used to scrub the product gases for removal of contaminants, compression condensates, and water of dehydration (57).

The quantity of process wastewater may be moderate compared with flows from large municipalities. Study done at the Pittsburgh Energy Technology Center (PETC) indicated "condensate production" ranging from 1.37 to 1.96 lb. of water per lb. of coal, on a moisture-and-ash-free basis (74). For a gasification plant with a capacity of 10,000 tons/day of coal, this would indicate a wastewater flow of 3.3 to 4.7 million gallons per day (mgd). Goldstein and Probstein provided estimates of water consumption for synthetic natural gas plants in two locations, and, based on a facility with 250 million scf/day capacity, indicated values of 3.80 and 5.50 mgd (26). This analysis considered a size of plant which has been discussed for commercial application.

Data on the chemical characteristics of coal gasification wastewater can be found in various sources. Generally, pollutant levels vary with the coal conversion processes that is used (66), the particular coal and its quality (lower grade coals tending to produce more contaminants) (66), reactor temperature and residence time (lower values being associated with higher levels of contaminants) (66), the reactor type, the "coal injection geometry" (48), and more. Table 4 summarizes selected data on the chemical characteristics of coal gasification wastewater.

The matter of toxic substances in the wastewater has been studied, and, despite the development of considerable data, a full evaluation has not been presented. Generally, numerous trace organic compounds can be found, as well as many trace elements (23,24,39,44,56,62,64,70,75).

ALTERNATIVES FOR WATER POLLUTION CONTROL

The major general alternatives for water pollution control from coal conversion facilities include:

1. Refinement of production process - Optimization of production processes well may include development of means for keeping pollutants out of the wastewater. The refinement of the Synthane process is a good example of what may be done (45).
2. Reuse of Wastewater and Materials - The major possibilities for materials recovery seem to be phenol, separated by solvent extraction, and ammonia, removed by a type of stripping. However, ammonia recovery may or may not be economical, and the recovered phenol might be useable mainly as fuel, unless there was extensive, costly refining. Reuse of wastewater for scrubbing product gas might require only rather simple removal of suspended solids (especially oil and grease) by settling and skimming, possibly supplemented by chemical precipitation, flotation, and sand filtration (61). Some wastewater would remain,

Table 4

Chemical Characteristics of Coal Gasification Wastewater

Source	Year	Parameter	Value
Forney et al. (22)	1975	Phenols	200-6,000 mg/l
		Thiocyanates	21-200
		Suspended Solids	23-600
		BOD (5 day)	2,500-22,000
		COD	1,700-43,000
		Ammonia	2,500-11,000
		Cyanides	0.1-0.6
		pH	7.9-9.3
PETC (70)	1976	TOC	8,000 mg/l
		COD	18,000
		Phenols	3,500
PETC (74)	1977	Ammonia	7,255 mg/l
		Total Sulfur	185
		Sulfide	10
		Phenols	2,120
		COD	22,200

requiring treatment and disposal, though the quantity would be reduced. This recycle may be widely applicable to coal gasification plants. Additionally, with higher order treatment, wastewater could be recycled for other purposes.

3. Joint Treatment with Municipal Sewage - At first examination, treatment of coal conversion waste in municipal plants would seem to have advantages (14). In a community of substantial size, the coal conversion waste might be a minor part of the total load on the treatment facilities. Municipal waste would provide dilution and nutrients. However, design of the facility would have to be based on inclusion of the coal conversion wastewater, so that, for example, adequate aeration could be provided and an alternative to chlorine used for disinfection (to avoid formation of chlorinated organics, especially chlorophenols) (61).
4. Separate Treatment - Generally, it appears realistic that at least some coal conversion wastewater of significant pollutant levels will require treatment. However, a substantial body of literature indicates that this may be accomplished.

Pretreatment

Equalization Tanks - Various biological treatment processes operate most effectively at constant loading. Thus, if variations in the rate of flow are expected, an influent equalization tank, sized to permit relatively constant flow, would be useful (61). Additionally, if variations in chemical characteristics are likely, the tank will also serve the function of maintaining constancy of chemical composition. Study might well be focused on the improvement in quality which might occur in long storage in an equalization tank, and how this could be enhanced.

Removal of Ammonia Nitrogen - Significant amounts of hydrogen sulfide and ammonia are found in refinery wastewater due to the breakdown of organic sulfur and nitrogen compounds that may be removed by air stripping (10). Ammonia stripping in combination with lime precipitation is considered to be the most low cost method in many situations (20).

The major product of ammonia stripping processes is ammonia. Ammonia recovery as fertilizer includes recovery of ammonia nitrogen in the form of common fertilizers,such as ammonium sulfate and aqua ammonia, which can be sold or used as by-product. Ammonia removal and recovery require that the ammonia be in the form of a dissolved gas. This means that the wastewaters must be at a high pH to accomplish conversion from ammonium ions to dissolved ammonia gas (37).

The major objection to ammonia stripping, discharge of ammonia to the air, may be overcome with an ammonia removal and recovery method. The process includes an ammonia stripping unit and an ammonia absorption unit (37). Both of these units are essentially sealed from the outside air, but are connected by appropriate ducting. The stripping unit recycles the gas stream rather than using outside air in a single-pass manner. Most of the ammonia discharged to the gas stream from the stripping unit is absorbed in the absorption unit, producing a much more highly concentrated solution than the original wastewater. The absorbing liquid is maintained at a low pH to convert any absorbed and dissolved gas to ammonium ions (37). This effectively retains the ammonia that has been absorbed and also has the effect of maintaining the full driving force for absorbing the ammonia,since dissolved ammonia does not build up in the absorbent (37).

An introductory investigation concerned removing nitrogen in supernatant from anaerobic digestors (20). With this method, carbon dioxide was removed by air, and lime was used for alkalization, after which ammonia was stripped by air. The ammonia was then absorbed in diluted sulfuric acid so air pollution effects would be lessened.

Ammonia stripping in the pilot plant was conducted at approximately pH 11 and a temperature of 18°C. This resulted in 75 percent ammonia nitrogen removal, with the ratio factor F = 2,100 (20). This is the ratio between the quantity of air supplied per time unit and the quantity of liquid supplied in the same time unit. An anti-scum agent (defoamer) was used during the stripping process. The effect of temperature on the theoretical yield for this pilot plant is shown in Figure 2.

Another study involving ammonia stripping was conducted at the National Environmental Research Center in Cincinnati, Ohio, in 1973. This investigation was conducted using large cooling towers with grids to promote airflow for better efficiency in the ammonia stripping process. The effect of influent wastewater pH on the efficiency of removal of ammonia was determined with wastewater temperature averaging 76°C. Influent wastewater pH was varied at pH 9.7, 10.5, 11.3, and pH 11.7. The efficiency of removal was dependent upon pH, with the highest removal (86.2%) obtained at pH 11.7 (7). However, the decrease in efficiency of removal from pH 11.7 to 10.5 was only approximately 6 percent. The decrease in inlet pH from 11.7 to 9.7, however, produced a marked decrease in total efficiency, from 86.2 to 51.8 percent (7).

Study at the Pittsburgh Energy Technology Center showed that high temperature air stripping could remove 78 percent of free ammonia. Removal of fixed ammonia (8) required more severe conditions, including raising the pH to 11 (67). Nuefeld, Drummond, and Johnson noted that removal of excess ammonia was a necessary part of pretreatment, and used air stripping on a batch basis to reduce the ammonia concentration from 10,000 mg/l to 500 mg/l. Concurrent with this, alkalinity was reduced by some 80 percent (48).

Removal of Oils, Tars and Greases - Study at the Pittsburgh Energy Technology Center showed that depression of pH, plus addition of alum, effectively reduced both suspended and dissolved tars (69). When H_2SO_4 was used for the pH suppression, and alum added as a coagulant, oils, tars and greases were reduced

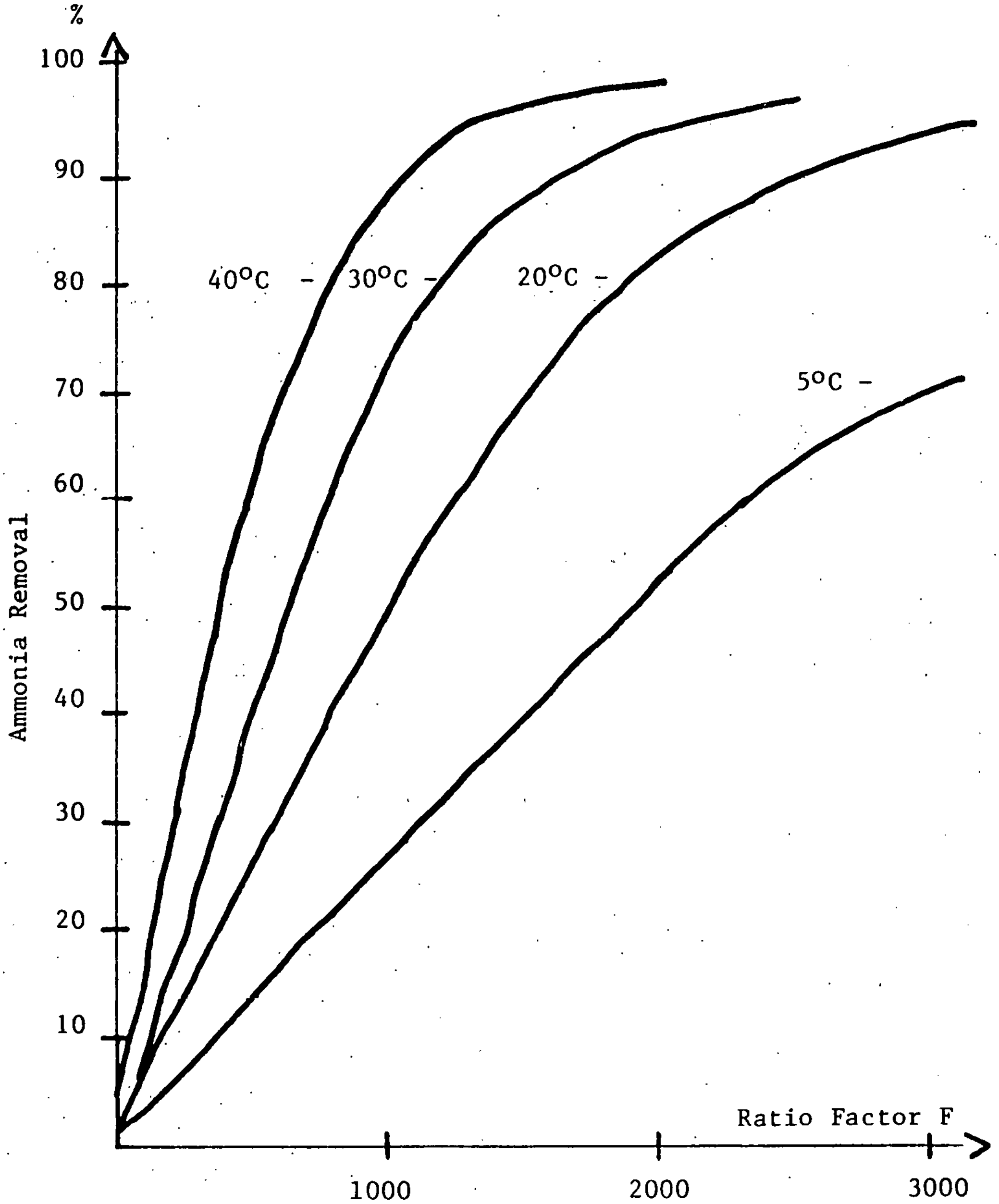


Figure 2

Theoretical Effect of Temperature on Ammonia Stripping in Pilot Plant (20) by 50 percent, and soluble total organic carbon (TOC) by 20 percent. It now appears that appropriate pH reduction, even without coagulant, reduces oils, tars, and greases. Filtration was then used (48), though dissolved air flotation was an alternative treatment. Subsequently, the waste was neutralized (11). In another process, Luthy and Tallon (40) used lime to precipitate $CaCO_3$, which was found to reduce oil and grease. The lime also helped raise the pH to facilitate the stripping of ammonia.

Biological Treatment

Several possibilities exist:

1. Waste Stabilization Ponds - The possibility of such treatment was suggested by the low pollutant concentrations found in water from the lagoon which received coal gasification wastewater at Morgantown. Other study also noted the possibility of lagooning, and considered it worthy of attention (61).

   A treatment facility might be similar to the following:

   a. Natural Aeration Stabilization Pond - Based on arbitrary values of four months detention, a water depth of 5 feet, and a flow of 5 mgd (for a 250 million scf/day gasification plant), approximately 370 acres of stabilization pond would be needed. However, actual design values would need to be determined. Although such a large area probably would not be available at most sites, perhaps it would be possible to increase pond depth and lessen detention time. Additionally, it might be possible to obtain some incidental treatment during storage in equalization tanks, suggested as having detentions as long as 30 days in particular cases (61).

   b. Stabilization Pond With Mechanical Aeration - Based on arbitrary values of 10 days detention, 10 feet depth, and a flow of 5 mgd, approximately 15 acres would be required for the gasification plant described above (250 million scf/day). Actual design values for coal gasification wastewater are not presently known.

2. <u>Fixed Position Biological Contactors</u> - These are exemplified by trickling filters, long thought to offer relatively good resistance to overload and to be less readily harmed by toxic substances. Wei and Goldstein suggested that there might be advantages to combining a trickling filter with activated sludge, including the incidental benefit of cooling of the heated process water. However, forced ventilation could be needed in the trickling filter (66). Other possibilities include revolving disc biological contactors. This entire subject remains to be studied in greater detail.

3. <u>Activated Sludge</u> - This process has been the subject of intensive study regarding application to coal gasification wastewater. Study has indicated considerable success in treating such wastewater by activated sludge (3). Some process details include:

   a. <u>Loading</u> - Study done at the Pittsburgh Energy Technology Center showed that aeration detention of some six days for undiluted waste produced comparable treatment to that obtained with diluted feed and 24 hour detention (22). Using diluted feed, a detention of one day (4), and food/microorganism ratios of 0.67 and 0.83 mg TOC/mg MLVSS/day, removals were over 50 percent for TOC and COD, and over 99 percent for phenols (71). Actual loads may be different. Later study yielded removals of 70 percent for TOC and 94 percent for BOD.

   b. <u>Reaction Kinetics</u> - Several authors have published works utilizing similar biokinetics models. In <u>Water Quality Engineering For</u>

Practicing Engineers, Eckenfelder gave a mathematical model for determining kinetic constants for removal of organic substances through biological treatment (19).

Several studies have been performed on sewage, but few references are available for kinetics of wastewaters from coal gasification plants. One study was done on the kinetics of activated sludge treatment of "Synthane" fluidized bed gasification wastewater by Ronald D. Neufeld, Charles J. Drummond, and Glenn E. Johnson (48). Another study was done on a wastewater similar to that to be used in this study. The authors, Richard G. Luthy and James T. Tallon, published their results in July, 1978 (40).

The biological reaction kinetics model used in this study was that presented by Metcalf and Eddy in Wastewater Engineering: Treatment, Disposal, Reuse, 1979 (42). To calculate K_s, the rate coefficient, and k, substrate removal rate coefficient, the following equation was utilized:

$$\frac{X\theta}{S_o - S} = \frac{K_s}{k}(S^{-1}) + k^{-1} \qquad (1)$$

where: S_o = influent substrate concentration, BOD, mg/l

S = effluent substrate concentration, BOD, mg/l

X = cell concentration in aeration chamber, MLVSS, mg/l

θ = hydraulic detention time in the aeration tank (volume/flow rate), days

This equation exhibits the linear form of:

$$Y - mX + B \qquad (2)$$

where: m = slope of a line graphed from this equation

B = y-intercept of that line

This makes it convenient to graphically determine K_s and k.

This linear form is also useful in determining Y, the biological yield coefficient, and k_d, the decay coefficient, according to the following formula:

$$\theta_c^{-1} = Y\frac{S_o - S}{X\theta} - k_d \qquad (3)$$

where: θ_c= mean cell residence time, days

A study by Luthy and Tallon (1978) produced a yield coefficient of 0.11 and a decay coefficient of 0.02/day. It was stated in the report that the decay coefficient seemed reasonable, but the yield coefficient was lower than expected (40).

A similar study performed by Neufeld, Drummond, and Johnson showed a yield coefficient of 0.37 lb. VSS/lb. BOD and a decay coefficient of 0.033/day (48).

c. Activated Sludge Modifications - Most study has centered on approximations to completely mixed activated sludge, with limited consideration of other possibilities:

(1) Two-Stage - This has been the major modification studied, but generally has been found to have little value for coal conversion waste (71,72).

(2) High-Purity Oxygen - Although usually a larger facility is required to justify use of high-purity oxygen instead of air, the availability of oxygen for other purposes at many coal conversion plants enhances prospects for use. A possible advantage would be increased oxygen transfer (66), facilitating maintenance of the higher MLVSS levels sometimes specified for coal conversion wastes.

(3) Return Sludge Aeration - This was noted to be of some value by Cooke and Graham, though their data were considered too limited to be definitive (14).

Other points might be mentioned regarding activated sludge. Nutrient addition would include at least phosphate (66). Acclimated microorganisms are essential, though mutant bacteria may show promise. Solids handling and disposal require additional study (47,61).

4. Anaerobic Biological Treatment - Study at the Pittsburgh Energy Technology Center showed TOC and COD reduced by 40 percent, phenols by 50 percent, and color reduced somewhat (72,73). Subsequent study showed (41) up to 80 percent reduction in COD using bench-scale anaerobic contact digestors. In related study, long-term (at least 45 days) anaerobic treatment made wastewater more amenable to biological treatment.

Chemical Precipitation

One of the problems encountered in the study of coal gasification wastewater treatment has been that, after biological oxidation in the activated sludge units, the effluent suspended solids and volatile suspended solids are relatively high. The wastewater, upon withdrawal from the activated sludge units, still contains a considerable amount of organic material. Some of this material is in the form of microorganisms carried out with the effluent, and has an adverse effect on treatment by lessening cell retention. Additionally, there also remains some organic material that could be toxic or even carcinogenic. It has been suggested that, to remove these organic materials, activated carbon should be utilized. The problem with activated carbon lies in the fact that it is easily clogged by suspended solids material, which reduces the effectiveness of adsorption by the granulated activated carbon. Thus, some means has been needed which could effectively reduce the suspended matter in the wastewater before it was passed through the carbon filter. Chemical coagulation seemed to be a promising method for this suspended solids removal.

This method of solids removal seems feasible because the major constituents of the suspended solids are bacterial. This has been deduced from the fact that very few suspended solids are added to the units in the coal gasification wastewater.

It has been found that bacteria have a charge at the sol membrane interface. This charge is anionic or negative in nature; this allows the bacteria to be amenable to chemical coagulation (with coagulants such as ferric chloride and aluminum sulfate) because in solution a positive ion species such as $Al+^3$ or $Fe+^3$ will exist. This positive charge will allow the colloid (bacteria) to be destabilized. The destabilization may occur in two different fashions, (1) charge neutralization; and (2) enmeshment.

In relation to the use of a polymer as a coagulant, an anionic (or negatively-charged) polymer is usually necessary, along with an alkaline substance, such as lime. The floc in the colloid polymer suspension is usually formed by interparticle bridging. The use of an anionic polymer plus a buffer seems most satisfactory in high colloid concentrations, although the reasons for this are not understood.

Efforts have not been successful in locating literature that specifically relates to the chemical coagulation of coal gasification wastewater. Most of the literature addressed the use of the ferric and aluminum salts, and also polymers, in the general case. Current literature suggests that four different conditions exist in a hydro-colloidal suspension. These are: (1) high colloid concentration - high alkalinity; (2) high colloid concentration - low alkalinity; (3) low colloid concentration - high alkalinity; (4) low colloid concentration - low alkalinity (65). In regard to treated coal gasification wastewater, the effluent exhibits the characteristics of high colloid concentration and high alkalinity (buffer capacity)(65). None of the available literature dealt with the property of high organic chemical concentration. These organic chemicals may affect the use of the inorganic chemical coagulants, but it is even more likely that they may react with the long chain polymers. This could be a positive interaction (such as increased chain length to allow for more particle/colloid bridging), or it may hinder the polymer by breaking the chain (which could produce floc too small to settle).

It has also been established that, with the use of polymers, an optimum dose is essential (43). When the iron or aluminum salts are used in doses greater then the optimum dose, usually no harm is done except that excess metal hydroxide species may be precipitated out when the K_{sp} (solubility product constant) is exceeded (50). When the polymer dose is increased beyond the optimum one, re-stabilization can occur in which the colloids are re-suspended into the solvent (43). This has especially been evident when bacteria are the colloidal particles in the hydro-colloid complex (60). The reaction between the colloid and polymer seems to be stoiciometric in nature.

Tertiary Treatment

Discoloration is a remaining problem. Although chemical oxidation has been suggested (49,68), activated carbon may be less costly (61). Tertiary treatment might be accomplished by sand filtration, followed by granular activated carbon in columns. The activated carbon also reduces TOC, phenol and odor. Although carbon adsorptuion has been studied for introductory treatment, or complete treatment (28,67), and is evidently effective in these roles, it has at least as much promise as a tertiary treatment (4).

Various treatment schemes utilizing granular activated carbon have been tested on process effluents from coal gasification operations. In pilot plant testing, it has been observed that up to 99% of the phenolics, TOC, and COD_{Mn} were removed upon direct application of activated carbon in a fixed-bed reactor to condensates from coking and gasification plants (36). However, these high efficiencies were obtained with adsorbate loadings of 85 Kg carbon/m^3 condensate and a maximum throughput of 300 liters/hour.

Commercial designs suggest a 70% carbon conversion for the gasification of coal in a large scale operation. Thus, for each pound of coal gasified, 0.3 pounds of solid waste remain. Char adsorption, which utilizes this solid residue (char) to adsorb contaminants from the gasifier's liquid waste, has been investigated (17). Typical chars and wastewaters from the Synthane process were used in this study. Average char surface area from the Synthane Process Development Unit was 330 m^2/g, or about one-third the surface area of activated carbons. At a loading rate of ten pounds of condensate throughput per pound of char, phenol removal exceeded 99% (approximately 3 mg/l phenol in the effluent) while COD and TOC removals were approximately 90% (1,500 and 680 mg/l in the effluent respectively).

Activated sludge processes are preferable to physical-chemical processes due to higher treatment efficiencies and ease of control (5). Yet effluent levels of phenolics, BOD, and TOC exceed allowable limits, so that further treatment will be required if discharge into the environment is anticipated.

It appears that no single operation will successfully treat the gasification wastewaters, and, at the same time, be economical. One possible solution to this problem is the application of activated carbon to the aerobically oxidized wastewaters. The use of activated carbon is not only simple and convenient (52), but also the cost of its application is relatively low as compared to other advanced treatment schemes (15).

Chapter 3

Methodology

Sampling

After the early stages of the study and the development of procedures, samples were collected at intervals of approximately one month. Samples were obtained near the discharge end of the decanter in service, using a scoop attached to a long handle. This sampling point was selected since it combines virtually all wastewater, is accessible, appears to contain well-mixed liquid, and, being subsequent to settling, provides maximum consistency in sample characteristics. The location was further identified as being at the Holston Defense Corporation, Coal Gasification Facility, Building 10. Sample was placed into two or three tin-coated, steel containers, using a funnel. Note that other containers, especially glass bottlies having capacity of about one gallon, also were used, early in the study.

The temperature of the wastewater was measured immediately upon collection, and preservation procedures were used for samples for special purposes (cyanide, sulfide, and thiocyanate). Routine procedure also provided for inquiry to be made regarding plant production, amount of coal used, variation in operation, and the presence of any special conditions. However, the answers were always the same, since the plant was in stable operation. Upon arrival at the laboratory, sample pH was determined immediately.

Table 5 gives sampling data.

Small-scale Studies of Pretreatment

Small-scale Studies of the Removal of Ammonia-Nitrogen - Test procedures were used to evaluate the removal of ammonia nitrogen as a function of pH, temperature, air flow rate, and length of time of treatment. The general tech-

Table 5

Data on Sampling Wastewater at the Holston Coal Gasification Plant

Sample Number	Date Collected	Amount Collected	Wastewater Temperature
1	10/10/78	3 liters	56 °C
2	10/17/78	2.5	55
3	10/24/78	2.5	57
4	10/31/78	-	57
5	11/7/78	-	57
6	11/15/78	5.3	55
7	11/21/78	-	56
8	11/28/78	-	54
9	12/5/78	13	55
10	12/18/78	11.5	-
11	1/9/79	20	52
12	1/16/79	7.5	53
13	1/22/79	10	53
14	1/29/79	25	54
15	2/5/79	22	-
16	2/12/79	20	54
17	2/20/79	25	55
18	2/28/79	-	-
19	3/5/79	40	55
20	3/26/79	20	-
21	4/2/79	-	-
22	4/9/79	20	-
23	4/17/79	-	-
24	4/23/79	32	-
25	5/1/79	-	-
26	5/14/79	30	-
27	5/21/79	30	-
28	7/21/79	30	-
29	8/13/79	40	54
30	9/19/79	57	54
31	10/15/79	40	57
32	11/8/79	40	-
33	11/26/79	40	45
34	1/7/80	40	53
35	2/21/80	40	54
36	4/2/80	44	56
37	4/25/80	35	56
38	5/23/80	33	58
Range	Year 1	2.5-40	52-57
	Total	2.5-57	45-58
Mean	Year 1	17.9	54.9
	Total	25.9	54.6
S.D.	Year 1	11.1	1.5
	Total	14.5	2.5
n	Year 1	19	16
	Total	30	25
Mode	Year 1	20	55
	Total	40	54

nique was to maintain three variables constant at levels expected to be generally satisfactory, while systematically varying the value of the fourth parameter. As soon as sample arrived at the laboratory, it was preserved by lowering the pH to 2.0 using concentrated H_2SO_4, and stored in a closed container kept refrigerated at 4°C.

The apparatus for these tests is shown in Figure 3. Sample was poured into a closed flask, and this was placed in a water bath controlled at a pre-set temperature. The flask contained 50 ml of preserved raw sample, plus three drops of defoamer (0.5% dilution by volume of Nalco 71-D5). Air was injected from an installed air source, and measured by an air-flow meter (rotameter). After treatment under the conditions prescribed for the particular test, the ammonia nitrogen concentration was determined, so that the percent reduction in ammonia nitrogen could be calculated. Exact conditions included:

1. Study of aeration rate: Aeration rate was varied at 5, 10, 15, and 20 liters of air per minute per liter of sample, while pH was held at 10, temperature at 70°C, and time at 30 minutes.
2. Study of temperature: Temperature was varied at 50, 60, 70, and 80°C, while pH was held constant at 10, time at 30 minutes, and aeration rate at 15 liters/minute/liter of sample.
3. Study of pH: The pH was varied at 9.0, 9.25, 9.5, 9.75, 10.0, 10.5, and 11.0, while time was held constant at 30 minutes, aeration rate at 15 liters per minute per liter of sample, and temperature at 70°C.
4. Study of length of treatment time: Length of treatment time was varied at 15, 30, 60, and 90 minutes, while temperature was held constant at 70°C, aeration rate at 15 liters/minute/liter of sample, and pH at 10.

After each test, the pH of the sample was lowered to 2.0, using H_2SO_4, and it was kept refrigerated at 4°C until analyzed, which generally was within 24 hours. Note that each test was done in duplicate.

Small-scale Studies of the Removal of Grease and Oil - Somewhat similar, though less extensive tests were performed in an attempt to evaluate the conditions related to removal of grease and oil. Again, the general procedure was

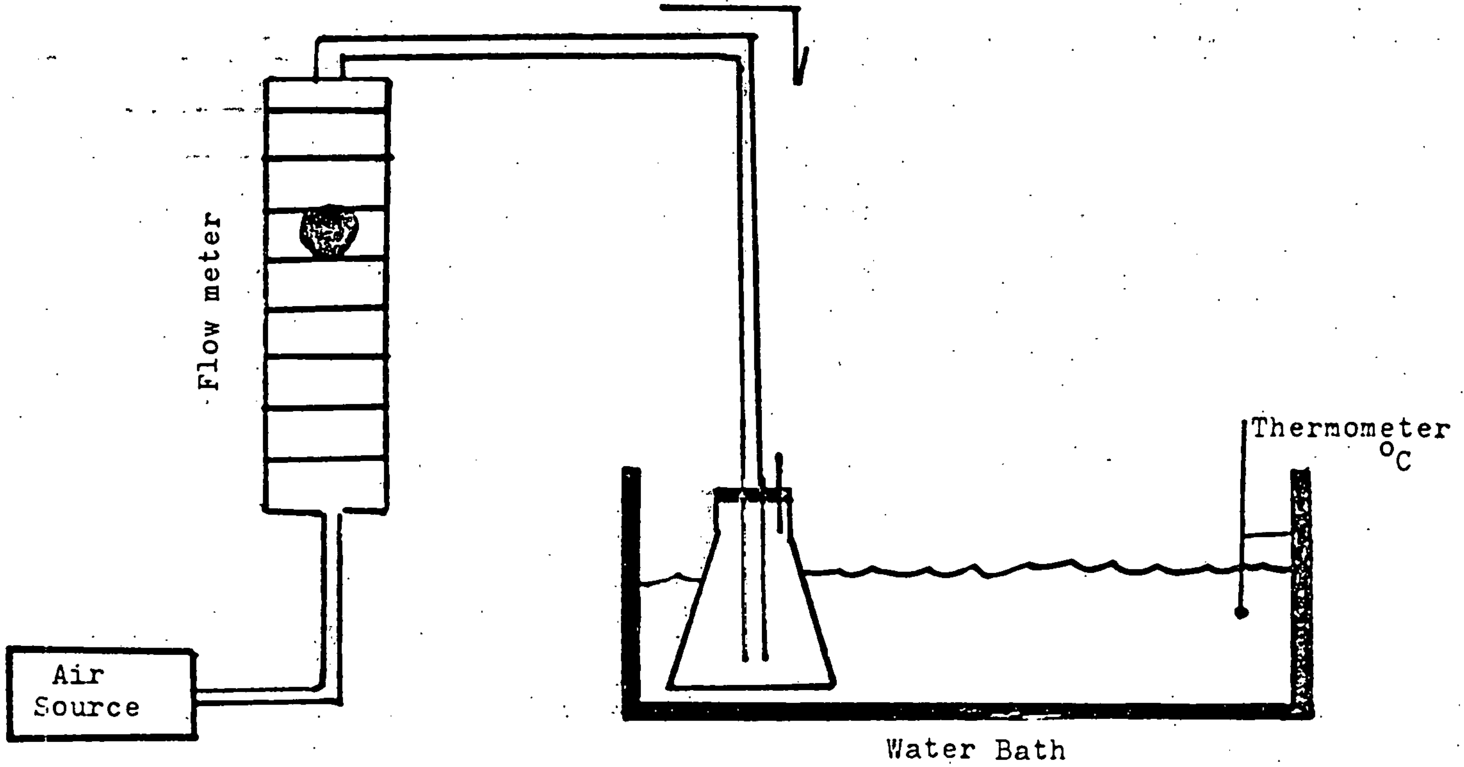


Figure 3
Apparatus for Small-Scale Studies
of the Removal of Ammonia Nitrogen

to hold one parameter constant, while varying others. The grease and oil concentration remaining after each test was determined, in order that the percent reduction could be calculated. The specific conditions studies were:

1. pH: The pH, in successive tests, was lowered to 3.0, 2.5, 2.0, and 1.5, while settling time was kept constant at 16 hours, and aeration not used.
2. Aeration rate: Aeration rate was varied at 0.4, 1.0, and 1.5 liters of air per minute per liter of sample, while pH was kept constant at 3.0, and length of time of treatment at 30 minutes.

Pretreatment of Batches of Wastewater For Use As Influent to Biological Treatment Units

Removal of Ammonia Nitrogen - The wastewater initially was treated to remove ammonia nitrogen by an air stripping procedure. Although various apparatus was used early in the study, the final equipment used for stripping was the modified bottom portion of a hot water heater, the top having been cut away to permit use under an enclosed exhaust hood. Figure 4 shows this equipment. Capacity of the unit was approximately 40 gallons. Air was used from an installed source, and delivered through flexible tubing (1 inch diameter), through a high-capacity air flow meter (rotameter) to perforated tubing located near the bottom of the tank.

Using 10 N NaOH, the pH of the wastewater was raised to approximately 9.75 or greater. The pK_a of ammonia is 9.75. Usually, wastewater in the stripping container was heated to approximately 70°C, after which aeration, at the rate of some 10 to 15 liters of air per minute per liter of sample, was applied. Heating and aeration were continued for 30 to 60 minutes, during which the temperature generally fell considerably, perhaps to 50°C (due to low heating capability). To minimize foaming during the stripping, four, 5 ml portions of concentrated Nalco anti-foam, 71-D5, were added to the wastewater. An improvised cover also was used to minimize splattering. A typical batch was approximately 30 to 40 liters in initial volume.

Figure 4
Equipment for Stripping Ammonia
from Batches of Wastewater for Influent to
Biological Treatment Units

Removal of Grease and Oil - After the stripping, the wastewater was treated with a mixture of 20% concentrated H_3PO_4 and 80% concentrated H_2SO_4, to lower the pH to 2.5 to 3.0, and also to provide nutrient phosphate for subsequent biological treatment. At this point, the wastewater was placed in a specialized settling chamber having a capacity of 44 liters, as shown in Figure 5. Air was then applied at a rate of 0.4 to 3 liters per minute per liter of sample, using an installed air source and measurement of air flow rate by a rotameter. Various solids,precipitated by the acidification, and especially grease and oil, were agglomerated by the turbulence, raised to the surface by flotation, and removed by gentle skimming.

Remaining solids in the acidified sample were removed by settling in the 44 liter plexiglass container for 24 to 36 hours. Subsequently, fractional portions were collected from the chamber, using a draw off located at its bottom, with the first fraction containing most of the settled solids, and the next fraction being clearer liquid. Each portion then was filtered through coarse paper filters to remove remaining solids. Fractions were combined, and treated with 10 N NaOH to adjust the pH to 7.0. Finally, the neutralized sample was placed in four liter, closed, polyethylene containers, and refrigerated at 40°C until used.

General Operation of Laboratory Scale Biological Treatment Units

The major biological treatment devices used were two Horizon Ecology "Bio-Oxidation Systems." These are laboratory scale units, each with a total capacity of 7.5 liters of liquid. Each system incorporates an air pump, air flow meter, wastewater pumps, aeration tank with interchangeable settling well, as well as diffusers and appurtenances. Recirculation of settled solids is induced by wastewater currents caused by the air injection. Air flow can be varied up to

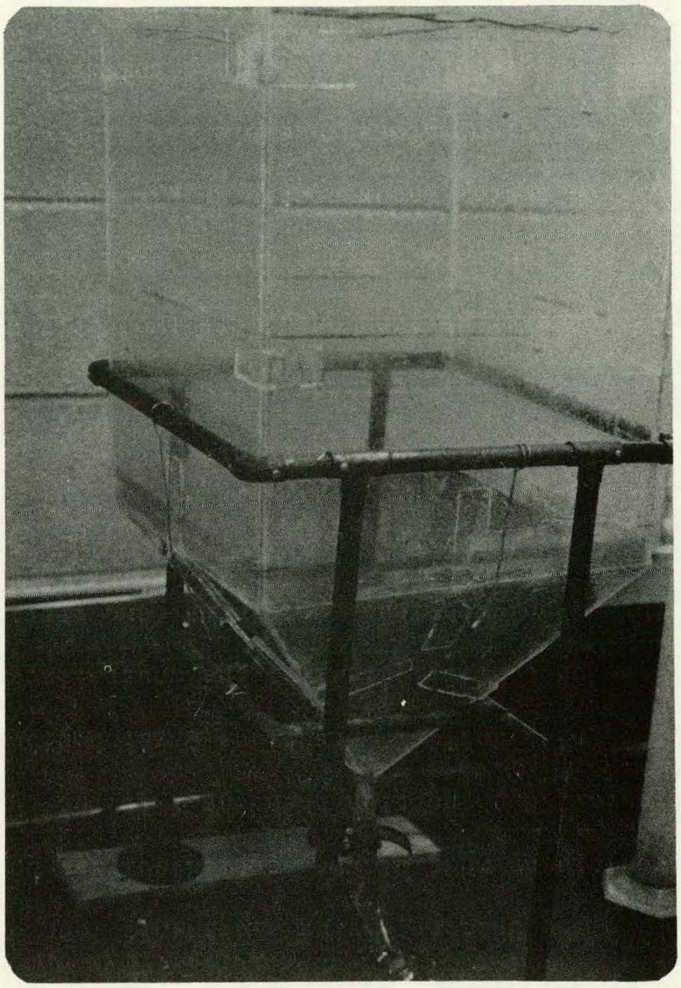


Figure 5
Settling Chamber Used in Removal
of Grease and Oil
from Batches of Wastewater

a maximum of 0.25 cfm, influent can be varied up to 14 gallons per day, and suspended solids, contained in the mixed liquor, may be removed at a fixed rate of 100 ml per minute. Figures 6 and 7 are diagrams of the apparatus and the control console respectively. Figure 8 shows the apparatus, as used in the study.

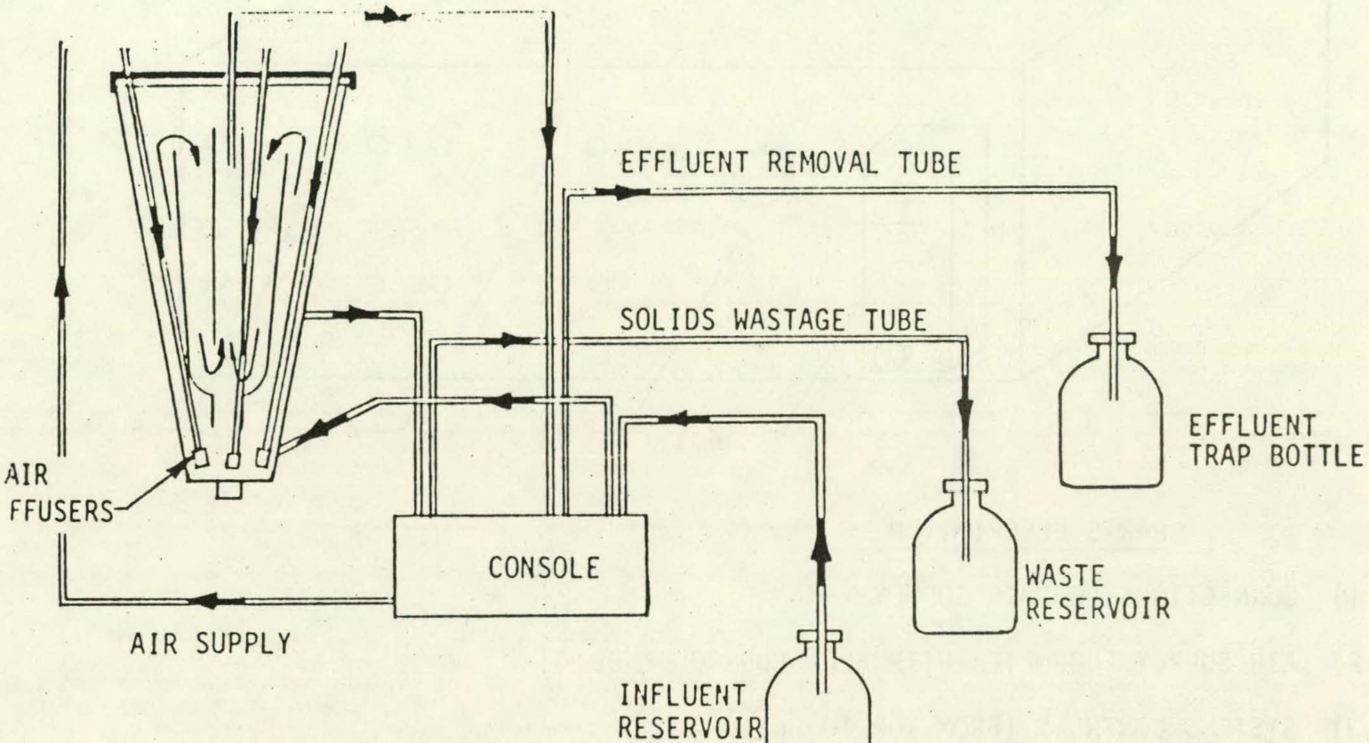
Units were started by adding a small amount of mixed liquor, brought frozen from laboratory-scale activated sludge units treating Synthane wastewater at the Pittsburgh Energy Technology Center. The Annual Report for the first year of study (89) gives details of early operation. However, Figure 9 shows the variation in the amount of pretreated waste in the flow, with time, during the period of this study. The Bio-Oxidation units drew waste from an influent reservoir, with a capacity of 32 gallons, serving each unit. The reservoir serving Unit 1 was seeded with a small amount of waste activated sludge, supplied with diffused air using an aerator, and operated as an aerated pond with a hydraulic detention of two weeks. A similar, 32 gallon effluent reservoir also was used for each Bio-Oxidation unit.

Details of the basic operation of these activated sludge units was as follows:

1. Addition of pretreated wastewater - For each Bio-Oxidation unit, a measured amount of pretreated wastewater was diluted with enough tap water to provide 7.5 liters for each day's feeding. The amount of pretreated wastewater added generally was greater for Unit 1 than Unit 2 throughout the second year of study because of the higher loading potential made possible by Unit 1's additional aeration pond.

2. Use of defoamer - A defoamer, Nalco 71-D5, was found necessary to limit foaming to an acceptable level. Until the end of September, 1979, one milliliter of a 0.5 percent dilution of defoamer was added to the influent dilution for the units for each 10 milliliters of pretreated wastewater in the mixture. In November, 1979, the amount of defoamer added per 10 milliliters of pretreated wastewater was decreased by one tenth of the original amount each day to determine the minimum concentration of defoamer required to maintain low foaming conditions. It was found that a concentration of 0.7 milliliters of defoamer per 10 milliliters of wastewater was a practical minimum. Defoamer conditions were thus maintained at this level through the end of the study.

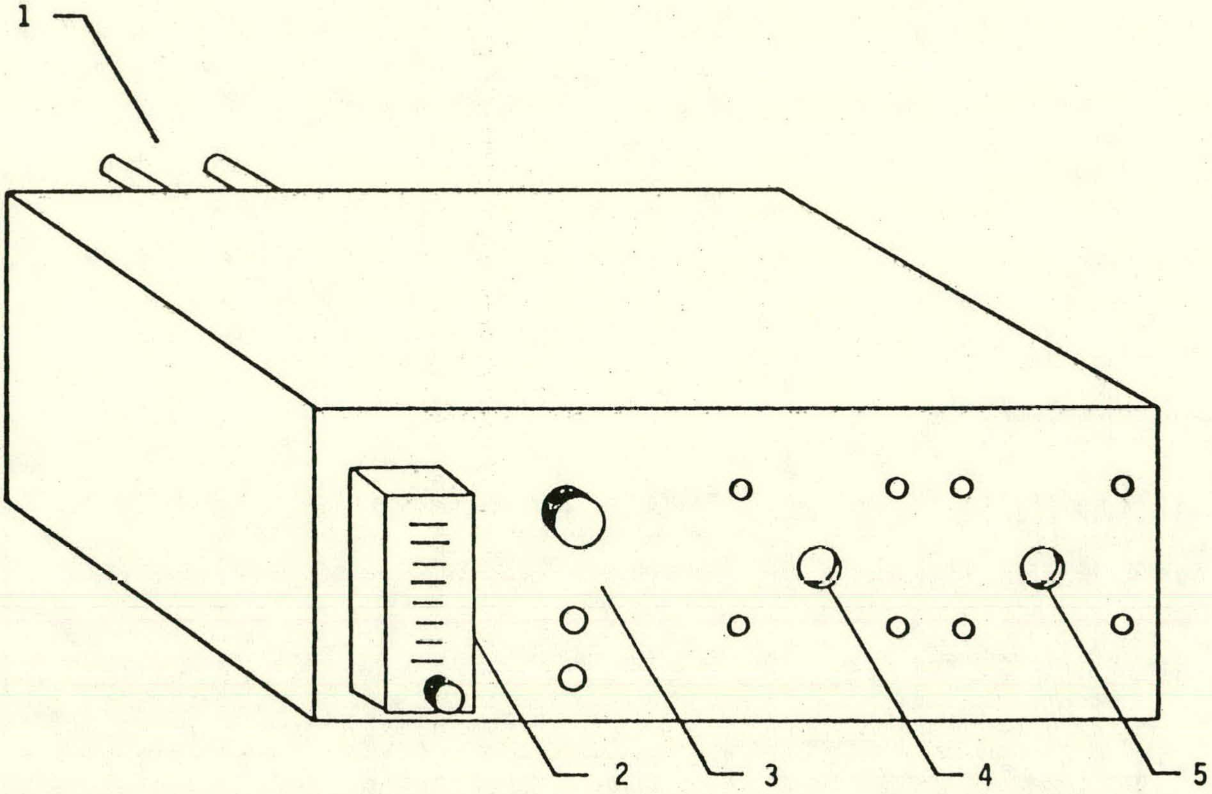
3. Hydraulic detention - Each laboratory scale activated sludge unit had a capacity of 7.5 liters.
   Since each unit received 7.5 liters per day of diluted wastewater, detention times were approximately 24 hours. This value fluctuated somewhat due



ARROWS SHOW DIRECTION OF AIR AND LIQUID FLOW

Figure 6
Schematic Diagram of
Bio-Oxidation System

Source: Horizon Ecology Co. (33)



PARTS DESCRIPTION

1) CONNECTIONS FOR AIR SUPPLY

2) AIR SUPPLY FLOWMETER WITH FLOW CONTROL KNOB

3) SYSTEMS CONTROLS (FROM TOP TO BOTTOM)
   A) EFFLUENT AND INFLUENT ON/OFF AND FLOW CONTROL
   B) SOLIDS IN SUSPENSION ON/OFF
   C) AIR SUPPLY ON/OFF

4) LOCATION OF PUMP FOR SOLIDS IN SUSPENSION (7017-20)

5) LOCATION OF TWO PUMPS
   INFLUENT USES 7017-20
   EFFLUENT USES 7018-20

Figure 7
Diagram of Console for
Bio-Oxidation System

Source: Horizon Ecology Co. (33)

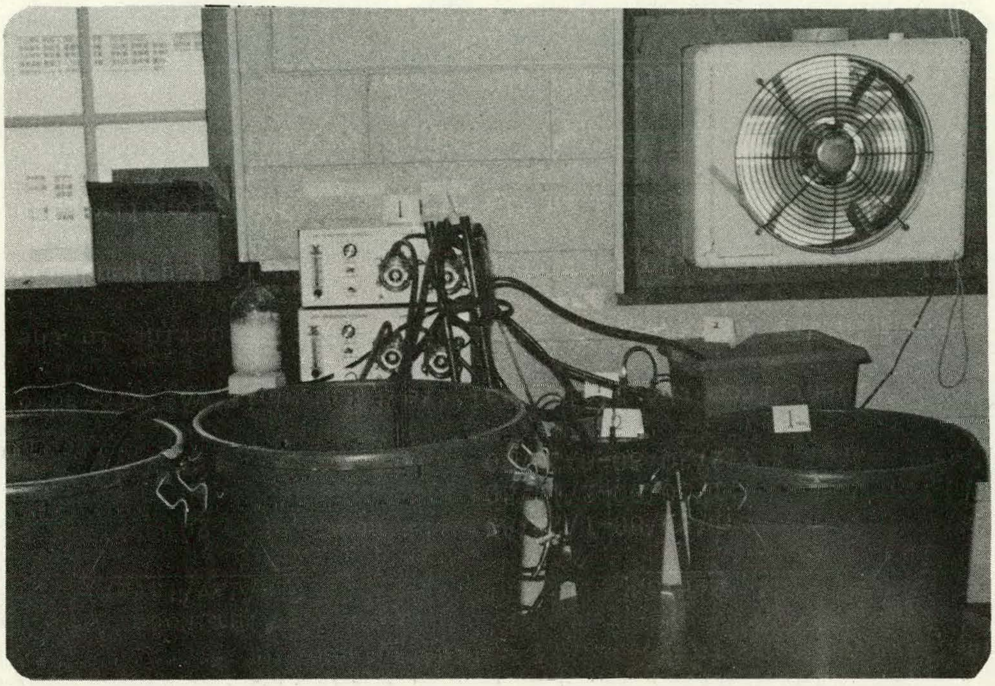
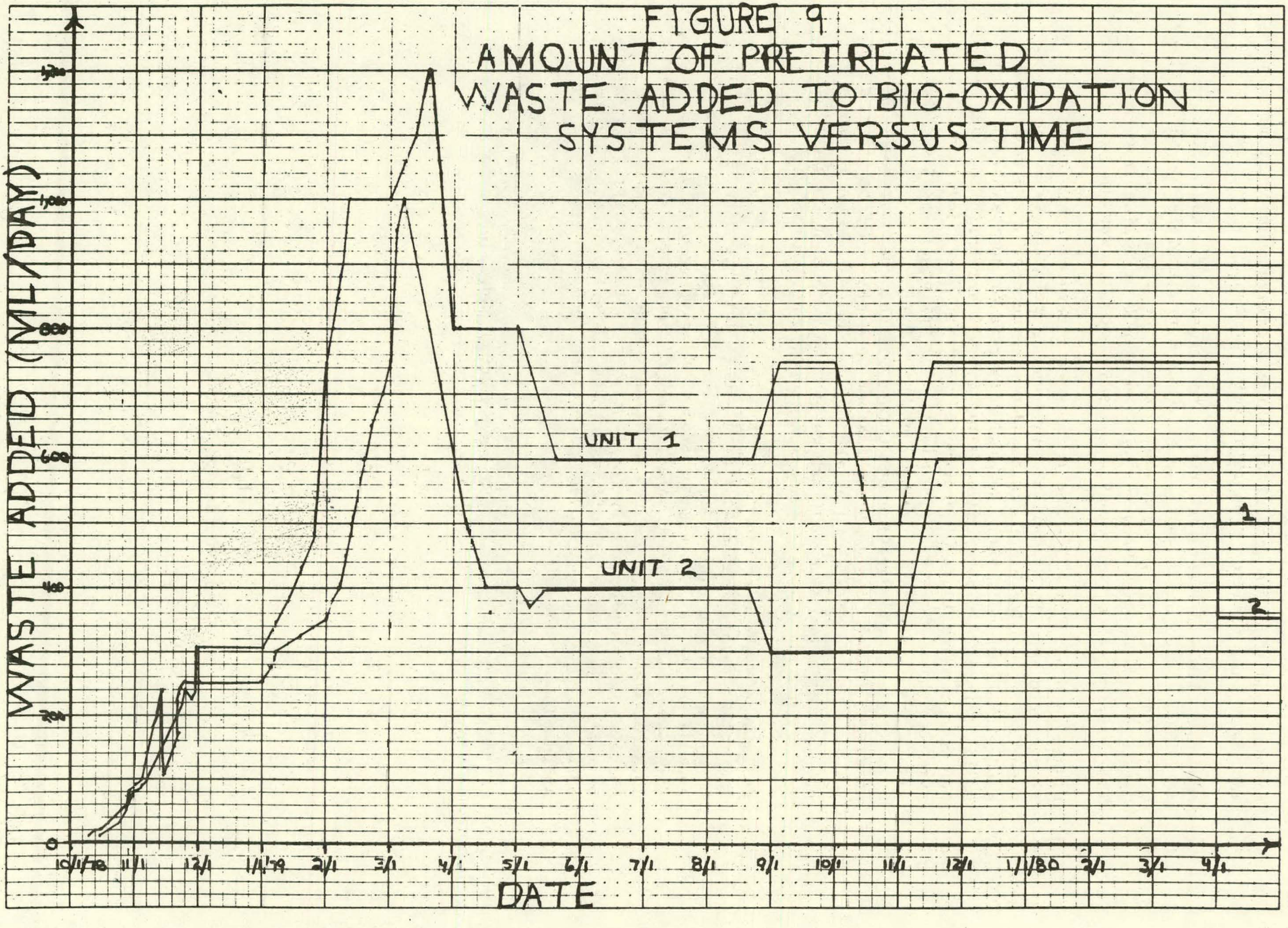


Figure 8
Bio-Oxidation Systems in Use

FIGURE 9
AMOUNT OF PRETREATED WASTE ADDED TO BIO-OXIDATION SYSTEMS VERSUS TIME



to such conditions as occasional tubing blockage, but daily maintenance kept the detention time relatively constant.

4. Aeration rate - The aeration rate into the aeration tanks of both activated sludge units was maintained at approximately 500 milliliters of air per minute. The aeration rate for the aerated pond serving Unit 1 was maintained between 1,500 and 2,000 milliliters per minute. The aeration rates were checked and adjusted each week.

5. Sludge reserve ("bank") - Ten to fifteen liters of waste activated sludge were kept in a 20 liter glass carboy referred to as the sludge reserve, or "sludge bank", to be used when needed by the units. The sludge bank was constantly aerated at a rate of approximately 2,000 milliliters of air per minute, using a small aerator. The sludge bank was fed 75 milliliters of pretreated wastewater per day, and was augmented by approximately 50 milliliters per week of waste mixed liquor from the aeration chamber of each unit.

   Each week the aeration was turned off for one hour to allow settling. Three liters of supernatant were drawn off to rid the system of wastes liberated by the microorganisms in the system. Approximately two liters of tap water also were dripped back into the system slowly - over a period of a few days during each week.

6. Addition of sludge to biological treatment units - At various times, low solids levels in the activated sludge units required that sludge be added to the aeration tanks to maintain effective treatment. The general procedure involved suspending the wasting of sludge, perhaps for several weeks, to evaluate recovery. Subsequently, if necessary, influent would be stopped and aeration turned off, in order to permit settling, for approximately one hour. Then, the appropriate amount of supernatant was drawn off, and an equivalent volume of liquid added from the sludge reserve. Additions from the sludge reserve included:

	Volume (liters) added to	
Date	Unit 1	Unit 2
4/5/79	0.5	1.5
4/26/79	0.5	0.5
10/19/79	3.0	-
11/27/79	2.0	1.0
3/5/80	1.0	0.5
5/26/80	1.0	0.5

7. Analyses and measurements used for routine operation - The pH and dissolved oxygen concentration were measured once each week in the aeration tank of each activated sludge unit, as well as in the aerated pond preceding Unit 1. See Table 6. Additionally, flow rate and aeration rate also were measured each week, and adjusted to maintain proper levels of these parameters. Though temperature was expected to be relatively constant, it was measured, as appropriate. For regular operation, influent and effluent biochemical oxygen demand were measured, as well as solids levels (suspended, volatile suspended, and settleable) for the mixed liquor. Numerous other analyses were performed, as appropriate.

Study of Alternatives For Biological Treatment

The major alternatives considered for biological treatment were as follows:

1. Activated sludge, without modification - The study of biological treatment in the first year was limited to basic operation of the laboratory scale activated sludge units, without modifications to stabilize treatment. The basic operation in this mode already has been described. Various loads were tried, the characteristics of the pretreated wastewater in the influent varying, especially early in the study when samples were collected from the Holston Coal Gasification Plant rather frequently (approximately every week). The effectiveness of treatment was evaluated by determining the levels of various parameters in the influent and effluent. Conditions related to process upset were observed.
2. Activated sludge preceded by aerated waste stabilization pond - This was studied as one means of stabilizing treatment in the activated sludge unit. However, an artificially aerated waste stabilization pond also might have potential as the major means of biological treatment used. Basic information on the unit has been given already. A hydraulic detention of two weeks was obtained by maintaining a liquid depth corresponding to a capacity of 105 liters. The pond was started by adding a small amount of waste activated sludge to the liquid, which

was in a 32 gallon container. A small aerator provided 1,500 to 2,000 ml per minute of air to the wastewater in the pond through a diffuser. The influent to Biological Treatment Unit 1, was drawn from mid-depth of the pond. Operation of the pond was monitored by measuring, each week, the dissolved oxygen concentration, pH, and air flow, as well as by analyzing samples of influent and effluent for several pollutant parameters. Influent was taken to be the pretreated wastewater diluted with tap water, with defoamer already added. Effluent was taken to be the pond contents, sampled at mid-depth.

Table 6

Dissolved Oxygen and pH in Biological Treatment Units

	Dissolved Oxygen (mg/l)			pH (units)		
Date	Unit 1 Pond	Unit 1 Bio.	Unit 2 Bio.	Unit 1 Pond	Unit 1 Bio.	Unit 2 Bio.
10/12/78	-	7.1	-	-	-	-
10/13/78	-	8.5	9.5	-	-	-
10/24/78	-	8.0	8.6	-	-	-
10/27/78	-	8.4	8.4	-	7.1	7.1
10/31/78	-	8.7	8.7	-	-	-
11/3/78	-	8.6	8.2	-	-	-
11/7/78	-	8.3	-			-
11/10/78	-	7.4	7.6	-	-	-
11/14/78	-	7.5	7.9	-	7.1	7.3
11/17/78	-	8.5	8.1	-	7.3	7.2
11/21/78	-	7.8	8.3	-	7.1	7.3
11/28/78	-	-	-	-	7.2	7.4
12/1/78	-	7.2	5.0	-	7.0	7.0
12/5/78	-	7.4	7.9	-	7.0	7.1
12/8/78	-	6.7	7.5	-	7.4	7.4
12/12/78	-	7.4	7.1	-	7.3	7.1
1/5/79	-	7.3	7.2	-	6.4	6.4
1/25/79	-	6.5	7.2	-	7.5	8.5
2/6/79	-	6.5	7.0	-	7.3	7.0
2/13/79	-	6.5	6.8	-	7.2	7.0
3/7/79	-	6.8	6.8	-	7.3	7.3
4/9/79	-	7.0	7.1	-	7.3	7.5
4/27/79	-	7.3	6.8	-	6.9	7.1
5/3/79	-	6.8	6.4	-	7.0	7.0
5/21/79	-	8.2	7.4	-	-	-
5/29/79	-	8.1	8.3	-	-	-
6/28/79	-	7.5	6.5	-	-	-
7/11/79	-	7.9	7.0	-	-	-
10/5/79	7.8	8.9	5.3	6.8	7.1	7.0
10/9/79	1.1	7.4	3.2	6.2	7.0	6.9
10/18/79	6.1	7.9	2.0	6.7	6.7	6.3
10/23/79	0.2	6.2	3.2	6.6	7.1	6.9
11/6/79	8.9	8.2	1.4	7.0	7.0	6.7
11/13/79	8.7	9.2	8.4	7.3	7.2	7.0
11/19/79	4.3	7.4	2.5	7.1	7.5	6.6
11/27/79	5.7	3.6	3.0	7.0	7.2	6.5
1/3/80	0.9	0.5	2.6	6.5	6.8	6.8
1/9/80	8.0	6.4	0.8	6.8	7.1	6.6
1/15/80	7.8	8.0	8.4	7.0	6.8	7.1
1/23/80	7.4	7.1	7.8	6.7	7.0	7.1
1/30/80	9.2	5.2	8.5	7.0	7.2	7.0
2/8/80	9.0	9.0	8.0	6.8	7.2	7.0
2/15/80	7.7	4.9	6.8	7.0	7.4	7.3

2/22/80		8.5	8.5	8.2	7.0	6.8	7.0
2/29/80		3.7	5.0	7.9	6.9	7.2	7.0
3/5/80		1.8	4.4	6.9	7.1	7.3	7.1
3/19/80		2.9	4.2	2.2	7.4	7.1	6.6
3/26/80		1.0	4.0	3.7	6.4	7.3	6.5
4/2/80		4.5	8.3	7.8	7.1	6.6	6.9
4/9/80		5.7	8.9	7.7	6.8	7.0	7.1
4/17/80		4.6	1.4	0.8	7.7	6.9	6.9
4/23/80		7.2	3.4	4.8	7.2	7.5	6.8
4/30/80		0.5	7.9	5.8	6.9	7.1	6.4
5/7/80		7.3	2.5	4.5	6.9	6.8	6.6
5/14/80		2.1	2.4	6.0	7.3	6.6	6.4
5/21/80		6.1	6.8	6.6	8.5	7.1	6.3
5/28/80		6.2	1.2	8.5	7.2	7.0	6.0
Range	Year 1	-	6.5 - 8.7	5.0 - 9.5	-	6.4 - 7.5	6.4 - 8.5
	Total	0.2 - 9.2	0.5 - 9.2	0.8 - 9.5	6.2 - 8.5	6.4 - 7.5	6.3 - 8.5
Mean	Year 1	-	7.6	7.5	-	7.1	7.2
	Total	5.3	6.7	6.3	7.0	7.1	6.9
S.D.	Year 1	-	0.7	0.9	-	0.25	0.41
	Total	2.9	2.1	2.3	0.4	0.24	0.41
n	Year 1	-	27	25	-	17	17
	Total	29	56	54	29	46	46
Mode	Year 1	-	6.5,7.4	6.8	-	7.3	7.0,7.1
	Total	-	7.4	6.8	7.0	7.3	7.0

3. Activated sludge with stabilized influent concentration of B.O.D. - Late in the first year of study, this mode of operation was attempted in order to simulate the effect of some technique dampening variations in the concentration of pollutants in the wastewater. Examples of ways that such variation could be reduced would include high recycle and perhaps use of an equalization tank. In this procedure, wastewater was diluted as necessary to provide a constant influent concentration of BOD, initially selected as 500 mg/l. Loading rates were calculated, and levels of various pollutant parameters were determined in both the biological influent and effluent.

4. Chemical precipitation in aeration tank - During the period of study of this alternative, Unit 1 was operated as usual, except that alum was dosed to the aeration tank. The dose was expressed as mg of alum per day per liter of aeration tank volume. This volume was taken to be 7.5 liters. The alum doses used were as follows:

Period	Alum Dose (mg/day/liter)
1/16/80-1/29/80	20
1/30/80-2/19/80	10
2/20/80-6/30/80	5

The effluent from the biological treatment unit was provided with supplementary settling, in addition to that occurring in the settling well of the unit. In particular, solids levels (suspended and volatile suspended) were measured in the effluent. Additionally, loadings were determined, and influent and effluent concentrations measured.

5. Activated sludge, with effluent chemical precipitation - Unit 1 was operated in the usual manner, except that the effluent was subjected to chemical precipitation. Small scale studies provided general information on the coagulant to be preferred ($FeCl_3$, rather than alum), and the

approximate dose needed. The general procedure was as follows:

a) The effluent from Unit 1 was collected for one week rising a 32 gallon plastic container (approximately 50 liters collected).

b) The volume of effluent was measured to determine the amount of coagulant to be added.

c) The effluent in the container was then stirred with sufficient agitation so that when the ferric chloride was added, thorough mixing would occur.

d) The ferric chloride was then added at a dose of 250 mg/l to the wastewater, during the stirring procedure.

e) After complete mixing had been accomplished (approximately 5 to 10 minutes), the mixture was slowly stirred in order to promote flocculation. Some 15 minutes was allowed for this process.

f) After the flocculation, the suspended matter was allowed to settle for approximately two hours.

g) The settled solids were then drawn off from the bottom of the container (approximately 10% of the wastewater volume was removed as sludge).

h) The collected solids were reintroduced to the activated sludge unit in equal daily increments. The remaining sludge was added to the sludge reserve.

i) Suspended solids analysis was used to determine the effectiveness of the precipitation procedure. Samples were taken before and after coagulation to determine suspended solids and volatile suspended solids.

j) The effluent from the coagulation container was neutralized with 1.0 N NaOH to be utilized in further analysis.

6. Joint treatment with municipal sewage ("cometabolism") - For this phase of the study, a specialized apparatus was assembled. Included were an aeration tank (glass jar), with a volume of 3 liters at the fill line, and a subsequent settling tank, having a liquid volume of approximately 3 liters. An aquarium aerator was used to supply air through a diffuser, and a magnetic stirrer helped to maintain the biological floc in suspension. Influent to the aeration tank was primary effluent, collected as needed from the Johnson City Brush Creek Sewage Treatment Plant, with the appropriate content of pretreated coal gasification wastewater. Feed was provided by a peristalic pump, set to deliver 3

liters in about 20 hours, for a detention of 0.83 day (20 hours). Pretreated wastewater was refrigerated at 4°C until used. Start up of the unit involved addition of mixed liquor from the aeration tank of the Brush Creek Plant, supplemented by a small amount of activated sludge from the coal gasification sludge reserve. The schedule of addition of wastewater was as follows:

Date	% of Total Wastewater	
	Primary Effluent	Pretreated Gasification
3/5/80	100	0
4/7/80	99.98	0.02
4/14/80	99.96	0.04
4/22/80	99.94	0.06
4/28/80	99.9	0.1
5/5/80	99.8	0.2
5/12/80	99.7	0.3

The air flow to the aeration tank was 2,000 ml/minute, with an additional 1,350 ml/minute being used in the airlift provided to return secondary settling solids to the aeration tank. Operational tests included dissolved oxygen, pH, temperature, suspended solids, and volatile suspended solids, all on the mixed liquor, as well as tests on both the influent and effluent to estimate the degree of treatment being provided.

Biological Reaction Kinetics

The basic technique used was to determine values of the relevant basic data for the same point in time. The basic data which were gathered included the following:

Item of Data	Model For Determining
MLVSS (X,mg/l)	Perform test for nonfilterable volatile residue on mixed liquor
Cell detention (θ_c, days)	Multiply MLVSS, in mg/l, by 7.5 liters. Divide product by total mg/day of volatile suspended solids removed, including that in sludge that was wasted, and that in effluent, as based on tests for volatile suspended solids and volumes.

Item of Data	Model For Determining
BOD of the Influent and Effluent (S_o and S, respectively, in mg/l)	Determine 5-day biochemical oxygen demand on influent and effluent.
Hydraulic Detention θ_c, days)	Divide aeration volume, 7.5 liters, by flow rate, in liters per day, based on measurement of amount delivered in a measured time.

It is essential to the effective use of this procedure that the cell retention be controlled, that it be maintained at each selected value for a sufficiently long time to obtain stable conditions in the effluent and that multiple data points may be obtained. Subsequently, the procedure is as follows:

1. The basis is the equation:

$$\frac{X\,\theta}{S_o - S} = \frac{K_s}{k}\left(\frac{1}{S}\right) + \frac{1}{k}$$

Here, K_s is the rate coefficient, and k is the substrate removal rate coefficient. Using linear graph paper, $y = \frac{X\,\theta}{S_o - S}$ is plotted on the vertical axis, versus $x = \frac{1}{s}$ on the horizontal axis. Following linear regression, $\frac{1}{k}$, and thus k, is found as the y intercept, and $\frac{K_s}{k}$, and thus K_s, is found as the slope.

2. The basis is the equation:

$$\frac{1}{\theta_c} = Y\,\frac{S_o - S}{X\theta} - k_d$$

Here, Y is the biological yield coefficient, and k_d is the decay coefficient. Using linear graph paper, $y = \frac{1}{\theta_c}$ is plotted on the vertical axis, versus $x = \frac{S_o - S}{X\,\theta}$ on the horizontal axis.

Following linear regression, $-k_d$ is found as the y intercept, and Y as the slope.

Tertiary Treatment

Tests have been conducted to determine the feasibility of utilizing tertiary activated carbon adsorption in the treatment of wastewater produced during coal gasification. These comments focus on determining criteria for optimizing equilibrium adsorption.

Effluent from the Biological Oxidation Unit 2 was used as the primary source of waste sample in this study. To evaluate the degree of adsorption, total organic carbon (TOC) analyses were performed.

The waste sample was initially investigated to determine if changes in pH altered, to a significant extent, the solubility of various components therein. Parameters employed to determine if precipitation occurred with changes in pH included total residue (TR), non-filterable residue (NFR), and TOC.

Subsequent to this preliminary work, actual adsorption testing was performed. The contact time required for the establishment of equilibrium conditions between the carbon and the waste sample was determined. Next, tests were conducted to determine the effect of waste sample pH on the activated carbon's adsorption capacity. Equilibrium adsorption isotherms (carbon dosage tests) were then developed to permit calculation of the equilibrium adsorption capacity.

Concurrent with these studies, tests were performed to measure the effectiveness of various methods of preservation of filtered effluent from Biological Oxidation Unit 2.

Waste samples were collected from the effluent stream of Biological Oxidation Unit 2. For each of the three equilibrium tests (contact time, pH variance, and carbon dosage), a sufficient volume of sample was collected to allow triplication of the particular procedure using the same quality of waste sample. The TOC, TR, and NFR of the waste sample were measured at collection. The bulk waste samples were then filtered through fine pore Gelman glass fiber filters to remove suspended material.

Waste samples were generally used within 48 hours of the completion of collection. Wastewater sample not immediately used was stored in 5 gallon cans at approximately 4°C, and sample thus stored was allowed to achieve room temperature equilibrium prior to testing.

Calgon Filtersorb 300 activated carbon was used in the adsorption tests. Physical characteristics of this carbon have been provided by Calgon Corporation and are listed in Table 7.

The carbon was prepared by washing with hot tap water to remove fines. These fines accounted for less than 1% (by weight) of the carbon. The carbon was then dried at 105°C for 72 hours and cooled in a desiccator. Particle size distribution of the desiccated carbon was determined using U.S. Standard Sieves. The results of this determination are listed in Table 8. To expedite the onset of equilibrium, a blender was used to grind the carbon small enough to pass through a #325 U.S. Standard Sieve (0.44μm).

Table 7

Physical Characteristics of Calgon Filtersorb 300

Characteristic	Unit	Value
Surface Area (N_2, BET Method)	m^2/g	950-1050
Apparent Density	g/cc	0.48
	lb/ft^3	30
Particle Density (Hg Displacement)	g/cc	0.75
Real Density (He Displacement)	g/cc	2.1
Pore Volume (Within Particle)	cc/g	0.85
Voids in Densely Packed Column	%	36

Table 8

Particle Size Distribution of Washed Carbon

U.S. Standard Sieve Number	Particle Size (mm)	% of Sample (x)
x > #10	x > 2.00	30
#10 > x > #14	2.00 > x > 1.41	40
#14 > x > #18	1.41 > x > 1.00	20
#18 > x > #25	1.00 > x > 0.707	7
#25 > x	0.707 > x	3

TOC determinations were performed by the Tennessee Eastman Company, Kingsport, Tennessee. Generally, treated samples were analyzed within 8 hours of carbon contacting. Samples were stored at 4°C in tightly capped vials until analysis.

The procedure for preparing the treated samples for TOC analysis involved removing inorganic carbon by acid sparging. Typically, a 25 ml portion of sample was treated with 2-3 drops of 50% HCl. Pre-purified nitrogen gas was then applied for approximately three minutes to purge carbon dioxide from the sample.

Two Model-915 Beckman Total Organic Carbon Analyzers with Beckman Model 215B Infrared Analyzers were used in the analyses. One was calibrated in the range 0-2000 mg/l TOC, and the other in the range 0-100 mg/l TOC. Any sample containing less than 100 mg/l TOC was analyzed on the TOC calibrated in the lower range.

Purified oxygen at a flow rate of 150 cc/min served as the carrier gas in both analyzers. Duplicate injections of 20 μl of sample were used to determine an average peak height.

<u>Preliminary pH Tests</u> - Since tests to define the optimum pH for adsorption were anticipated, it was necessary to determine the effect of pH adjustments on the TOC, TR, and NFR of the waste sample. The pH of eight, 200 ml aliquots of waste sample was varied from 4 to 11 in increments of 1.0 pH units using 0.1 N H_2SO_4 and 0.1 N NaOH. Since less than 2 ml of acid or base were required for each adjustment, no dilution correction was performed. Samples were then agitated in capped 300 ml BOD bottles for 60 minutes. After agitation, 50.0 ml of each treated sample were analyzed for TR and 25.0 ml for NFR.

<u>Preservation Test</u> - A test was developed to determine the effect of various methods of preservation on the TOC concentration. A three-liter portion of waste sample was filtered and divided into three one-liter aliquots. One aliquot was stored at room temperature in a Parafilm-covered amber bottle. The second aliquot

was stored in a ground glass container at 4^oC. The third aliquot was treated to contain 40 mg/l HgCl and likewise stored in a ground glass container at 4^oC. At timed intervals, 50 ml portions were removed from each container, filtered, and analyzed for TOC.

Contact Time Equlibrium Test - The purpose of this test was to determine the extent of adsorption with respect to the time the sample was in contact with the activated carbon. From a plot of TOC versus contact time, the point at which equilibrium is established was estimated.

Into each of eight 300 ml BOD bottles, 1.000 gram of prepared activated carbon was analytically weighed. Then, 200.0 ml of filtered waste sample were volumetrically measured into each of the bottles. The containers were then agitated, and, at specified intervals, treated samples were removed, filtered through Gelman glass fiber filters to remove carbon particles, and stored in polyethylene capped vials at 4^oC until analysis.

This procedure was performed in triplicate.

pH Variance Equilibrium Test - This test was conducted to determine the optimum pH (or range of pH values) for maximizing the adsorption capacity of the carbon.

Generally, 0.5000 gram of prepared carbon was weighed into each of eight 300 ml BOD bottles. The pH of 200.0 ml aliquots of filtered waste sample was adjusted from 4 to 11 in increments of 1.0 pH unit using 0.1 N H_2SO_4 and 0.1 N NaOH. The waste samples were added to the bottles and agitated for the time period previously determined. After reacting, the carbon was separated by filtration and the treated samples prepared for analysis.

This procedure was triplicated.

Carbon Dosage Test - To estimate the ultimate capacity of the carbon for the adsorbable components in the waste sample, carbon dosage tests were performed.

In this test, varying amounts of carbon were used to treat constant volumes of waste sample. From 0.01 to 1.00 gram of prepared carbon was analytically weighed into seven, 300 ml BOD bottles. The waste sample pH was adjusted as defined in the previous test. Waste sample in 200.0 ml aliquots was added to the seven containers. An additional BOD bottle containing 200.0 ml of waste sample served as a blank. The containers were agitated until equilibrium was achieved. Treated samples were removed, filtered, and stored as described above.

This procedure was performed four times.

Analytical Methods

Analysis was instituted promptly in the project laboratory at East Tennessee State University. The procedures used were those specified in Standard Methods For the Examination of Water and Wastewater (1), 14th edition, using adaptations described by R. G. Luthy in Manual of Methods: Preservation and Analysis of Coal Gasification Wastewater (38). However, adapted methods were used for sulfides and thiocyanates. General descriptions of procedures used are as follows:

1. Alkalinity - The procedure utilized was potentiometric titration to a pre-selected pH. Because of the turbiduty and color present in the wastewater, it was not possible to use the color indicator endpoint for titration. The pre-selected pH of the endpoint was 4.3. A 50 ml sample was titrated with a standard 0.02 N H_2SO_4 solution until the endpoint pH was reached. The amount of alkalinity was then calculated using the amount of sample, amount of titrant used, and the normality of the acid, with a multiplication factor of 50,000.

$$\frac{\text{ml of acid X N X 50,000}}{\text{ml of cample}} = \frac{\text{alkalinity}}{\text{mg/l}}$$

2. Ammonia Nitrogen - The samples were preserved by adding sulfuric acid to a pH of less than 2. The sample flasks were steamed until there was no

ammonia present. The samples, in 35 ml portions, were filtered through a fine glass fiber filter. Borate buffer solution (25 ml) was added to the sample, and the pH was adjusted to 9.5 with 6 N NaOH. The sample was then distilled with the Kjeldahl apparatus (See Figure 10). The distillate was then collected below a 50 ml portion of boric acid indicator solution in a 500 ml Erlenmeyer flask. After 300 ml were collected, the outlet tube was placed above the collected distillate, and the condeser was allowed to steam for five minutes. The samples were then titrated with 0.02 N H_2SO_4 solution until they turned from a green to a pale lavender color. A blank was also carried through all of the above steps.

$$\text{mg/l } NH_3\text{-}N = \frac{(\text{ml } H_2SO_4 \text{ for sample}) - (\text{ml } H_2SO_4 \text{ for Blank}) \times 280}{\text{ml of sample}}$$

3. Biochemical Oxygen Demand - BOD is an empirical bioassay determination of the amount of dissolved oxygen consumed in a 5 day period as a result of stabilization under standard conditions. A deionized dilution water is first obtained. Then 1 ml per liter aliquots are added of phosphate buffer solution, ferric chloride solution, magnesium sulfate solution, and calcium chloride solution. Dilution water and several control blanks are then set up before adding seed to the dilution water. Samples are then added to the BOD bottles, and diluted with seeded dilution water to 300 ml. Initial dissolved oxygen (D.O.) tests are made on all samples. After five days incubation at $20^{\circ}C$, the final D.O. is read on all the samples. The D.O. uptake is then calculated for the seed blanks and dilution water blanks. The values for the seed blank and dilution water blanks are then added together and used as a correction factor against each sample dilution. This correction factor is then subtracted from the final D.O. of each sample dilution.

$$\underset{(\text{mg/l})}{\text{BOD - 5}} = \frac{\text{Final D.O. - Correction Factor} \times 100}{\text{\% of sample in bottle}}$$

Figure 11 shows a member of the project staff, Miss Donna Reed, performing a test for biochemical oxygen demand.

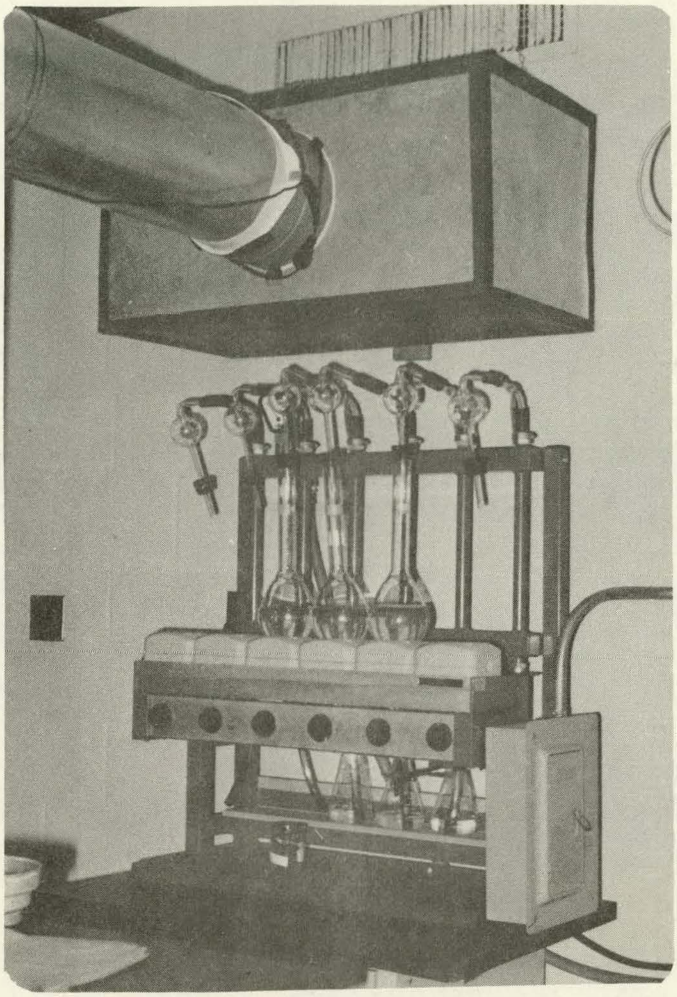


Figure 10
Kjeldahl Apparatus for
Distilling Ammonia Nitrogen Samples

Figure 11
Miss Donna Reed, a Member of the
Project Staff, Performs Tests
for Biochemical Oxygen Demand

4. Cyanide - The sample was first preserved by removing oxidizing agents with ascorbic acid. Then the sample was treated with lead nitrate to remove sulfide. Nest, the pH of the solution is raised to 12.0 to 12.5 with concentrated NaOH. A sample of the preserved solution was placed in the cyanide distillation apparatus (Figure 12), and an air purge was applied. The sample was then acidified and refluxed, which caused HCN to be liberated. The HCN gas was collected in a NaOH scrubbing solution. The concentration of the cyanide in the NaOH solution was determined by a colorimetric procedure.

5. Dissolved Oxygen - A YSI standard meter was used. With the electrode immersed in the liquid being studied, the dissolved oxygen concentration is read directly on the meter scale. See Figure 11. Note the instruments for recording temperature and atmospheric pressure, necessary for calibration, in this photograph.

6. Grease and Oil - A sample was acidified to a pH of less than 2. A boiling flask was tared, after being dried and stored in a dessicator. Fluorocarbon was added to the sample bottle in the amount of 30 ml. After being transferred to a separatory funnel, the funnel was shaken vigorously for approximately two minutes, and the layers allowed to separate. The solvent layer was filtered into the tared flask, and the process repeated twice using fresh solvent each time. The solvent was then distilled off. The flask was cooled in a dessicator for 30 minutes and then weighed. The residue weight was divided by the sample volume, and the amount of grease and oil determined in mg/l.

7. pH - pH was determined using a Fisher pH meter with a combination electrode, which was immersed in the sample solution. Figure 13 is the instrument used in the study.

8. Phenols - The direct photometric method was utilized for this determination. A 500 ml sample was preserved with 5 ml of copper sulfate solution and the

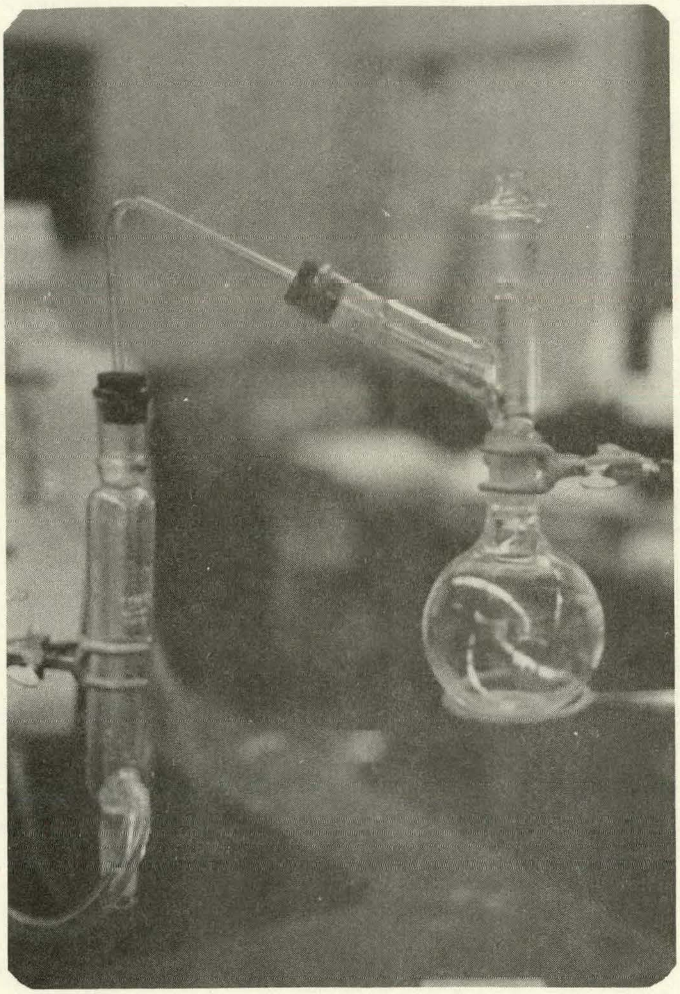


Figure 12
Distillation Apparatus Used for Cyanide
Determination (Exhaust Hood Required)

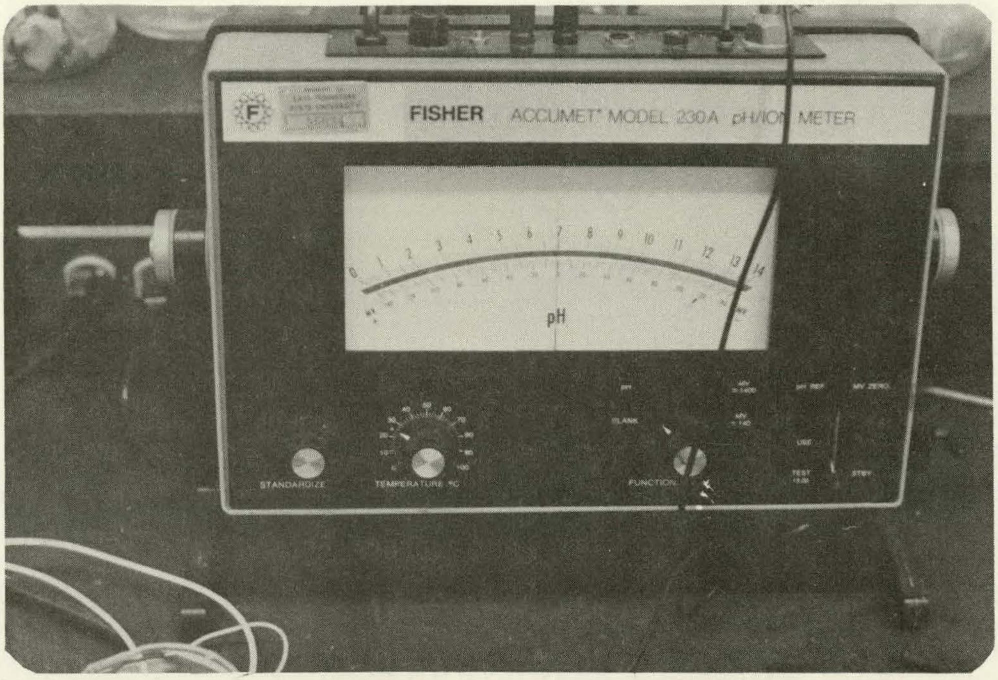


Figure 13
Meter for Determining pH Used
in Study

pH was adjusted to 4.0 with H_3PO_4 solution. Approximately 450 ml were distilled from the total volume, and distillation was stopped. Then 50 ml of phenol free water were added to the remaining 50 ml and then 50 ml more were distilled into the previous 450 ml. Then 100 ml of the distillate or a suitable portion containing not more than 0.5 mg of phenol were diluted to 100 ml in a 250 ml beaker. A phenol free water blank was also prepared. The blank and samples were treated by: (1) adding 2.0 ml NH_4Cl solution and adjusting with concentrated ammonium hydroxide; (2) adding 2 ml 4-amino antipurine solution, mixing, adding 2.0 ml of potassium ferrcyanide solution and mixing again; (3) after approximately 15 minutes, the amino phenol dye is read in a Spectrophotometer at 510 NM. The values obtained were then compared against a standard phenol calibration curve, and the phenol concentrations calculated. Figure 14 shows the spectrophotometer used for rountine determinations in this study.

9. Residue Determinations

   a. Total residue - A 25 ml sample was put in a 50 ml weighed beaker. The sample and beaker were weighed again. The water was then allowed to evaporate at 103 105°C. The beaker then was allowed to cool in a desiccator, and weighed again. The difference in weight between the sample weight and the dried weight determined the total amount of solids present in the sample, expressed as mg/l of total residue.

   b. Volatile Residue - The residue obtained from the total solids analysis was then fired at approximately 550°C in a muffle furnace. After the 100 ml beaker had cooled, it was weighed again. The difference between the total solids and the amount of residue not volatilized determined the volatile residue.

   c. Non-filterable Residue - An aliquot of well mixed sample was passed through a glass fiber filter using vacuum. The filter was then dried at 103-105°C until constant weight was obtained. The initial filter weight was then subtracted from the weight of the filter, plus the sample, and the amount of solids retained by the filter after drying was thus obtained in mg/l.

   d. Volatile Non-filterable Residue - The filter that was dried in the non-filterable residue procedure was fired at 550°C for approximately 15 minutes. It was then cooled and weighed again. The difference between the weight of the filter before firing and the weight after firing determined the volatile material present in the non-filterable residue sample, expressed as mg/l.

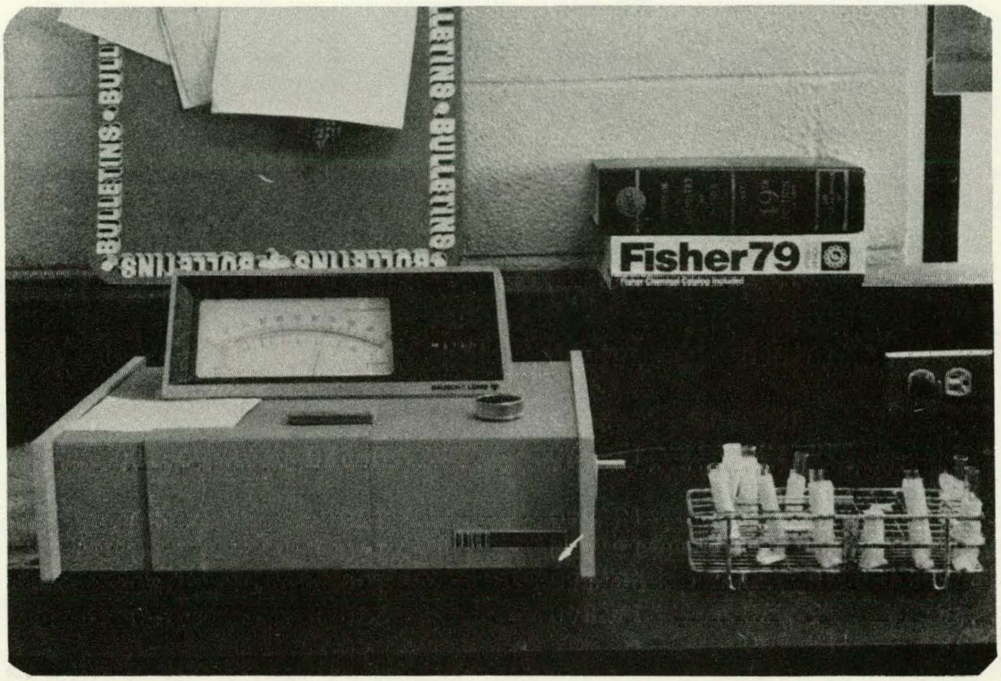


Figure 14
Spectrophotometer Used for
Routine Determinations

10. Settleable Solids - A one liter portion of the contents of the biological reaction chamber (aeration tank mixed liquor) was obtained and allowed to settle for one hour. The volume occupied by the sludge at the end of this period was then recorded, as provided in the standard method.

11. Sulfide - A 200 ml sample was stirred, and 2 N zinc acetate and 6 N NaOH added to preserve the sample. The sample was then filtered through a fine glass fiber filter. Next, there were added 150 ml of distilled water, 3 ml of 6 N HCl, and an amount of 0.025 N iodine solution that was in excess of the amount of sulfide thought to be present in the sample. All of the preceding were added in sequence to a 250 ml beaker. The filter paper was placed in the beaker along with the reagents, and then stirred gently for about five minutes to show that the iodine was not completely consumed. Starch solution indicator was added, and the sulfide solution titrated with .025 N sodium thiosulfate solution until the blue color disappeared. The amount of this sulfate solution was then subtracted from the amount of iodine solution added. This was then multiplied by a factor of 400, and, divided by the amount of sample in mililiters, this gave the sulfide concentration in mg/l. See Appendix B for details of this procedure, as adapted for use in the present study, where an amperometric titration was used.

12. Thiocyanate - The procedure used was a modified version of the spectrophotometric method given in Standard Methods For the Examination of Water and Wastewater (1). See Appendix C for details of the method, as adapted in this study for coal gasification wastewater.

13. Total Organic Carbon - A Beckman carbon analyzer was used for this procedure. The samples were filtered through a glass fiber filter to remove suspended matter. A carbon standard was then injected into the analyzer in both the total and inorganic carbon sides of the instrument. Then waste in the amount of 20 microliters for each sample was injected into the sample ports. The

standard peaks were calculated to determine their area. The total carbon was then calculated for each sample as a simple ratio against the standard. The same technique was used for the inorganic sample peaks. The difference between the peaks was calculated, which yielded the total organic carbon value for each sample. Figure 15 shows the instrument used in the study.

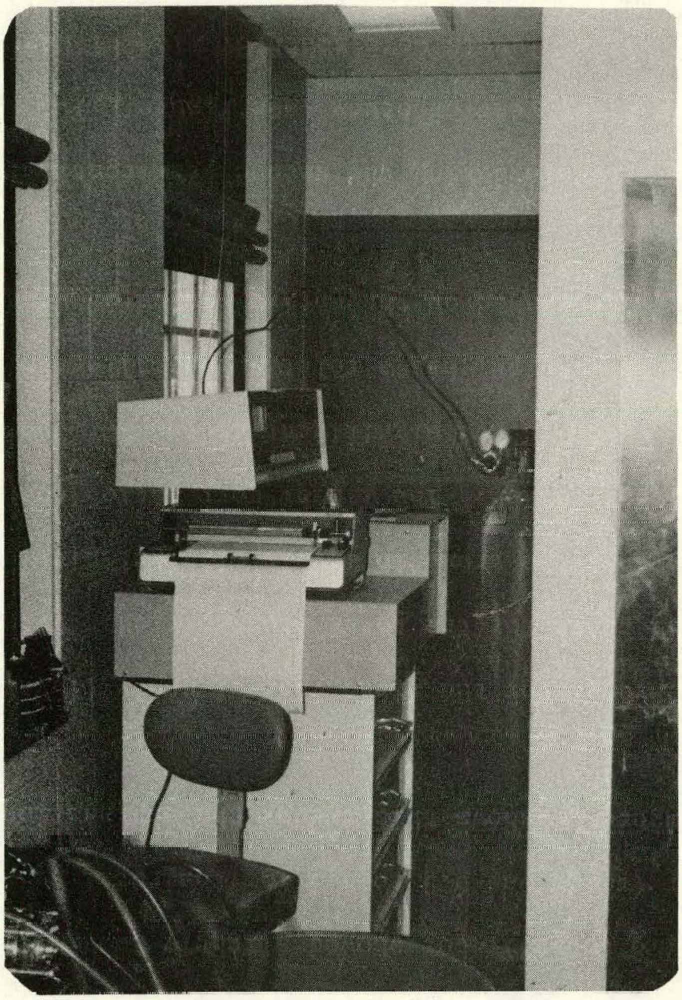


Figure 15
Total Organic Carbon Analyzer

Chapter 4

Results For Characterization of Untreated Wastewater

Tables 9 through 11 list levels of the various chemical parameters which were found. Comments on these data are as follows:

pH: Generally, pH was relatively stable during the first year of study (range of 7.8 to 8.3), but showed slightly lower values during the second year (range was 6.9 to 8.3 for the total study period). The graph in Figure 16 shows this trend, the explanation for which is not clear.

Alkalinity: The range for the first year of study (1,362 to 2,008 mg/l) also was the range for the total study period. From Figure 17, it can be seen that the trend in levels of alkalinity was only somewhat similar to that for pH. The linear correlation coefficient was found to be 0.13, which is not significant at the 90% confidence level. Alkalinity, as with pH, has a relatively small standard deviation (only 9.6% of the mean, based on the entire period of study, versus 4.2% for pH).

Ammonia Nitrogen: Levels during the second year continued the trend observable in the first year of study (see Figure 18). However, during the second year higher levels were reached. The highest level was nearly 250% of the average value. Thus, the standard deviation was relatively high, 1,470 mg/l for the entire study, which was 45.9% of the mean of 3,201 mg/l.

Biochemical Oxygen Demand (5 day): Levels in the pretreated wastewater showed considerable variation, the standard deviation of 2,561 mg/l for the entire study being 33.8% of the mean of 7,581 mg/l. Variability was less during the second year of the study than during the first year. In part, this may reflect better standardization of the pretreatment

Table 9

Chemical Characteristics of Untreated Wastewater:
pH, Alkalinity, BOD-5, Ammonia Nitrogen, TOC, and COD

Date	pH	Alkalinity (mg/l)	BOD(Mg/l) (Pretreated)	Ammonia Nitrogen (mg/l)	TOC (mg/l)	COD (mg/l)
10/10/78	7.8	-	5,290	-	-	-
10/17/78	8.2	-	14,130	-	-	-
10/24/78	8.2	2,008	12,690	-	-	-
10/31/78	8.1	1,650	12,240	-	-	-
11/7/78	8.3	1,638	12,960	-	-	-
11/15/78	8.2	1,688	5,612	-	-	-
12/5/78	8.0	1,699	6,230	-	-	-
12/18/78	8.0	1,807	-	-	-	-
1/9/79	8.0	1,362	3,640	-	-	
1/16/79	8.0	1,362	4,838	-	-	-
1/22/79	8.0	1,546	7,320	1,961	-	-
1/29/79	8.1	1,490	6,790	2,250	-	-
2/5/79	8.2	1,600	6,898	2,189	-	-
2/12/79	8.2	1,520	5,500	2,083	-	-
2/20/79	8.1	1,546	4,848	1,907	13,730	-
2/28/79	8.0	1,500	7,120	1,926	71,000	-
3/5/79	7.9	1,584	7,840	2,020	-	-
3/26/79	8.0	1,475	6,770	-	-	-
4/9/79	7.8	1,500	7,948	2,929	-	19,500
4/17/79	8.0	1,684	6,350	3,179	-	19,500
4/23/79	8.0	1,832	9,953	3,609	-	49,132
5/1/79	7.9	1,760	9,500	-	-	-
5/14/79	7.9	1,877	9,493	3,095	13,600	31,904
5/21/79	7.8	1,663		3,135	-	-
7/21/79	-	-	6,747	-	-	-
8/13/79	8.0	1,700	6,400	-	-	-
9/19/79	-	1,670	6,710	3,463	-	-
10/15/79	7.5	-	6,403	3,388	-	-
11/8/79	-	1,828	6,688	2,716		
11/26/79	7.7	-	7,853	2,175	-	-
1/7/80	7.5	-	5,383	2,781	-	-
2/21/80	7.4	1,404	5,919	3,743	-	-
4/2/80	8.2	1,664	8,959	4,919	-	-
4/25/80	7.0	1,664	-	7,812	-	-
5/23/80	6.9	1,578	-	5,940	-	-
Range						
Year 1	7.8 - 8.3	1,362 - 2,008	3,640 - 14,130	1,907 - 3,609	13,600 - 71,000	19,500 - 49,132
Total	6.9 8.3	1,362 - 2,008	3,640 - 14,130	1,907 - 7,812	13,600 - 71,000	19,500 - 49,132
Mean						
Year 1	8.03	1,627	7,907	2,524	32,777	30,009
Total	7.90	1,631	7,581	3,201	32,777	30,009

S.D.						
Year 1	0.14	163	2,926	615	33,102	14,026
Total	0.33	153	2,561	1,470	33,102	14,026
N						
Year 1	24	22	22	12	3	4
Total	32	29	31	21	3	4
Mode						
Year 1	8.0	-	-	-	-	-
Total	8.0	-	-	-	-	-

Table 10

Chemical Characteristics of Untreated Wastewater: Residue Determinations

Date	Total Residue		Nonfilterable Residue	
	TR (mg/l)	TVR (mg/l)	NFR (mg/l)	VNFR (mg/l)
10/10/78	16,630	-	40	-
10/24/78	16,870	16,840	220	160
10/31/78	28,350	28,150	150	70
11/7/78	14,780	11,470	140	60
11/15/78	18,670	18,540	150	80
Range	14,780 - 28,350	11,470 - 28,150	40-220	60-160
Mean	19,060	18,750	140	92.5
S.D.	5,733	6,953	64.4	45.7
N	5	4	5	4

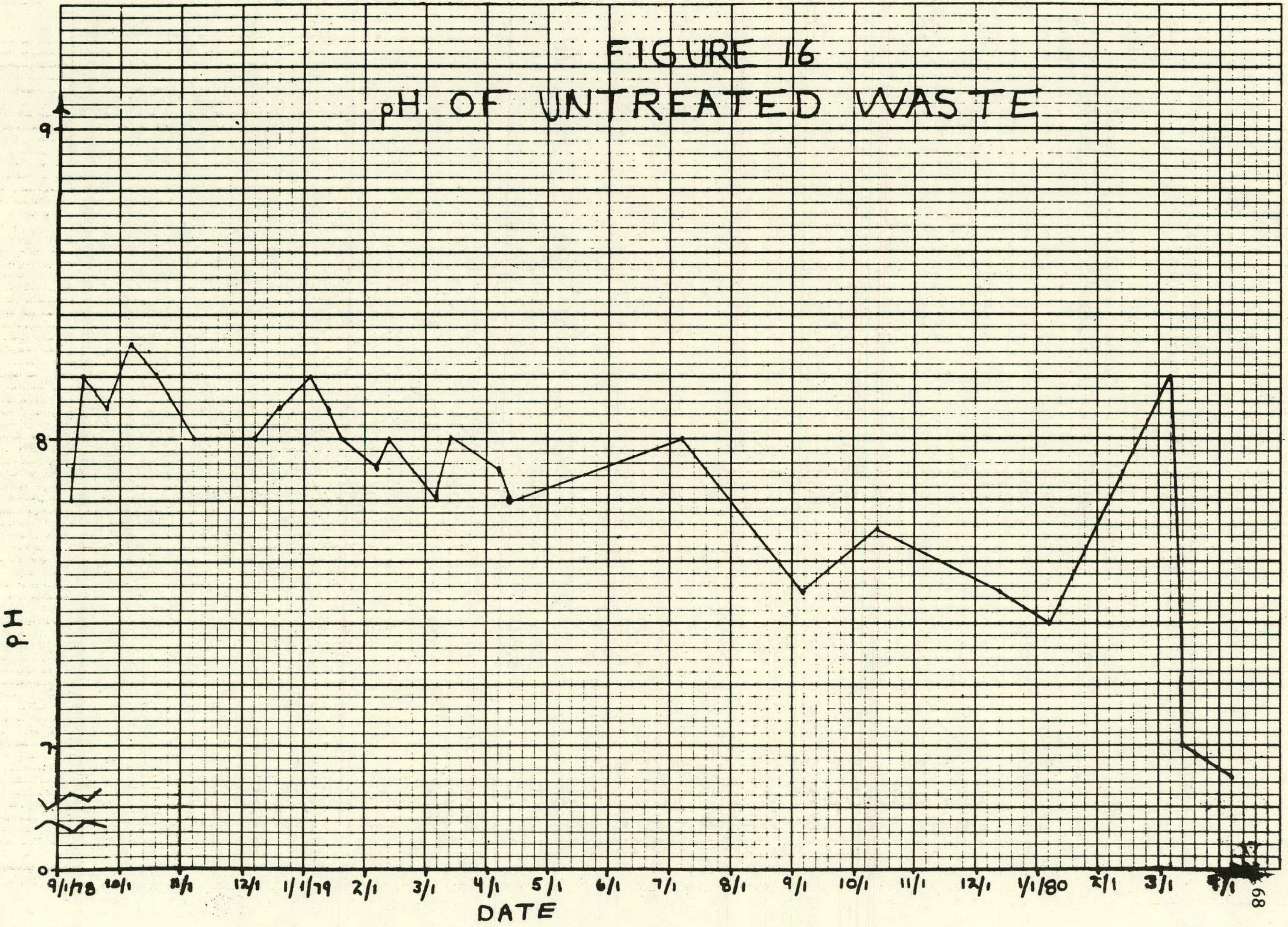
Table 11

Chemical Characteristics of Untreated Wastewater: Sulfide, Thiocyanate, Grease and Oil, and Phenols

Date	Sulfide (mg/l)	Thiocyanate (mg/l)	Grease and Oil (mg/l)	Phenols (mg/l)
1/23/79	-	160	-	-
2/12/79	829	700	-	-
3/5/79	-	235	-	1,700
4/9/79	-	452	697	-
5/1/79	-	-	-	1,800
5/14/79	-	402	-	-
5/21/79	-	784	624	-
6/20/79	-	653	-	-
7/2/79	-	706	-	-
7/10/79	-	-	2,443	-
7/21/79	-	601	6,535	-
8/13/79	-	860	-	-
9/19/79	-	922	-	2,061
10/15/79	-	-	-	1,707
11/8/79	-	879	1,009	-
11/26/79	1,757	-	-	-
1/7/80	-	-	-	-
2/21/80	-	-	1,508	-
4/2/80	8,857	-	3,320	1,868
4/25/80	8,166	-	-	-
5/23/80	7,270	-	4,161	2,410
Range				
Year 1	-	160-784	624-2,443	1,700-1,800
Total	829 - 8,857	160-922	624-6,535	1,700-2,410
Mean				
Year 1	-	512	1,255	1,750
Total	5,376	613	2,537	1,924
S.D.				
Year 1	-	234	1,030	71
Total	3,784	251	2,059	272
n				
Year 1	1	8	3	2
Total	5	12	8	6

FIGURE 16

pH OF UNTREATED WASTE



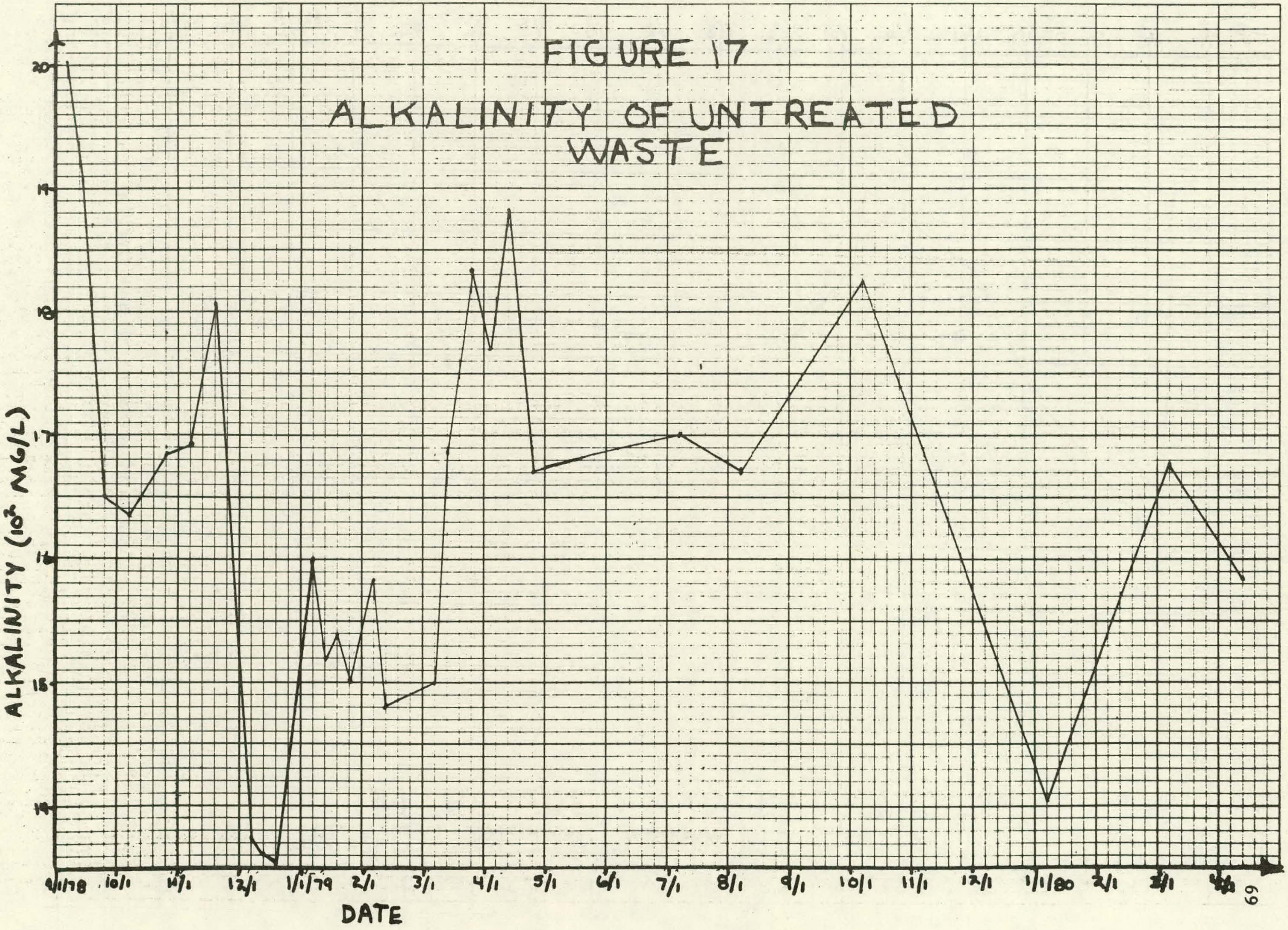


FIGURE 17

ALKALINITY OF UNTREATED WASTE

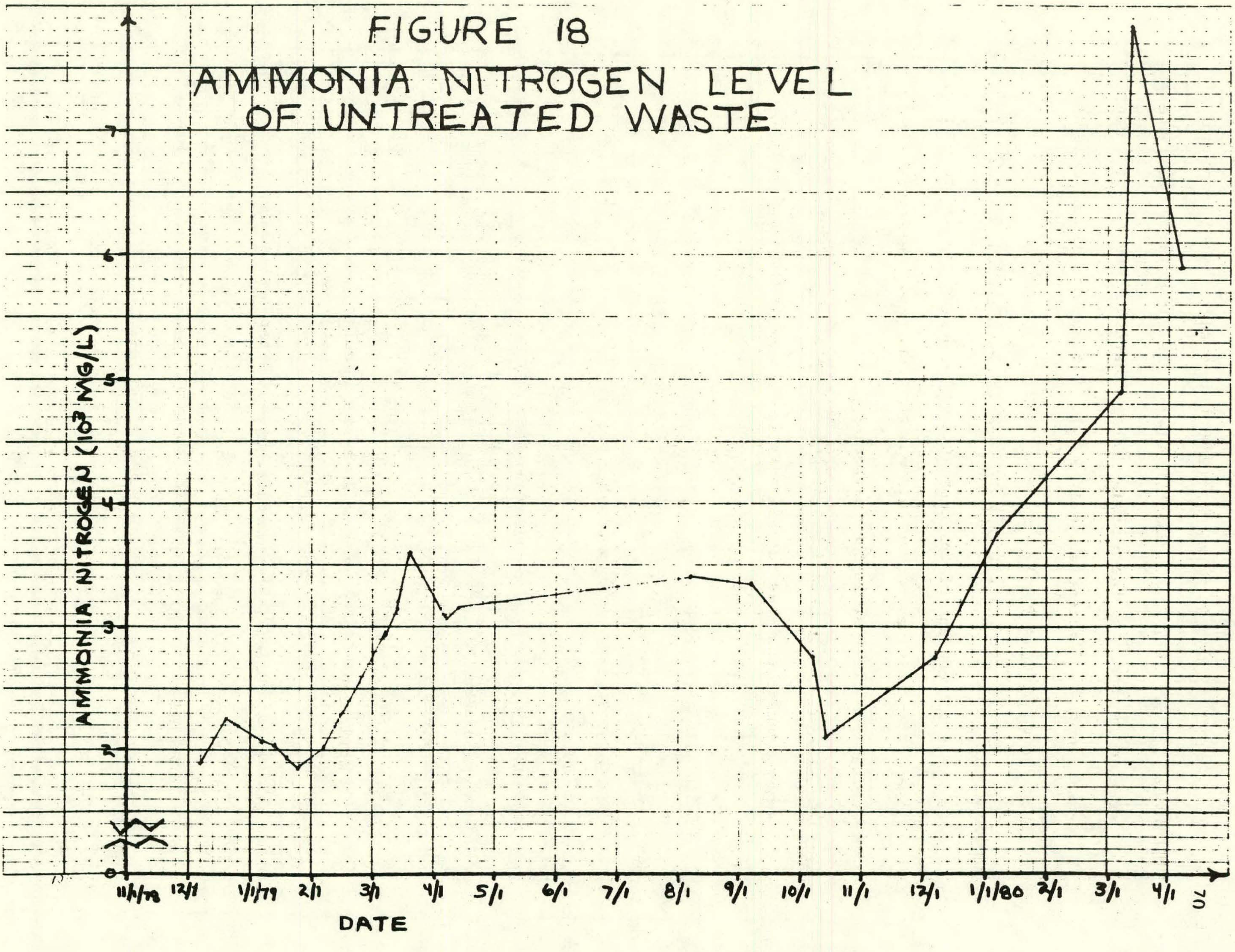


FIGURE 18

AMMONIA NITROGEN LEVEL OF UNTREATED WASTE procedure. Figure 19 shows the variation of the data on biochemical oxygen demand with time. Some aspects of the variation in data are similar to those for the ammonia nitrogen data. However, the linear correlation coefficient was only 0.37, which was not significant at the 95% confidence level.

Total Organic Carbon: Additional data were not gathered on the total organic carbon (TOC) content of the untreated waste during the second year of study. The main reason for this was that untreated sample tended to degrade the catalyst in the instrument.

Chemical Oxygen Demand: Despite repeated attempts, a procedure for chemical oxygen demand that was satisfactory for the wastewater under study was not developed. The data listed in Table 9 , therefore, must be considered preliminary.

Residue: Major findings, all in the first year of the study, were:

1. Total residue had a mean of 19,060 mg/l, and a standard deviation of 5,733 mg/l.
2. Volatile residue comprised most of the total residue, having a mean of 18,750 mg/l (98.4 % of the mean for total residue),and a standard deviation of 6,953 mg/l.
3. Nonfilterable residue had a mean of only 140 mg/l and a standard deviation of 64.4 mg/l, and was 66.1% volatile material.

Sulfide: To derive meaningful data, it was considered necessary to develop a modified procedure for sulfide, one more appropriate to the wastewater under study. See Appendix B . The three most recent values (8,857; 8,166; and 7,270 mg/l) were considered the most reliable. The mean of these was 8,098 mg/l, with a standard deviation of 796 mg/l (9.8% of the mean). For comparison, four replicate determinations of sulfide in the sample collected on 11/26/79 showed a standard deviation of 51 mg/l,

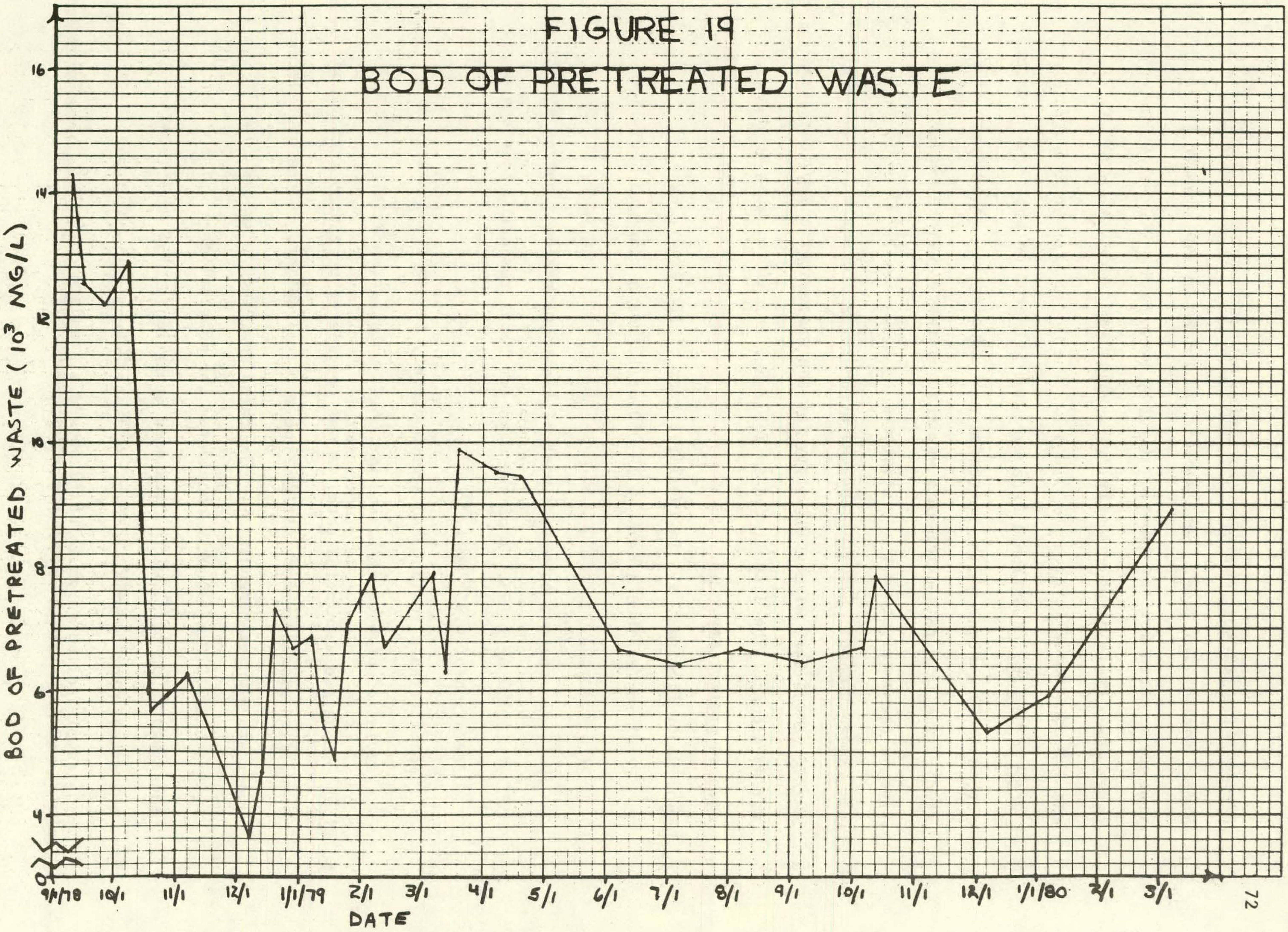


FIGURE 19

BOD OF PRETREATED WASTE

which was 2.9% of the mean of 1,757 mg/l.

Thiocyanate: A modified procedure also was developed for thiocyanate. See Appendix C . In this case, also, the most recent data, gathered during the second year of the study, were considered the most reliable. These data showed a mean of 816 mg/l, and a standard deviation of 145 mg/l (17.8% of the mean).

Grease and Oil: Data were characterized by a range of 624 to 6,535 mg/l. Variability was especially great in data gathered during the second year of the study. The mean for the entire study was 2,537 mg/l, with a standard deviation of 2,059 mg/l (81.2% of the mean).

Phenols: Concentrations of phenols ranged from 1,700 to 2,410 mg/l. The mean for the entire study was 1,924 mg/l, and the standard deviation was 272 mg/l (14.1% of the mean).

Cyanide: Cyanide was measured in three samples:

Date	CN(mg/l)
10/15/79	0.2
11/8/79	0.9
11/26/79	2.8

The mean of these values was 1.3 mg/l, compared with a standard deviation of 1.3 mg/l.

Chloride: Several analytical techniques were tried, though a full basis for comparison was not developed. Appendix D discusses the analytical techniques. Data for the chloride content of the raw waste were:

Date	Cl(mg/l)
1/7/80	94,300
4/25/80	12,373

Chapter 5

Results For Study of Wastewater Pretreatment

Removal of Ammonia Nitrogen

Most detailed study of the removal of ammonia nitrogen was performed during the first year of the study. Table 12 presents data from small scale studies in which air from an installed, pressurized source was injected into the untreated wastewater. Conditions studied included pH ranging from 9.0 to 11.0, temperature ranging from 50°C to 80°C, aeration rate ranging from 5 to 20 liters of air per minute per liter of sample (l/m/l), and stripping time ranging from 15 minutes to 90 minutes. Under various combinations of conditions, the removal of ammonia nitrogen ranged from 28.2% (pH of 9.0, 30 minutes, 70°C, and 15 l/m/l) to 97.4% (pH 10.0, 90 minutes, 70°C, and 15 l/m/l).

Using the data from small scale studies, multi-variant linear regression yielded an equation which included the effect of all four of the variables studied:

$$y = 30.08\, x_1 + 1.05\, x_2 + 1.94\, x_3 + 0.318\, x_4 - 332.15$$

y = removal of ammonia nitrogen (%)
x_1 = pH (units)
x_2 = temperature of solution being stripped (°C)
x_3 = aeration rate (l/m/l)
x_4 = stripping time (minutes)

It appeared that ammonia nitrogen could be removed to well beyond the level required to protect biological treatment processes, and possibly to essentially any extent desired.

Information obtained from the small scale studies was used in refining the stripping process. Table 13 summarizes information on the stripping of ammonia nitrogen in batches large enough to use as influent in the study of biological treatment. Note that data for the samples collected 7/21/79 and 8/13/79 were not included in this study. It is clear that, although the formula above gives

Table 12

Small-scale Studies of the Stripping of Ammonia Nitrogen

	Stripping Conditions				Ammonia Nitrogen	
pH	Time (min.)	Temp. (^{o}C)	Aeration (l/m/l)	Raw (mg/l)	Treated (mg/l)	Removal %
9.0	30	70	15	3,179	2,283	28.2
9.25	"	"	"	"	1,674	47.3
9.5	"	"	"	"	950	70.3
9.75	"	"	"	"	674	78.8
10.0	"	"	"	"	588	81.5
10.5	"	"	"	"	226	93.0
11.0	"	"	"	"	243	92.3
9.0	30	70	15	3,612	2,250	37.0
9.25	"	"	"	"	1,695	53.1
9.5	"	"	"	"	974	73.0
9.75	"	"	"	"	703	80.5
10.0	"	"	"	"	567	84.3
10.5	"	"	"	"	214	94.0
11.0	"	"	"	"	258	93.0
10.0	30	50	15	3,179	1,261	60.3
"	"	60	"	"	893	71.9
"	"	70	"	"	481	84.9
"	"	80	"	"	187	94.1
10.0	30	50	15	3,179	1,299	59.1
"	"	60	"	"	852	73.2
"	"	70	"	"	519	83.6
"	"	80	"	"	207	93.4
10.0	30	70	5	3,179	1,223	61.5
"	"	"	10	"	778	75.5
"	"	"	15	"	338	89.4
"	"	"	20	"	163	95.0
10.0	30	70	5	3,179	1,270	60.0
"	"	"	10	"	766	75.9
"	"	"	15	"	359	88.7
"	"	"	20	"	154	95.1
10.0	15	70	15	3,179	822	74.1
"	30	"	"	"	543	82.9
"	60	"	"	"	223	93.0
"	90	"	"	"	68	97.9
10.0	15	70	15	3,179	867	72.7
"	30	"	"	"	573	81.9
"	60	"	"	"	249	92.1
"	90	"	"	"	83	97.4

Table 13

Stripping of Batches of Wastewater For Influent in Studies of Biological Treatment

	Stripping Conditions				Ammonia Nitrogen			
Date	pH (units)	Time (min.)	Temp. (C)	Aeration (l/m/l)	Raw (mg/l)	Pre-treated (mg/l)	Re-moval (%)	Expected Removal (%)
1/22/79	10.0	30	60	8	1,961	1,149	41.4	56.7
1/29/79	10.0	30	60	9	2,250	1,210	46.2	58.7
2/5/79	10.0	30	55	9	2,189	1,095	50.0	53.4
2/12/79	10.0	30	65	9	2,083	689	66.9	63.9
2/20/79	10.0	30	60-45	8	1,907	560	70.6	48.8
2/28/79	10.0	30	60	15	1,926	773	59.6	70.3
3/5/79	10.0	30	62-55	10	2,020	809	60.0	59.0
4/9/79	10.0	45	70	15	2,929	496	83.1	85.6
4/18/79	10.0	30	70	15	3,179	543	82.9	80.8
4/23/79	10.0	45	70	15	3,609	944	73.8	85.6
5/14/79	10.0	45	70	10	3,095	526	83.0	75.9
5/21/79	10.0	45	70	15	3,135	407	87.0	85.6
9/19/79	10.0	30	60	9.3	3,463	1,190	65.6	59.2
10/15/79	9.75	40	65	9	3,388	938	72.3	59.6
11/8/79	9.75	60	70	15	2,716	734	73.0	82.8
11/26/79	9.75	30	70	15	2,175	630	71.0	73.3
1/7/80	9.75	30	70	15	2,781	476	82.9	73.3
2/21/80	9.75	30	65	15	3,743	1,348	64.0	68.0
4/2/80	9.8	60	70	4	4,919	1,372	72.1	63.0
4/25/80	9.7	60	60	10	7,812	2,752	64.8	60.1
5/23/80	10.1	60	61	9.5	5,940	1,670	71.9	72.2
<u>Range</u>								
Year 1	-	30-45	52.5 - 70	8 - 15	1,907 - 3,609	407 - 1,210	41.4 - 87.0	48.8 - 85.6
Total	9.7 - 10.1	30-60	52.5 - 70	4-15	1,907 - 7,812	407 - 2,752	41.4 - 87.0	48.8 - 85.6
<u>Mean</u>								
Year 1	10.0	35	63.4	11.5	2,524	767	67.0	68.7
Total	9.92	39.0	64.4	11.4	3,201	967	68.7	68.4
<u>S.D.</u>								
Year 1	-	7.4	6.5	3.1	615	277	15.7	13.6
Total	0.13	12.0	5.7	3.4	1,470	537	12.3	11.4
<u>n</u>								
Year 1	12	12	12	12	12	12	12	12
Total	21	21	21	21	21	21	21	21
<u>Mode</u>								
Year 1	10.0	30	70	15	-	-	-	-
Total	10.0	30	70	15	-	-	-	-

a reasonable estimate of the reduction in ammonia nitrogen to be expected (correlation coefficient is 0.697, significant at the 99.9% confidence level), that there are differences.

Removal of Grease and Oil

A limited series of small-scale tests was performed to estimate appropriate conditions for removal of grease and oil. Results are shown in Table 14. It was deduced from these data that the injection of a small amount of air at the low point in the suppression of the pH could greatly increase the removal of grease and oil. These data were used as the basis for the development of a preliminary equation summarizing the effect of the several parameters (multivariant regression), and for the pretreatment of larger batches of wastewater.

Table 15 summarizes available data on full-scale grease and oil removal for use as biological treatment influent. Note that, after an early high degree removal (96.7% for the sample collected on 7/21/79), results were less satisfactory, and conditions were gradually modified to improve the removal of grease and oil. Thus, aeration rate was increased to 3 liters/minute/liter of sample, aeration time raised to 45 minutes, and pH suppression modified to 2.6. The result was a gradual increase in the removal of grease and oil, from the 33.0 percent for the sample collected on 11/8/79, to 73.4% for the sample collected on 5/23/80.

Table 14

Results of Small Scale Tests For Estimating Parameters For Removal of Grease and Oil

Removal Conditions			Grease and Oil		
pH	Time (min.)	Aeration (1/m/1)	Untreated (mg/1)	Treated (mg/1)	Removal (%)
3.0	960	0	624	538	13.8
2.5	960	0	624	490	21.5
2.0	960	0	624	393	36.2
1.5	960	0	624	237	62.0
3.0	30	0.4	2,443	289	88.2
3.0	30	1.0	2,443	371	84.8
3.0	30	1.5	2,443	312	87.2

Result of multi-variant linear regression using above data:

$$y = 185.87 - 31.86\, x_1 - 0.0842\, x_2 - 1.066\, x_3$$

where: y = removal of grease and oil (%)

x_1 = pH at low point

x_2 = treatment time (minutes)

x_3 = aeration rate (1/m/1)

multiple correlation coefficient = 0.9929

Table 15

Result of Full Scale Grease and Oil Removal For Wastewater to be Used as Biological Influent

	Removal Conditions			Grease and Oil		
Date	pH	Time (min.)	Aeration (1/m/1)	Untreated (mg/1)	Treated (mg/1)	Removal (%)
4/9/79	2.5	960	0	697	563	19.2
5/21/79	2.5	960	0	618	507	18.0
7/21/79	3.0	30	0.4	6,535	214	96.7
11/8/79	3.0	30	0.4	1,009	676	33.0
2/21/80	3.0	30	0.4	1,508	672	55.4
4/2/80	3.0	30	0.4	3,320	1,099	66.9
4/25/80	3.0	45	3	-	432	-
5/23/80	2.6	45	3	4,161	1,105	73.4
Range						
Year 1	-	-	-	618 - 697	507 - 563	18.0 - 19.2
Total	2.5 - 3.0	30 - 960	0 - 3	618 - 6,535	507 - 1,105	18.0 - 96.7
Mean						
Year 1	2.5	960	0	658	535	18.6
Total	2.83	266	3.45	2,550	659	51.8
S.D.						
Year 1	-	-	-	56	40	0.8
Total	0.243	428	6.80	2,225	310	26.7
n						
Year 1	2	2	2	2	2	2
Total	8	8	8	7	8	7
Mode						
Year 1	2.5	960	0	-	-	-
Total	3.0	30	0.4	-	-	-

Removal of Other Substances in Pretreatment

Limited data are available for several substances that are significant as pollutants, including:

1. Sulfide: For the sample collected 5/23/80, results were:

Location	Sulfide (mg/l)	Removal (%)
Untreated	7,270	-
Stripped	1,633	77.5
Entire pretreatment	1,113	84.7

For comparison, in the sample collected 4/25/80, the original sulfide of 8,166 mg/l was reduced to 580 mg/l, for a total of 92.9 removal, with no breakdown available as to where the removal occurred. Evidently, relatively high degree removal of sulfide is obtained, and this is mainly due to stripping, the first process.

2. Phenols: Data were summarized as follows:

Date	Raw (mg/l)	Pretreated (mg/l)	Removal %
8/13/79	-	2,010	-
9/19/79	2,061	1,527	25.9
4/25/80	1,868	1,622	13.2
5/23/80	2,410	1,470	39.0
Mean	2,113	1,657	26.0
S.D.	275	243	12.9
n	3	4	3

3. Thiocyanate: Data were as follows:

Date	Raw (mg/l)	Pretreated (mg/l)	Removal %
1/23/79	160	182	-
1/30/79	-	186	-
2/12/79	700	86	87.7
3/7/79	235	294	-
4/10/79	452	371	17.9
5/23/79	-	938	-
7/21/79	-	601	-
8/13/79	860	-	-
9/19/79	922	1,145	-
11/8/79	879	-	-

Data are not extensive enough to be definitive. In several samples for which both a raw and a pretreated result were available, there was an increase in thiocyanate in pretreatment. This could have been due to several mechanisms, including reaction between sulfide and cyanide. In any event, there apparently was little removal of thiocyanate in pretreatment, and there even may have been an increase in some cases.

4. Biochemical Oxygen Demand: Only a small amount of data are available to show the effect of pretreatment on biochemical oxygen demand:

Date	Raw (mg/l)	Pretreated (mg/l)	Removal (%)
7/21/79	12,800	6,747	43.8
2/21/80	9,145	5,919	35.3
5/23/80	8,700	-	-

Evidently, there can be substantial reduction in biochemical oxygen demand, whether by volatilization, precipitation, or another mechanism.

5. Alkalinity: Data on the change in alkalinity in pretreatment are as follows:

Date	Raw (mg/l)	Pretreated (mg/l)	Removal (%)
10/24/78	2,008	1,815	9.6
10/31/78	1,650	1,388	15.9
8/13/79	1,700	676	60.2
9/19/79	1,670	520	68.9
11/8/79	1,828	656	64.1
2/21/79	1,404	540	61.5
4/2/80	1,664	1,450	12.9
4/25/80	1,664	1,326	20.3
5/23/80	1,578	1,488	5.7
Range	1,578 - 2,008	520 - 1,815	5.7 - 68.9
Mean	1,685	1,095	35.5
S.D.	165	493	27.2
n	9	9	9

Some of the results, such as the low degree of removal of alkalinity in recent samples, are difficult to explain.

Sludge Production in Pretreatment

Table 16 lists the total reduction in volume in pretreatment. Apparently, some 18.9% reduction in volume (standard deviation was 12.2%) may be expected in pretreatment. There are several explanations for this loss, including the stripping operation (mainly volatilization of water and organics), the grease and oil removal (mainly removal of settled solids and floating material), and neutralization (mainly settled material). A limited breakdown is available:

	Loss in Volume				
Date	Stripping (%)	Grease and Oil (%)	Neutralization (%)	Made -up by Reagents (%)	Total
11/8/79	5.8	5.0	15.0	(0.8)	25.8
1/7/80	-	2.5	-	(2.6)	13.9
2/21/80	-	9.0	-	(3.8)	28.8
4/2/80	18.9	2.3	4.7	(5.4)	25.9
4/25/80	11.8	3.2	10.3	(6.7)	25.3
5/23/80	14.7	5.3	9.7	(11.5)	29.7
Range	5.8-18.9	2.3-9.0	4.7-15.0	0.8-11.5	13.9-29.7
Mean	12.8	4.6	9.9	5.1	24.9
S.D.	5.5	2.5	4.2	3.7	5.7
n	4	6	4	6	6

Thus, the greatest loss in volume appeared to be in stripping, followed by neutralization, and, again, followed by the grease and oil removal.

Table 16
Decrease in Volume in Pretreatment

Date	Total Decrease (%)
10/10/78	2.0
10/24/78	5.2
10/31/78	1.9
11/7/78	3.3
12/5/78	2.3
12/18/78	12.5
1/9/79	23.5
1/16/79	13.0
1/22/79	47.9
1/29/79	41.4
2/5/79	37.8
2/12/79	18.4
2/28/79	12.8
3/5/79	14.4
4/2/79	21.0
4/9/79	14.0
4/23/79	12.5
5/1/79	17.5
5/14/79	8.7
5/21/79	31.5
11/8/79	25.8
11/26/79	19.6
1/7/80	13.9
2/21/80	28.8
4/2/80	25.9
4/25/80	25.3
5/23/80	29.7
Range	
Year 1	1.9 - 47.9
Total	1.9 - 47.9
Mean	
Year 1	17.1
Total	18.9
S.D.	
Year 1	13.4
Total	12.2
n	
Year 1	20
Total	27

Chapter 6

Results For Study of Biological Treatment

Activated Sludge Without Aerated Waste Stabilization Pond

Tables 17 through 26 provide data for the activated sludge unit operated without a preceding aerated waste stabilization pond. The mode of operation is further identified as follows:

1. Operation as activated sludge without modification: Unit 1, from beginning of study, through June 6, 1979; and Unit 2, from beginning of study through June 6, 1979, and from January 1, 1980, through end of study.
2. Operation as activated sludge with stabilized influent level of BOD: Unit 2, from June 7, 1979, through December 31, 1979.

Activated Sludge With Aerated Waste Stabilization Pond

Tables 27 through 35 provide data for activated sludge Unit 1, preceded by an aerated waste stabilization pond, with operation in several modes:

1. Operation as activated sludge, without modification of the Bio-Oxidation Unit, but with a preceding aerated waste stabilization pond: Unit 1, from June 7, 1979, through January 16, 1980.
2. Operation as activated sludge, with chemical precipitation in the aeration tank: Unit 1, beginning January 17, 1980, and extending through June 30, 1980.

Activated Sludge With Effluent Chemical Precipitation

Data from small scale tests already have been reported. Data obtained in these studies generally showed poor removal of suspended solids from the effluent. These data are not repeated here since precipitation of larger volumes of wastewater revealed a totally different picture, with much greater removal of suspended solids. Data from the larger-volume precipitation are as follows:

Trial No:	1	2
Date:	6/17/80	6/24/80
Volume Precipitated:	48 liters	50 liters
Coagulant:	$FeCl_3$	$FeCl_3$
Dose:	250 mg/l	250 mg/l
pH: Raw:	7.0	7.0
Precipitated:	3.2	3.1
Suspended solids:		
Raw:	142 mg/l	75 mg/l
Precipitated:	7.3 mg/l	9.3 mg/l
Reduction:	94.9%	87.6%
Volatile Suspended Solids:		
Raw:	106 mg/l	55 mg/l
Precipitated:	3 mg/l	4.3 mg/l
Reduction:	97.2%	92.2%
Turbidity:		
Raw:	470 NTU	48.0 NTU
Precipitated:	19.0 NTU	27.5 NTU
Reduction:	59.6%	42.7%
Sludge Production:	4.3 liters	4.5 liters

The sludge collected was neutralized with 1 N NaOH, with 75% being returned to the aeration tank of Unit 1 in small, daily portions, and the balance being placed in the sludge reserve.

Joint Treatment With Municipal Sewage (Cometabolism)

Table 36 shows temperature, pH, and dissolved oxygen concentrations in the joint treatment unit, Table 37 shows solids levels in the aeration tank, Table 38 shows the effect of treatment on ammonia nitrogen, Table 39 lists data on biochemical oxygen demand, and Table 40 lists data on several other pollutant parameters.

Biological Reaction Kinetics

Several efforts were made to develop data on biological reaction kinetics, including:

1. <u>Assembly of existing data</u> - Data were assembled, although, data for cell detention and hydraulic detention were incomplete. Results were:
   a. <u>Basic data</u> for estimating parameters of biological reaction kinetics:

Unit	Trial	Cell Detention (θ_c, days)	Influent BOD (S_o, mg/l)	Effluent BOD (S, mg/l)	MLVSS (X, mg/l)	Hydraulic Detention (θ, days)
1	1	5.8	186	58	692	1
	2	8.1	81	48	1,008	1
	3	10.3	111	44	1,324	1
	4	10.6	35	25	1,182	1
	5	10.5	159	91	965	1
2	1	11.6	49	43	914	1
	2	9.2	183	47	975	1
	3	7.8	265	18	1,035	1
	4	10.6	342	32	1,205	1
	5	15.6	322	42	1,392	1

b. Processed data for calculating K_s and k in the equation:

$$\frac{X\theta}{S_o - S} = \frac{K_s}{k}\left(\frac{1}{S}\right) + \frac{1}{k}:$$

Unit	Trial	$y = \dfrac{X\theta}{S_o - S}$	$x = \dfrac{1}{S}$
1	1	5.41	0.0172
	2	30.5	0.0208
	3	19.8	0.0227
	4	118.2	0.0400
	5	14.2	0.0110
2	1	152.3	0.0238
	2	7.17	0.0213
	3	4.19	0.0556
	4	3.89	0.0313
	5	4.97	0.0238

Linear regression yielded the equation:

$$\frac{X\theta}{S_o - S} = 453\left(\frac{1}{S}\right) + 23.9$$

Thus, K_s was found to be 19, and k was determined as 0.042. The correlation coefficient in this case was 0.11, which is significant at less than the 50% confidence level.

c. Processed data for calculating Y and k_d in the equation:

$$\frac{1}{\theta_c} = Y\,\frac{S_o - S}{X\theta} - k_d:$$

Unit	Trial	$y = \frac{1}{\theta_c}$	$x = \frac{S_o - S}{X\ \theta}$
1	1	0.17	0.185
	2	0.12	0.0328
	3	0.097	0.0505
	4	0.094	0.00846
	5	0.095	0.0704
2	1	0.086	0.00657
	2	0.11	0.139
	3	0.13	0.239
	4	0.094	0.257
	5	0.064	0.201

Linear regression yielded the equation:

$$\frac{1}{\theta_c} = 0.0665 \frac{S_o - S}{X\ \theta} + 0.0981$$

Thus, Y was found to be 0.067, and k_d was determined as -0.098. The correlation coefficient in this case was determined as 0.22, which is significant at less than the 50% confidence level.

2. Use of data various measures to improve quality of data (especially cell detention and hydraulic detention) - Results were:

   a. Basic data:

Unit	Date	Trial	Cell Detention (θ_c,days)	Influent BOD (S_o,mg/l)	Effluent BOD (S,mg/l)	MLVSS (X,mg/l)	Hydraulic Detention (θ,days)
1	4/10/80	6	11.1	231	35	748	1.07
	4/17/80	7	6.8	137	100	1,212	0.74
	4/24/80	8	6.8	155	119	1,292	0.40
	5/1/80	9	12.2	172	81	1,192	1.36
	5/8/80	10	16.8	190	122	1,216	1.74
2	4/10/80	6	33.7	414	51	1,580	1.36
	4/17/80	7	19.4	374	146	1,684	0.94
	4/24/80	8	13.6	378	87	1,556	0.50
	5/1/80	9	19.7	412	67	2,156	1.04
	5/8/80	10			137	1,860	1.15

   b. Processed data for calculating K_s and k in the equation:

$$\frac{X\ \theta}{S_o - S} = \frac{K_s}{k} \left(\frac{1}{s}\right) + \frac{1}{k} :$$

Unit	Date	Trial	$y = \frac{X\,\theta}{S_o - S}$	$x = \frac{1}{S}$
1	4/10/80	6	4.08	0.02857
	4/17/80	7	24.24	0.01000
	4/24/80	8	14.36	0.00840
	5/1/80	9	17.81	0.01235
	5/8/80	10	31.12	0.00820
2	4/10/80	6	5.92	0.01961
	4/17/80	7	6.94	0.00685
	4/24/80	8	2.67	0.01149
	5/1/80	9	6.50	0.01493
	5/8/80	10	20.18	0.00730

Linear regression yielded the equation:

$$\frac{X\,\theta}{S_o - S} = -759\left(\frac{1}{S}\right) + 23.1$$

Thus, K_S was found to be -33, and k was determined as 0.043. The correlation coefficient in this case was 0.53, which is significant at the 90% confidence level.

c. Processed data for calculating Y and k_d in the equation:

$$\frac{1}{\theta_c} = Y\,\frac{S_o - S}{X\,\theta} - k_d:$$

Unit	Date	Trial	$y = \frac{1}{0_c}$	$x = \frac{S_o - S}{X\,\theta}$
1	4/10/80	6	0.090	0.245
	4/17/80	7	0.147	0.041
	4/24/80	8	0.147	0.070
	5/1/80	9	0.082	0.056
	5/8/80	10	0.060	0.032
2	4/10/80	6	0.030	0.169
	4/17/80	7	0.052	0.144
	4/24/80	8	0.074	0.375
	5/1/80	9	0.051	0.154
	5/8/80	10	0.034	0.050

Linear regression yielded the equation:

$$\frac{1}{\theta_c} = {}^{-}0.0713\,\frac{S_o - S}{X\,\theta} + 0.0862$$

Thus, Y was found to be $^{-}0.071$, and k_d was determined as $^{-}0.086$. The correlation coefficient in this case was found to be 0.19, which is significant at less than the 50% confidence level.

3. Use of further measures to improve quality of data, including effluent precipitation and return of a portion of solids to the aeration tank - Results were:

   a. Basic data:

Unit	Date	Trial	Cell Detention (θ_c,days)	Inf. BOD (S_o,mg/l)	Eff. BOD (S,mg/l)	MLVSS (X,mg/l)	Hydraulic Detention (θ,days)
1	5/15/80	11	7.5	254	117	1,084	1.12
	5/22/80	12	7.4	261	151	712	1.04
	6/12/80	13	3.9	267	145	880	0.66
	6/19/80	14	13.0	510	232	676	2.26
2	5/15/80	11	58.4	209	71	1,644	1.36
	5/22/80	12	9.7	125	60	816	1.25
	6/12/80	13	28.3	294	144	1,020	1.37
	6/19/80	14	26.0	376	292	1,016	3.25

   b. Processed data for calculating K_s and k in equation:

$$\frac{X\,\theta}{S_o - S} = \frac{K_s}{k}\left(\frac{1}{S}\right) + \frac{1}{k}:$$

Unit	Date	Trial	$y = \frac{X\,\theta}{S_o - S}$	$x = \frac{1}{s}$
1	5/15/80	11	8.86	0.00855
	5/22/80	12	6.73	0.00662
	6/12/80	13	4.76	0.00690
	6/19/80	14	5.50	0.00431
2	5/15/80	11	16.20	0.01408
	5/22/80	12	15.69	0.01667
	6/12/80	13	9.32	0.00694
	6/19/80	14	39.31	0.00342

Linear regression yielded the equation:

$$\frac{X\,\theta}{S_o - S} = -212\left(\frac{1}{s}\right) + 15.1$$

Thus, K_s was found to be -13.9, and k was determined as 0.066. The correlation coefficient in this case was 0.09, which is significant at less than the 50% confidence level.

   c. Processed data for calculating Y and k_d in the equation:

$$\frac{1}{\theta_c} = Y\,\frac{S_o - S}{X\,\theta} - k_d:$$

Unit	Date	Trial	$y = \frac{1}{\theta_c}$	$x = \frac{S_o - S}{X\,\theta}$
1	5/15/80	11	0.133	0.133
	5/22/80	12	0.135	0.149
	6/12/80	13	0.256	0.210
	6/19/80	14	0.077	0.182
2	5/15/80	11	0.017	0.062
	5/22/80	12	0.103	0.064
	6/12/80	13	0.035	0.107
	6/19/80	14	0.038	0.025

Linear regression yielded the equation:

$$\frac{1}{\theta_c} = 0.876\ \frac{S_o - S}{X\,\theta} - 0.000633$$

Thus, Y was found to be 0.88, and k_d was determined as 0.00063. The correlation coefficient in this case was found to be 0.72, which is significant at the 95% confidence level.

Combining all of the data listed thus far yielded the following:

Equation	Correlation Coefficient	Values of Constants
$\frac{X\,\theta}{S_o - S} = 706\ (\frac{1}{S}) + 9.79$	0.25 (significant at 80%)	$K_s = 71$ $k = 0.10$
$\frac{1}{\theta_c} = 0.0894\ \frac{S_o - S}{X\,\theta} + 0.0826$	0.16 (significant at more than 50%)	$Y = 0.089$ $k_d = -0.083$

The correlation may be improved slightly if the first data, which were assembled from existing information, are excluded:

Equation	Correlation Coefficient	Values of Constants
$\frac{X\,\theta}{S_o - S} = 532\ (\frac{1}{S}) + 19.1$	0.32 (significant at 80%)	$K_s = -28$ $k = 0.052$
$\frac{1}{\theta_c} = 0.109\ \frac{S_o - S}{X\,\theta} + 0.0731$	0.17 (significant at more than 50%)	$Y = 0.11$ $k_d = -0.073$

Table 17
BOD Data for Activated Sludge without Modification

	Unit 1			Unit 2		
Date	Inf.BOD (mg/l)	Eff.BOD (mg/l)	Reduction (%)	Inf.BOD (mg/l)	Eff.BOD (mg/l)	Reduction (%)
12/1/78	288	72	68.4	187	111	40.6
12/8/78	257	4	98.4	206	7	96.6
1/9/79	138	9	93.5	148	12	91.9
2/5/79	758	130	82.8	379	67	82.3
2/19/79	-	-	-	-	-	-
2/26/79	-	-	-	-	-	-
3/2/79	906	145	84.0	695	92	86.8
3/9/79	1,370	782	42.9	917	807	12.0
3/26/79	877	228	74.0	696	510	26.7
4/10/79	677	298	56.0	376	214	43.1
4/20/79	-	-	-	-	-	-
4/21/79	602	411	31.7	307	176	42.7
4/26/79	732	344	53.0	361	114	68.4
4/30/79	-	-	-	-	-	-
5/1/79	-	-	-	-	-	-
5/5/79	1,138	578	49.2	564	222	60.6
5/11/79	1,183	550	53.5	565	153	72.9
5/12/79	-	-	-	-	-	-
5/16/79	-	-	-	-	-	-
5/17/79	-	-	-	-	-	-
5/21/79	681	402	40.9	444	192	56.8
5/23/79	-	-	-	-	-	-
5/25/79	-	-	-	-	-	-
5/29/79	-	-	-	-	-	-
6/6/79	589	160	72.8	503	151	70.0
	Unit 1 was operated with preceding aerated waste stabilization pond after 6/6/79, until end of study.					
7/4/79				320	82	74.4
7/13/79				554	157	71.7
7/21/79				396	238	39.9
7/27/79				448	176	60.7
8/3/79				434	252	41.9
8/31/79				305	71	76.6
9/22/79				109	18	83.4
9/28/79				533	79	85.2
10/5/79				471	136	71.2
10/12/79				487	180	63.0
10/19/79				487	144	70.4
11/2/79				502	216	57.0
11/8/79				495	212	57.2
11/15/79				402	96	76.1
11/29/79				506	156	69.2
1/4/80				212	16	92.5

(Table 17 continued)

1/10/80					215	18	91.6
1/17/80					155	59	61.9
1/24/80					126	4	96.8
1/31/80					296	31	89.5
2/7/80					306	34	88.9
2/14/80					246	23	90.7
2/21/80					257	55	78.6
2/29/80					170	21	87.6
3/6/80					49	43	12.2
3/13/80					183	47	74.3
3/20/80					265	18	93.2
3/27/80					342	32	90.6
4/3/80					322	42	87.0
4/10/80					414	51	87.7
4/17/80					374	146	61.0
4/24/80					378	87	77.0
5/1/80					412	67	83.7
5/8/80					243	137	43.6
5/15/80					209	71	65.9
5/22/80					125	60	51.6
6/12/80					294	144	51.0
<u>Range</u>	Year 1	138-1,370	4-782	31.7-98.6	148-917	7-807	12.0-96.6
	Total	138-1,370	4-782	31.7-98.6	109-917	4-807	12.0-96.8
<u>Mean</u>	Year 1	728	294	64.4	457	192	62.3
	Total	728	294	64.4	361	122	68.7
<u>S.D.</u>	Year 1	356	232	20.6	212	200	23.9
	Total	356	232	20.6	170	133	21.0
<u>n</u>	Year 1	14	14	14	16	16	16
	Total	14	14	14	51	51	51

Table 18
TOC Data For Activated Sludge Without Modification

	Unit 1			Unit 2		
Date	Inf.TOC (mg/l)	Eff.TOC (mg/l)	Reduction (%)	Inf.TOC (mg/l)	Eff.TOC (mg/l)	Reduction (%)
2/19/79	464	1,495	-	302	865	-
2/26/79	7,207	395	94.5	5,045	182	96.4
4/30/79	833	650	22.0	550	321	41.6
5/12/79	855	735	14.0	570	388	31.9
5/17/79	745	760	-	744	630	15.3
5/23/79	610	526	13.8	495	375	24.2
5/29/79	605	505	16.6	525	330	37.1
1/4/80	Unit 1 was operated with a preceding aerated waste stabilization pond after this time, until end of study.			249	257	-
1/10/80				193	179	7.3
1/15/80				205	122	40.5
1/22/80				216	128	40.7
1/31/80				263	124	52.9
2/5/80				279	137	50.9
2/26/80				288	207	28.1
3/12/80				291	150	48.5
3/20/80				301	146	51.5
5/8/80				333	226	32.1
5/22/80				328	231	29.6
5/28/80				366	197	46.2
Range						
Year 1	464 - 7,207	395 - 1,495	13.8 - 94.5	302 - 5,045	182 - 630	15.3 - 96.4
Total	464 - 7,207	395 - 1,495	13.8 - 94.5	193 - 5,045	122 - 630	7.3 - 96.4
Mean						
Year 1	1,617	724	32.2	1,176	442	41.1
Total	1,617	724	32.2	608	273	39.7
S.D.						
Year 1	2,469	364	35.0	1,711	230	28.7
Total	2,469	364	35.0	1,085	191	19.4
n						
Year 1	7	7	5	7	7	6
Total	7	7	5	19	19	17

Table 19
COD Data For Activated Sludge Without Modification

	Unit 1			Unit 2		
Date	Inf.COD (mg/l)	Eff.COD (mg/l)	Reduction (%)	Inf.COD (mg/l)	Eff.COD (mg/l)	Reduction (%)
4/10/79	-	12,700	-	-	22,400	-
4/20/79	-	8,900	-	-	17,900	-
5/1/79	3,400	1,700	50.0	800	800	0
5/11/79	3,000	2,600	13.3	1,700	600	64.7
5/16/79	4,700	3,200	31.9	2,600	1,400	46.2
5/25/79	1,700	850	50.0	1,700	1,500	11.8
Range	1,700 - 4,700	850 - 12,700	13.3 - 50.0	800 - 2,600	600 - 22,400	0 - 64.7
Mean	3,200	4,992	36.3	1,700	7,433	30.7
S.D.	1,236	4,725	17.5	735	9,958	30.0
n	4	6	4	4	6	4

Table 20
Data on Phenols for Activated Sludge without Modification

		Unit 1			Unit 2		
Date		Inf.Phenols (mg/l)	Eff.Phenols (mg/l)	Reduction (%)	Inf.Phenols (mg/l)	Eff.Phenols (mg/l)	Reduction (%)
5/1/79		175	125	28.6	125	50	60.0
5/11/79		-	-	-	125	50	60.0
5/17/79		135	90	33.3	110	53	51.8
		Unit 1 was operated with a preceding aerated waste stabilization pond after this, until end of study.					
10/25/79					404	1.51	99.63
11/2/79					113	60	46.9
11/8/79					122	21	82.8
11/14/79					124	25	79.8
11/21/79					119	47	60.5
1/16/80					66	0.65	99.02
1/23/80					49	1.52	96.9
2/5/80					22	0.39	98.2
2/12/80					45	0.32	99.29
2/19/80					44	0.38	99.14
2/28/80					53	0.41	99.23
3/20/80					57	0.05	99.91
3/26/80					52	0.12	99.77
4/11/80					16	0.09	99.44
4/23/80					69	0.70	99.0
5/8/80					15	0.67	95.5
5/27/80					24	0.16	99.33
Range	Year 1	135-175	90-125	28.6-33.3	110-125	50-53	51.8-60.0
	Total	135-175	90-125	28.6 33.3	15-404	0.05-60	46.9-99.91
Mean	Year 1	155	107.5	31.0	120.0	51.0	57.3
	Total	155	107.5	31.0	87.7	15.6	86.3
S.D.	Year 1	28.3	24.8	3.3	8.7	1.7	4.7
	Total	28.3	24.8	3.3	84.5	22.7	19.1
n	Year 1	2	2	2	3	3	3
	Total	2	2	2	20	20	20

Table 21
Ammonia Nitrogen Data For Activated Sludge Without Modification

	Unit 1			Unit 2		
Date	Inf.NH_3^-N (mg/l)	Eff.NH_3^-N (mg/l)	Reduction (%)	Inf.NH_3^-N (mg/l)	Eff.NH_3^-N (mg/l)	Reduction (%)
4/11/79	53.0	56.0	-	68.0	83.0	-
4/27/79	74.2	50.5	31.9	26.7	32.6	-
5/3/79	92.0	89.0	3.3	38.6	41.6	-
5/11/79	115.0	84.0	27.0	20.0	50.0	-
5/18/79	78.4	100.4	-	72.8	61.6	15.4
5/25/79	156.8	498.4	-	100.8	84.0	16.7
10/1/79				91.5	100.8	-
10/10/79	Unit 1 was operated with a preceding aerated waste stabilization pond after this time, until end of study.			83.1	81.2	2.3
10/15/79				-	87.3	-
10/23/79				66.7	75.1	-
10/30/79				65.3	69.1	-
11/8/79				37.3	47.6	-
11/14/79				45.7	56.9	-
11/20/79				46.7	51.8	-
1/16/80				34	38	-
1/25/80				38	46	-
2/1/80				41	44	-
2/7/80				10	15	-
2/15/80				42	46	-
2/22/80				56	44	21.4
2/29/80				45	45	0
3/6/80				75	73	2.7
3/25/80				88.7	80.3	9.5
4/1/80				65.3	95.2	-
4/15/80				79.3	85.9	-
4/22/80				67.2	63.8	5.1
4/29/80				65.0	87.4	-
5/5/80				10.3	6.2	39.8
Range						
Year 1	53.0 - 156.8	50.5 - 498.4	3.3 - 31.9	20.0 - 100.8	32.6 - 84.0	15.4 - 16.7
Total	53.0 - 156.8	50.5 - 498.4	3.3 - 31.9	20.0 - 100.8	6.2 - 100.8	2.3 - 39.8
Mean						
Year 1	94.9	146.4	20.7	54.5	58.8	16.1
Total	94.9	146.4	20.7	54.8	60.4	12.5
S.D.						
Year 1	36.6	173.5	15.3	31.2	21.4	0.9
Total	36.6	173.5	15.3	24.3	23.9	12.6
n						
Year 1	6	6	3	6	6	2
Total	6	6	3	27	28	9

Table 22
Thiocyanate Data For Activated Sludge Without Modification

	Unit 1			Unit 2		
Date	Inf. (mg/l)	Eff. (mg/l)	Reduction (%)	Inf. (mg/l)	Eff. (mg/l)	Reduction (%)
4/10/79	-	<1	-	-	<1	-
5/23/79	-	30.6	-	-	39.0	-
5/25/79	-	44.3	-	-	-	-
7/6/79	-	-	-	45.0	35.4	21.3
7/17/79	-	-	-	43.7	60.0	-
10/2/79	Unit 1 was operated with a preceding aerated waste stabilization pond after this time, until the end of the study.			71.6	20.9	70.8
10/12/79				70.2	48.7	30.6
10/26/79				75.1	59.0	21.4
Range	-	<1 - 44.3	-	43.7 - 75.1	<1 - 60.0	21.3 - 70.8
Mean	-	25.3	-	61.1	37.7	36.0
S.D.	-	22.1	-	15.4	21.2	23.6
n	-	3	-	5	7	4

Table 23

Mixed Liquor Solids for Activated Sludge without Modification

	Unit 1				Unit 2			
Date	MLSS (mg/l)	MLVSS (mg/l)	Sett. Solids (mg/l)	S.V.I.	MLSS (mg/l)	MLVSS (mg/l)	Sett. Solids (mg/l)	S.V.I.
10/31/78	340	160	15.5	45.6	150	80	8.6	57.3
11/7/78	530	400	21.5	40.6	380	260	10.1	26.6
11/15/78	640	440	30.5	47.7	330	210	20	60.6
12/6/78	536	432	52	97.0	384	288	38	99.0
12/11/78	486	380	58	119.3	290	214	42	144.8
12/18/78	760	658	64	84.2	452	360	54	119.5
1/8/79	1,680	1,557	74	44.0	560	468	68	121.4
1/15/79	1,980	1,520	86	43.4	660	500	76	115.2
1/23/79	2,620	2,095	88	33.6	1,215	965	56	46.1
1/30/79	2,524	1,898	78	30.9	1,401	1,056	68	48.5
2/8/79	2,305	1,797	88	38.2	1,675	1,075	76	45.4
2/12/79	1,729	1,160	60	34.7	1,895	1,267	78	41.2
2/19/79	1,879	1,113	60	31.9	2,173	1,198	76	35.0
2/26/79	2,030	1,314	60	29.6	1,854	1,115	76	41.0
3/7/79	2,453	1,525	64	26.1	2,218	1,436	72	32.5
3/18/79	1,770	1,165	39	22.0	1,788	1,142	48	26.8
4/2/79	2,154	1,452	30	13.9	1,826	1,208	44	24.1
4/10/79	2,173	1,408	30	13.8	1,755	1,031	80	45.6
4/17/79	1,450	990	40	27.6	1,650	1,140	64	38.8
4/23/79	1,700	1,140	68	40.0	1,890	1,240	76	40.2
5/1/79	1,740	1,300	68	39.1	2,020	1,380	100	49.5
5/7/79	1,970	1,370	86	43.7	2,010	1,340	100	49.8
5/14/79	2,120	1,310	56	26.4	2,000	1,410	108	54.0
5/21/79	1,880	990	26	13.8	1,630	1,140	80	49.1
5/29/79	1,720	980	48	27.9	1,760	1,220	64	36.4
6/5/79	-	-	48	-	-	-	62	-
6/14/79	Unit 1 was operated				-	-	88	-
6/26/79	with a preceding				1,140	630	-	-
7/10/79	aerated waste sta-				1,400	720	54	38.6
7/23/79	bilization pond				1,100	844	38	34.5
7/31/79	after this time,				956	624	56	58.6
8/8/79	until end of study.				1,072	740	41	38.2
9/28/79					1,184	1,028	56	47.3
10/4/79					1,068	976	80	74.9
10/10/79					1,172	960	78	66.6
10/25/79					776	640	44	56.7
10/31/79					808	692	36	44.6
11/7/79					868	696	30	34.6
11/14/79					584	528	28	47.9
1/4/80					1,356	1,080	45	33.2
1/14/80					960	888	64	66.7
1/28/80					1,616	1,592	100	61.9
2/7/80					744	720	48	64.5

(Table 23 continued)

2/12/80						830	744	54	65.1
2/18/80						1,104	896	60	54.3
2/26/80						1,016	804	64	63.0
3/3/80						1,016	888	64	63.0
3/21/80						1,108	1,044	76	68.6
4/10/80						1,640	1,580	102	62.2
4/17/80						1,764	1,684	100	56.7
4/24/80						1,684	1,556	72	42.8
5/1/80						2,192	2,156	88	40.1
5/8/80						1,996	1,860	88	44.1
5/15/80						1,820	1,644	100	54.9
5/22/80						864	816	30	34.7
6/12/80						1,124	1,020	20	17.8
6/19/80						1,248	1,016	30	24.0
<u>Range</u>	Year 1	340–2,620	160–2,095	15.5–88	13.8–119.3	150–2,218	80–1,436	8.6–108	24.1–144.8
	Total	340–2,620	160–2,095	15.5–88	13.8–119.3	150–2,218	80–2,156	8.6–108	17.8–144.8
<u>Mean</u>	Year 1	1,647	1,142	55	40.6	1,352	892	64	57.2
	Total	1,647	1,142	55	40.6	1,276	978	62	53.9
<u>S.D.</u>	Year 1	691	503	21	25.0	681	436	25	33.1
	Total	691	503	21	25.0	559	435	25	25.3
<u>n</u>	Year 1	25	25	26	25	27	27	28	25
	Total	25	25	26	25	55	55	56	54

Table 24

BOD Loads for Activated Sludge without Modification

Date	Unit No. 1		Unit No. 2	
	Lb.BOD/Day per Th.Ft^3	Mg BOD/Day per mg MLVSS	Lb. BOD/Day per Th.Ft^3	Mg BOD/Day per mg MLVSS
10/31/78	10.2	1.02	10.2	2.12
11/7/78	19.6	0.82	19.6	1.26
11/15/78	32.3	1.18	32.3	2.47
12/11/78	15.8	0.67	13.0	0.97
12/16/78	15.8	0.59	13.0	0.72
12/18/78	15.8	0.39	13.0	0.58
1/15/79	13.3	0.14	5.1	0.16
1/23/79	10.0	0.076	7.6	0.13
1/30/79	24.2	0.20	10.1	0.15
2/8/79	45.9	0.41	23.0	0.34
2/12/79	45.8	0.67	25.8	0.33
2/19/79	45.8	0.66	29.8	0.40
3/7/79	65.2	0.68	56.3	0.63
4/2/79	54.8	0.60	54.8	0.73
4/10/79	54.8	0.62	34.3	0.53
4/17/79	54.8	0.89	27.4	0.39
4/21/79	37.6	0.55	19.2	0.25
4/26/79	45.7	0.61	22.5	0.28
5/5/79	71.0	0.84	35.2	0.42
5/11/79	73.8	0.89	35.3	0.41
5/21/79	42.5	0.69	27.7	0.39
6/6/79	36.7	-	31.4	-
7/4/79	Unit 1 was operated with a preceding aerated waste stabilization pond after this time, until end of study.		20.0	0.47
7/13/79			34.6	-
7/23/79			25.8	0.49
7/31/79			27.5	0.71
9/28/79			33.2	0.52
10/5/79			29.4	0.48
10/12/79			30.4	0.50
10/19/79			30.3	0.63
11/2/79			31.3	0.73
11/8/79			30.8	0.74
11/15/79			25.0	0.75
1/4/80			13.2	0.20
1/10/80			13.4	0.22
1/17/80			9.7	0.15
1/24/80			7.9	0.09
1/31/80			18.5	0.22
2/7/80			19.1	0.43
2/14/80			15.3	0.31
2/21/80			16.0	0.30
2/29/80			10.6	0.20
3/6/80			3.1	0.05
3/13/80			11.4	0.19

(Table 24 continued)

3/20/80				16.5	0.26
3/27/80				21.3	0.28
4/3/80				20.1	0.23
4/10/80				25.8	0.26
4/17/80				23.3	0.22
4/24/80				23.6	0.24
5/1/80				25.7	0.19
5/8/80				15.2	0.13
5/15/80				13.0	0.13
5/22/80				7.8	0.15
6/12/80				18.3	0.29
<u>Range</u>	Year 1	10.0-73.8	0.076-1.18	5.1-56.3	0.13-2.47
	Total	10.0-73.8	0.076-1.18	3.1-56.3	0.05-2.47
<u>Mean</u>	Year 1	37.8	0.63	25.1	0.64
	Total	37.8	0.28	22.0	0.46
<u>S.D.</u>	Year 1	20.0	0.63	13.3	0.60
	Total	20.0	0.28	10.9	0.44
<u>n</u>	Year 1	22	21	24	22
	Total	22	21	55	53

Table 25
COD and TOC Loads for Activated Sludge Units without Modification

		Unit No. 1				Unit No. 2		
Date		Lb.COD/Day per Th.Ft^3	Mg COD/Day per mg MLVSS	Lb.TOC/Day per Th.Ft^3	Mg TOC/ Day per mg MLVSS	Lb.COD/Day per Th.Ft^3	Mg COD/Day per mg MLVSS	Lb.TOC/Day per Th.Ft^3	Mg TOC/ Day per mg MLVSS
4/30/79		-	-	52.0	0.65	-	-	34.3	0.40
5/1/79		209.9	2.59	-	-	52.5	0.61	-	-
5/11/79		85.8	-	-	-	106.2	-	-	-
5/16/79		291.9	3.84	-	-	159.2	1.91	-	-
5/17/79		-	-	46.5	0.64	-	-	46.4	0.57
5/23/79		-	-	38.1	0.62	-	-	30.9	0.43
5/25/79		106.2	1.73	-	-	106.2	1.44	-	-
5/29/79		-	-	37.7	0.62	-	-	32.8	0.43
1/4/80		Unit 1 was operated with a preceding aerated waste stabilization pond after this time, until end of study.						15.5	0.23
1/10/80								12.0	0.20
1/15/80								12.8	0.22
1/22/80								13.4	0.17
1/31/80								16.4	0.20
2/5/80								17.4	0.31
2/26/80								18.0	0.36
3/12/80								18.2	0.30
3/20/80								18.8	0.29
5/8/80								20.8	0.18
5/22/80								20.5	0.40
5/28/80								32.8	0.42
Range	Year 1	85.8-291.9	1.73-3.84	37.7-52.0	0.62-0.65	52.5-159.2	0.61-1.91	30.9-46.4	0.40-0.57
	Total	85.8-291.9	1.73-3.84	37.7-52.0	0.62-0.65	52.5-159.2	0.61-1.91	12.0-46.4	0.17-0.57
Mean	Year 1	173.5	2.72	43.6	0.63	106.0	1.32	36.1	0.46
	Total	173.5	2.72	43.6	0.63	106.0	1.32	22.6	0.32
S.D.	Year 1	95.9	1.06	6.9	0.02	43.6	0.66	7.0	0.08
	Total	95.9	1.06	6.9	0.02	43.6	0.66	9.8	0.12
n	Year 1	4	3	4	4	4	3	4	4
	Total	4	3	4	4	4	3	16	16

Table 26
Effluent Solids Data for Activated Sludge Unit 2 without Modification

Date	ss (mg/l)	vss (mg/l)
9/28/79	80	56
10/4/79	108	100
10/10/79	48	39
10/25/79	136	132
11/7/79	120	80
11/14/79	204	180
1/14/80	116	116
1/28/80	30	24
2/7/80	184	60
2/12/80	172	124
2/18/80	184	72
2/28/80	92	32
3/3/80	208	68
3/21/80	140	136
4/10/80	80	64
4/17/80	80	80
4/24/80	92	56
5/1/80	152	112
5/8/80	92	72
5/15/80	48	36
5/22/80	120	104
6/12/80	60	48
6/19/80	148	124
Range	30- 208	24- 180
Mean	117	83
S.D.	51	40
n	23	23

Table 27
BOD Data For Activated Sludge Unit 1 Preceded by Aerated Waste Stabilization Pond

	BOD			Reduction		
Date	Pond Inf. (mg/l)	Pond Eff. (mg/l)	Act.S.Eff. (mg/l)	Pond (%)	Act.S. (%)	Total (%)
7/4/79	-	455	287	-	36.9	-
7/13/79	764	552	234	27.7	57.6	69.4
7/21/79	-	326	228	-	30.1	-
7/27/70	638	481	193	24.6	59.9	69.7
8/3/79	687	-	200	-	-	70.9
8/31/79	-	108	28	-	74.1	-
9/22/79	-	114	46	-	59.6	-
9/28/79	630	272	-	56.8	-	-
10/5/79	2,153	94	56	95.6	40.4	97.4
10/12/79	493	90	101	81.7	-	79.5
11/2/79	726	197	181	72.9	8.1	75.1
11/8/79	697	262	184	62.4	29.8	73.6
11/15/79	738	92	146	87.5	-	80.2
11/29/79	1,308	292	196	77.7	32.9	81.1
1/4/80	327	128	96	60.9	60.9	70.6
1/10/80	426	172	48	59.6	59.6	88.7
1/17/80	416	158	37	62.0	76.6	91.1
1/24/80	231	16	36	93.1	-	84.4
1/31/80	228	-	-	-	-	-
2/7/80	427	129	43	69.8	66.7	89.1
2/14/80	387	196	36	49.4	81.6	90.7
2/21/80	451	134	37	70.3	72.4	91.8
2/29/80	437	117	37	73.2	68.4	91.5
3/6/80	449	186	58	58.6	68.8	87.1
3/13/80	-	81	48	-	40.7	-
3/20/80	405	111	44	72.6	60.4	89.1
3/27/80	360	35	25	90.3	28.6	93.1
4/3/80	518	159	91	69.3	42.8	82.6
4/10/80	513	231	35	55.0	89.2	93.2
4/17/80	223	137	100	38.6	27.0	55.2
4/24/80	628	155	119	75.2	23.2	81.1
5/1/80	507	172	81	66.1	52.9	84.0
5/8/80	270	190	122	29.6	35.8	54.8
5/15/80	747	254	117	66.0	53.9	84.3
5/22/80	493	261	151	47.1	42.1	69.4
6/12/80	414	267	145	35.5	45.7	65.0
Range						
7-8/79	630 - 764	108 - 552	28 - 287	24.6 - 27.7	30.1 - 74.1	69.4 - 70.9
9/22/79- 1/10/80	327 - 2,153	90 - 292	46 - 196	56.8 - 95.6	8.1 - 60.9	70.6 - 97.4
1/17/80- end	223 - 518	16 - 267	25 - 151	29.6 - 93.1	23.2 - 89.2	55.2 - 93.2
Total	223 - 2,153	16 - 552	25 - 287	24.6 - 95.6	8.1 - 89.2	55.2 - 97.4

Table 27 - continued

	BOD			Reduction		
Date	Pond.Inf. (mg/l)	Pond.Eff. (mg/l)	Act.S.Eff. (mg/l)	Pond (%)	Act.S. (%)	Total (%)
Mean						
7-8/79	696	384	195	26.2	51.7	70.0
9/22/79-1/10/80	833	171	117	72.8	41.6	80.8
1/17/80-end	427	157	72	62.3	54.3	82.1
Total	571	195	106	63.1	50.9	80.5
S.D.						
7-8/79	64	175	88	2.2	18.0	0.8
9/22/79-1/10/80	568	80	61	13.8	19.8	8.7
1/17/80-end	134	70	42	17.4	19.8	12.5
Total	364	121	72	19.1	19.6	11.3
n						
7-8/79	3	5	6	2	5	3
9/22/79-1/10/80	9	10	9	9	7	8
1/17/80-end	19	19	19	18	18	18
Total	31	34	34	29	30	29

Note: July through August was considered to be a period of start-up for the aerated pond. Beginning 1/17/80, a chemical coagulant was dosed to the aeration tank of activated Sludge Unit 1.

Table 28
TOC Data For Activated Sludge Unit 1 Preceded by Aerated Waste Stabilization Pond

	TOC			Reduction		
Date	Pond.Inf. (mg/1)	Pond Eff. (mg/1)	Act.S.Eff. (mg/1)	Pond (%)	Act.S. (%)	Total (%)
1/4/80	-	206	176	-	14.6	-
1/10/80	-	198	307	-	-	-
1/15/80	-	199	185	-	7.0	-
1/22/80	-	162	157	-	3.1	-
1/31/80	-	162	153	-	5.6	-
2/5/80	-	178	174	-	2.2	-
2/26/80	390	202	175	48.2	13.4	55.1
3/12/80	446	185	184	58.5	0.5	58.7
3/20/80	413	195	204	52.8	-	50.6
5/8/80	551	254	281	53.9	-	49.0
5/22/80	540	417	319	22.8	23.5	40.9
5/28/80	527	296	325	43.8	-	38.3
Range	390 - 551	162 - 417	153 - 325	22.8 - 58.5	0.5 - 23.5	38.3 - 58.7
Mean	478	221	220	46.7	8.7	48.8
S.D.	70	72	67	12.7	7.8	7.9
n	6	12	12	6	8	6

Table 29
Data on Phenols For Activated Sludge Unit 1 Preceded By Aerated Waste Stabilization Pond

	Phenols			Reduction		
Date	Pond Inf. (mg/1)	Pond Eff. (mg/1)	Act.S.Eff. (mg/1)	Pond (%)	Act.S. (%)	Total (%)
10/10/79	-	3.06	1.46	-	52.3	-
10/16/79	-	4.32	1.24	-	71.3	-
10/25/79	-	1.10	-	-	-	-
11/2/79	-	4.32	1.47	-	66.0	-
11/8/79	-	27	3.5	-	87.0	-
11/14/79	-	16	1.8	-	88.8	-
1/16/80	-	4.28	1.86	-	56.5	-
1/23/80	-	2.00	1.63	-	18.5	-
2/5/80	-	4.21	2.40	-	43.0	-
2/12/80	-	21	0.48	-	97.7	-
2/19/80	-	22	0.29	-	98.7	-
2/28/80	61	7.60	0.58	87.5	92.4	99.05
3/20/80	81	0.11	0.11	99.86	0	99.86
3/26/80	80	16	0.038	80.0	99.76	99.95
4/11/80	108	0.34	0.13	99.69	61.8	99.87
4/23/80	95	16	0.19	83.2	98.8	99.80
5/8/80	87	0.23	0.12	99.74	47.8	99.86
5/27/80	89	20	0.47	77.5	97.7	99.47
Range	61 - 108	0.11 - 27	0.038 - 305	77.5 - 99.86	0 - 99.76	99.05 - 99.95
Mean	85.9	9.4	1.05	89.6	69.3	99.69
S.D.	14.5	9.0	0.99	9.9	30.2	0.33
n	7	18	17	7	17	7

Table 30
Ammonia Nitrogen Data For Activated Sludge Unit 1
Preceded by Aerated Waste Stabilization Pond

	Ammonia Nitrogen			Reduction		
Date	Pond Inf. (mg/l)	Pond Eff. (mg/l)	Act.S.Eff. (mg/l)	Pond (%)	Act.S. (%)	Total (%)
10/1/79	176.4	105.5	84.0	40.2	20.4	52.4
10/10/79	-	98.3	97.1	-	1.2	-
10/15/79	-	98.5	101.3	-	-	-
10/23/79	-	99.9	114.8	-	-	-
10/30/79	-	91.5	100.8	-	-	-
11/8/79	-	80.3	86.8	-	-	-
11/14/79	-	84	97.1	-	-	-
11/20/79	-	77	121.3	-	-	-
1/16/80	-	46	48	-	-	-
1/25/80	-	49	60	-	-	-
2/1/80	-	52	62	-	-	-
2/7/80	-	12	16	-	-	-
2/15/80	-	54	63	-	-	-
2/22/80	-	59	68	-	-	-
2/29/80	-	62	68	-	-	-
3/6/80	-	55	84	-	-	-
3/25/80	-	112	70	-	46.4	-
4/1/80	-	110.1	112	-	-	-
4/15/80	-	157.7	121.3	-	23.1	-
4/22/80	-	112.0	122.0	-	-	-
4/29/80	-	110.9	133.3	-	-	-
5/5/80	-	11.1	11.2	-	-	-
Range	-	11.1 - 157.7	11.2 - 133.3	-	1.2 - 46.4	-
Mean	(176.4)	79.0	83.7	(40.2)	22.8	(52.4)
S.D.	-	35.3	32.9	-	18.5	-
n	1	22	22	1	4	1

Table 31
Thiocyanate Data For Activated Sludge Unit 1 Preceded by Aerated Waste Stabilization Pond

Date	Thiocyanate Pond Eff. (mg/l)	Thiocyanate Act.S.Eff. (mg/l)	Reduction (%)
7/6/79	59.8	53.6	10.4
7/17/79	79.1	77.4	2.1
10/2/79	83.4	52.4	37.2
10/12/79	72.0	56.6	21.4
10/26/79	53.7	18.6	65.4
Range	53.7 - 83.4	18.6 - 77.4	2.1 - 65.4
Mean	69.6	51.7	27.3
S.D.	12.6	21.1	25.0
n	5	5	5

Table 32

Mixed Liquor Solids For Activated Sludge
Unit 1 Preceded by Aerated Waste Stabilization Pond

Date	MLSS (mg/1)	MLVSS (mg/1)	Sett.Solids (mg/1)	S.V.I.
6/14/79	-	-	28	-
6/26/79	1,020	550	-	-
7/10/79	1,420	800	50	35.2
7/23/79	616	384	28	45.5
7/31/79	724	452	46	63.5
8/8/79	880	544	38	42.2
9/28/79	1,404	1,184	140	99.7
10/4/79	996	894	96	96.4
10/10/79	1,228	1,068	87	70.8
10/25/79	852	720	48	56.3
10/31/79	964	764	30	31.1
11/7/79	787	548	24	30.5
11/14/79	444	336	16	36.0
1/4/80	788	720	34	43.1
1/14/80	1,096	992	50	45.6
1/28/80	1,776	1,536	>200	>113.0
2/7/80	1,396	1,224	104	74.5
2/12/80	1,042	882	96	92.1
2/18/80	1,320	1,048	56	42.4
2/26/80	936	788	43	45.9
3/3/80	908	556	28	30.8
3/21/80	1,448	1,368	124	85.6
4/10/80	820	748	52	63.4
4/17/80	1,312	1,212	48	36.6
4/24/80	1,472	1,292	44	29.9
5/1/80	1,432	1,192	40	27.9
5/8/80	1,264	1,216	30	23.7
5/15/80	1,228	1,084	30	24.4
5/22/80	722	712	20	25.9
6/12/80	1,048	880	36	34.4
6/19/80	792	676	12	15.2
Range				
Year 1	1,020 - 1,420	550 - 800	28 - 50	-
Total	616 - 1,776	336 - 1,536	12 - >200	15.2 - >113.0
Mean				
Year 1	1,220	675	39	(35.2)
Total	1,071	879	56	50.4
S.D.				
Year 1	283	177	16	-
Total	309	312	42	26.2
n				
Year 1	2	2	2	1
Total	30	30	30	29

Table 33
BOD Loads for Activated Sludge Unit 1 Preceded by Aerated Waste Stabilization Pond

Date		Lb. BOD/Day per Th. Ft^3	Mg BOD/Day per Mg MLVSS
7/4/79		28.4	0.66
7/13/79		34.4	-
7/23/79		23.6	0.98
9/28/79		17.0	0.23
10/5/79		5.9	0.09
10/12/79		5.6	0.08
11/2/79		11.3	0.28
11/8/79		16.3	0.51
11/15/79		5.7	0.27
1/4/80		8.0	0.18
1/10/80		10.7	0.19
1/17/80		9.9	0.14
1/24/80		1.0	0.01
2/7/80		8.0	0.11
2/14/80		12.2	0.21
2/21/80		8.4	0.14
2/29/80		7.3	0.17
3/6/80		11.6	0.27
3/13/80		5.1	0.08
3/20/80		6.9	0.08
3/27/80		2.2	0.03
4/3/80		9.9	0.16
4/10/80		14.4	0.31
4/17/80		8.5	0.11
4/24/80		9.7	0.12
5/1/80		10.7	0.14
5/8/80		11.9	0.16
5/15/80		15.8	0.23
5/22/80		16.3	0.37
6/12/80		16.7	0.30
Range	Year 1	28.4- 34.4	- -
	Total	1.0- 34.4	0.01- 0.98
Mean	Year 1	31.4	(0.66)
	Total	11.8	0.23
S.D.	Year 1	4.2	-
	Total	7.2	0.20
n	Year 1	2	1
	Total	30	29

Table 34
TOC Loads for Activated Sludge
Unit 1 Preceded by Aerated Waste Stabilization Pond

Date	Lb. TOC/Day per Th. Ft^3	Mg TOC/Day per mg MLVSS
1/4/80	12.9	0.29
1/10/80	12.3	0.22
1/15/80	12.4	0.19
1/22/80	10.1	0.12
1/31/80	10.1	0.11
2/5/80	11.1	0.14
2/26/80	12.6	0.26
3/12/80	11.5	0.19
3/20/80	12.7	0.15
5/8/80	15.8	0.21
5/22/80	26.0	0.59
5/28/80	18.5	0.39
Range	10.1-26.0	0.11-0.59
Mean	13.8	0.24
S.D.	4.5	0.14
n	12	12

Table 35
Effluent Solids Data for Activated Sludge Unit 1 Preceded by Aerated Waste Stabilization Pond

Date	SS (mg/1)	VSS (mg/1)
9/28/79	68	68
10/4/79	230	146
10/10/79	50	42
10/25/79	144	120
11/7/79	308	184
11/14/79	228	132
1/14/80	116	100
1/28/80	10	10
2/7/80	114	56
2/12/80	508	264
2/18/80	172	24
2/28/80	144	120
3/3/80	208	120
3/21/80	136	128
4/10/80	96	72
4/17/80	148	132
4/24/80	124	76
5/1/80	230	132
5/8/80	152	124
5/15/80	180	160
5/22/80	114	100
6/12/80	212	148
6/19/80	196	116
Range	10- 508	10- 264
Mean	169	112
S.D.	100	55
n	23	23

Table 36
Temperature, pH, and Dissolved Oxygen Concentrations in Aeration Tank of Joint Treatment Unit

Period	Addition of C.C. Waste (Vol.%)	Temperature (°C) Range	Temperature (°C) Median	pH Range	pH Median	D.O. (mg/l) Range	D.O. (mg/l) Median
3/5/80-4/3/80	0	18 to 25	21.3	7.3 to 8.0	7.7	6.8 to 8.9	8.2
4/7/80-4/11/80	0.02	20 to 22	21.0	7.6 to 7.9	7.7	7.9 to 9.4	8.1
4/14/80-4/21/80	0.04	15 to 25	18.8	7.5 to 7.8	7.7	7.1 to 9.0	8.7
4/22/80-4/25/80	0.06	24 to 25	24.8	7.2 to 7.4	7.3	7.0 to 7.2	7.1
4/28/80-5/2/80	0.1	20 to 21	20	7.4 to 7.6	7.5	-	6.8
5/5/80-5/7/80	0.2	24 to 26.5	26	7.3 to 7.4	7.4	5.8 to 6.9	6.8
5/8/80-5/9/80	0.2	-	-	-	7.3	-	5.7
5/12/80-5/17/80	0.3	20 to 28	22.3	7.1 to 7.3	7.2	3.1 to 6.0	6.0
5/19/80-5/29/80	0.3	23 to 27	24	6.8 to 8.0	7.1	2.6 to 8.0	5.0
6/4/80-6/13/80	0.3	22 to 24	23	6.9 to 7.5	7.1	0.3 to 5.9	4.0
6/14/80-6/29/80	0.3	22 to 25	24	7.0 to 7.6	7.1	0.5 to 7.4	6.0

Table 37
Solids Levels in Aeration Tank
of Joint Treatment Unit

Date	MLSS (mg/l)	MLVSS (mg/l)
4/9/80	30	15
4/16/80	438	301
4/18/80	451	365
4/23/80	672	278
4/25/80	689	260
4/30/80	893	474
5/2/80	964	413
5/7/80	935	416
5/14/80	1,313	902

Table 38
Reduction in Ammonia Nitrogen in
Joint Treatment Unit

Date	NH_3-N Influent (mg/l)	Effluent (mg/l)	% Reduction
4/11/80	3.36	0	100
4/16/80	10.08	0	100
4/18/80	8.54	0	100
4/23/80	8.96	0	100

Table 39
Reduction in Biochemical Oxygen Demand in Joint Treatment Unit

Date	Biochemical Oxygen Demand Aeration Influent (mg/l)	Effluent (mg/l)	% Reduction
3/28/80	44.0	32.7	35.7
4/2/80	22.6	4.7	79.2
4/9/80	44.4	19.9	55.2
4/10/80	60.5	38.9	35.7
4/16/80	118.7	34.8	70.7
4/17/80	131	17.5	86.6
4/18/80	104.8	37.9	63.8
4/24/80	255	75	70.6
4/25/80	74.5	11.5	84.6
5/1/80	345.8	6.1	98.2
5/8/80	184.4	36.5	80.2
5/9/80	190.6	33.0	82.7
5/14/80	254.4	14.7	94.2
5/16/80	220.3	17.1	92.2

Table 40
Other Data for Joint Treatment Unit

Date	Parameter	In Influent (mg/l) From Sewage	In Influent (mg/l) From C.G. Waste	In Influent (mg/l) Total	In Effluent (mg/l)	Reduction (%)
7/2/80	Phenols	-	4.2	4.2	0.02	99.5
7/3/80	Sulfate	28	21	49	85	-
7/3/80	Ortho-phosphate	18.0	3.4	21.4	16.1	24.8
7/3/80	Nitrate Nitrogen	1.5	0.6	2.1	8.5	-

Chapter 7

Results of Study of Tertiary Treatment

Preliminary Tests

Figures 20, 21, and 22 illustrate the effects of changes in pH on the total residue, nonfilterable residue and TOC, respectively.

In Figure 20, a general trend is established and maintained in all three trial runs, namely, little change in total residue occurs between pH 4 and pH 8. However, above pH 8, a significant increase in total residue is observed. A 15% increase in total residue is shown between pH 8 and pH 11. One possible rationale for this phenomenon involves the formation of hydroxy complexes which under the mild thermal evaporation conditions (105°C) fail to give up their water of hydration. One such candidate for these hydroxy complexes is calcium.

A similar plot for non filterable residue versus pH is illustrated in Figure 21. No clear trend is established in these data and the results of this test are inconclusive.

Figure 22 suggests that a significant portion of the organic contaminants in the waste sample may be volatilized during agitation. However, again no clear conclusion may be stated.

Preservation Test

As illustrated by Figure 23 and Table 41, all three preservation samples were marked by an initial increase in TOC during the first 48 hours. This phenomenon was also observed in bulk samples for the equilibrium tests. Since the samples were filtered prior to preservation, little microbiological activity would be expected. Formation of compounds somewhat more resistant to volatilization during the TOC acid sparging procedure provides one possible explanation for these results.

After four days, all three preservation samples begin to show a generalized

Figure 20

Effect of pH on Total Residue

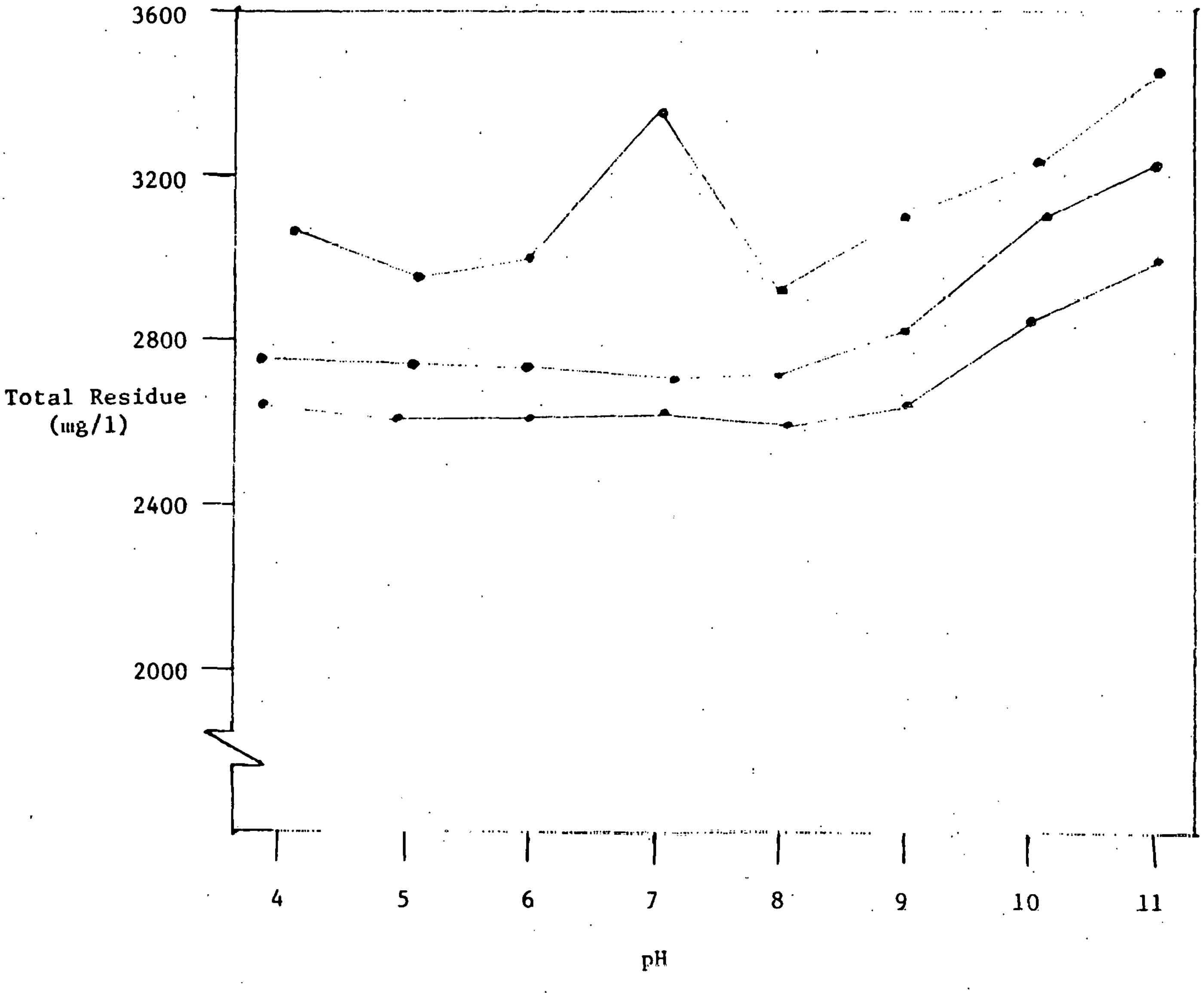
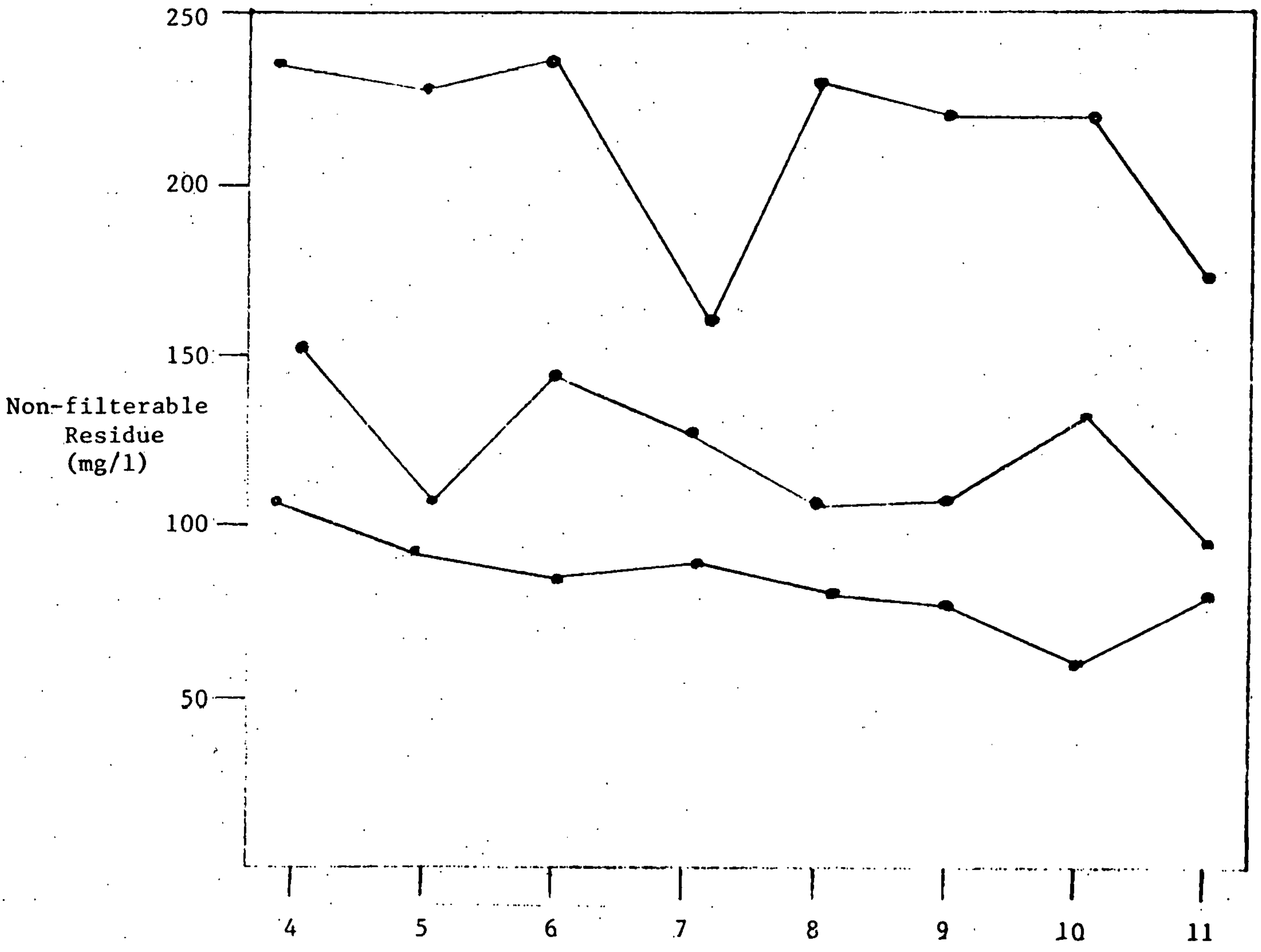


Figure 21

Effect of pH on Non-filterable Residue

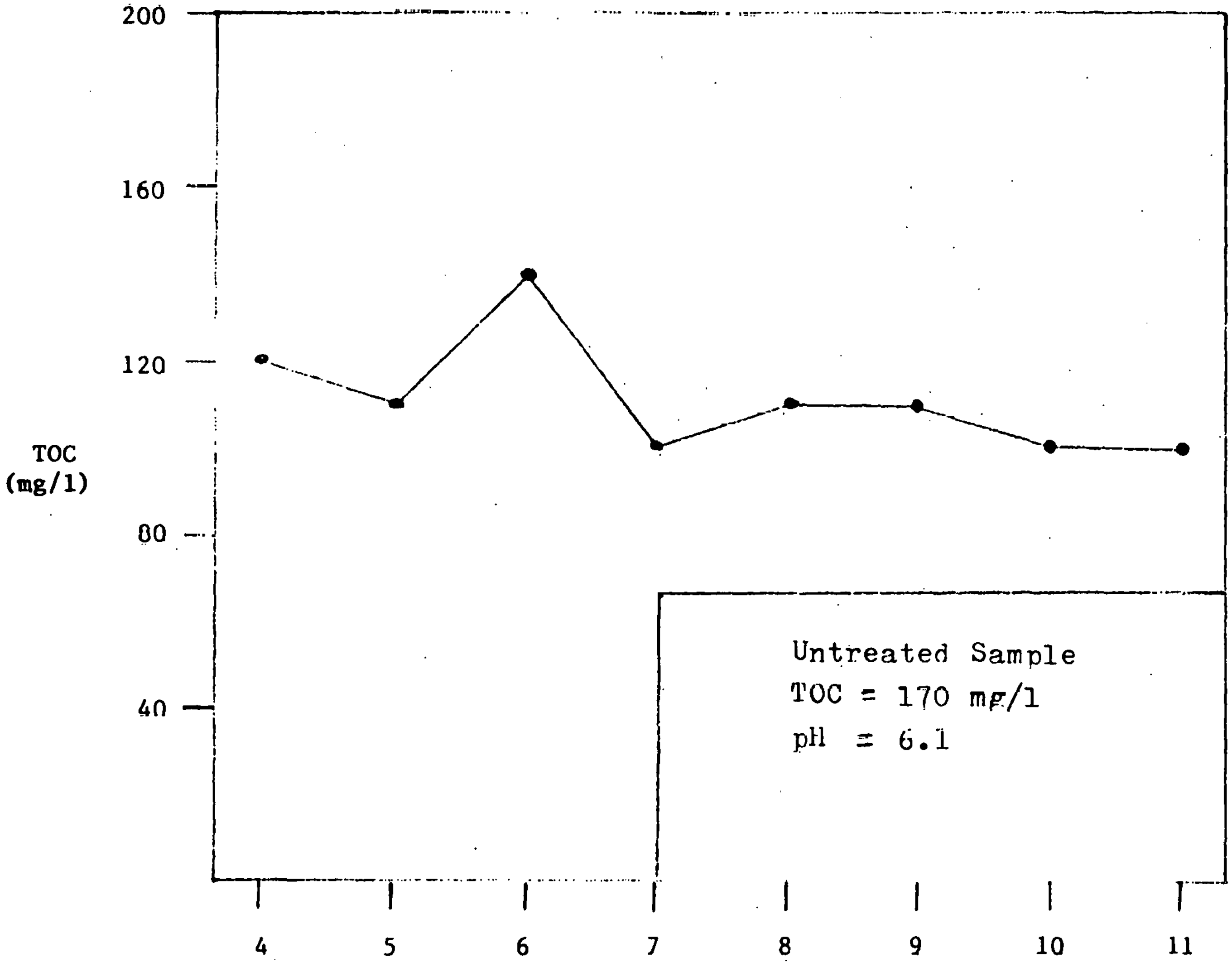


pH

(prior to treatment)

Figure 22

Effect of pH on TOC

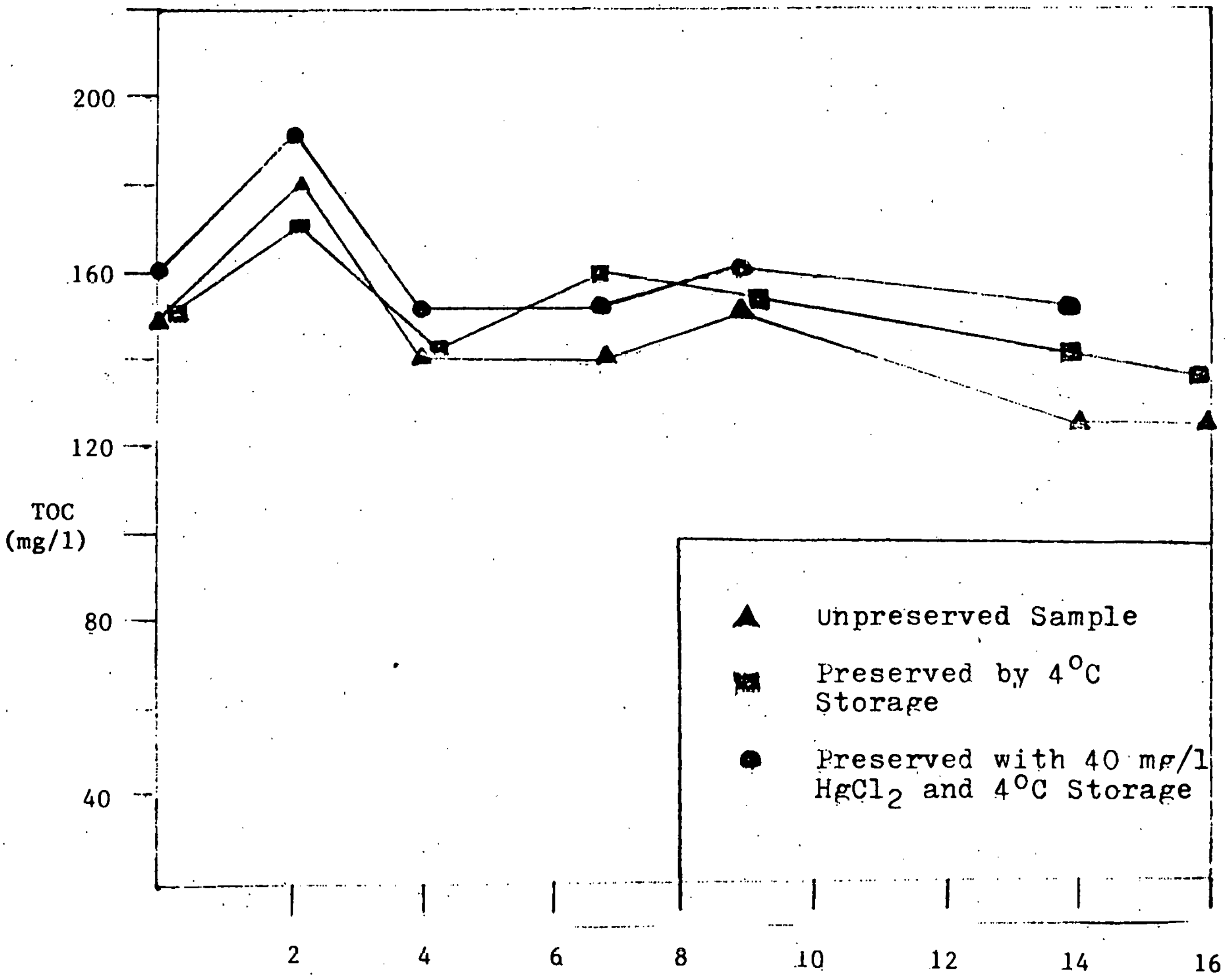


pH

(prior to treatment)

Figure 23

Plot of Preservation Data



reduction in TOC, although minor variations were observed. Samples preserved with 40 mg/l $HgCl_2$ and 4°C storage appeared to be the most stable with respect to TOC, while untreated sample was more susceptible to loss of TOC, although only marginally so ($\leq$ 10%).

Table 41
Preservation Test Data

	TOC (mg/l)		
Date	Untreated	Storage at 4°C	Storage at 4°C plus $Hg\ Cl_2$
5/12/80	130	130	140
5/14/80	160	150	170
5/16/80	120	120	130
5/19/80	120	140	130
5/21/80	130	130	140
5/26/80	100	120	130
5/28/80	100	110	-

Contact Time Equilibrium Test

It was evident from Figure 24 and Table 42 that the vast majority ($>$95%) of the adsorbable components were adsorbed within the first thirty minutes. After this time, the plot illustrates a rapid asymptotic approach to equilibrium. By the time the carbon had been in contact with the waste sample for 2.5 hours, equilibrium was achieved.

This rapid establishment of equilibrium was due primarily to the small particle size of the carbon used ($\leq$0.45μ). Thus, the rate controlling step in achieving equilibrium (penetration of the adsorbate into the internal porous network of the carbon) was significantly shortened.

Figure 24

Equilibrium Contact Time Plot

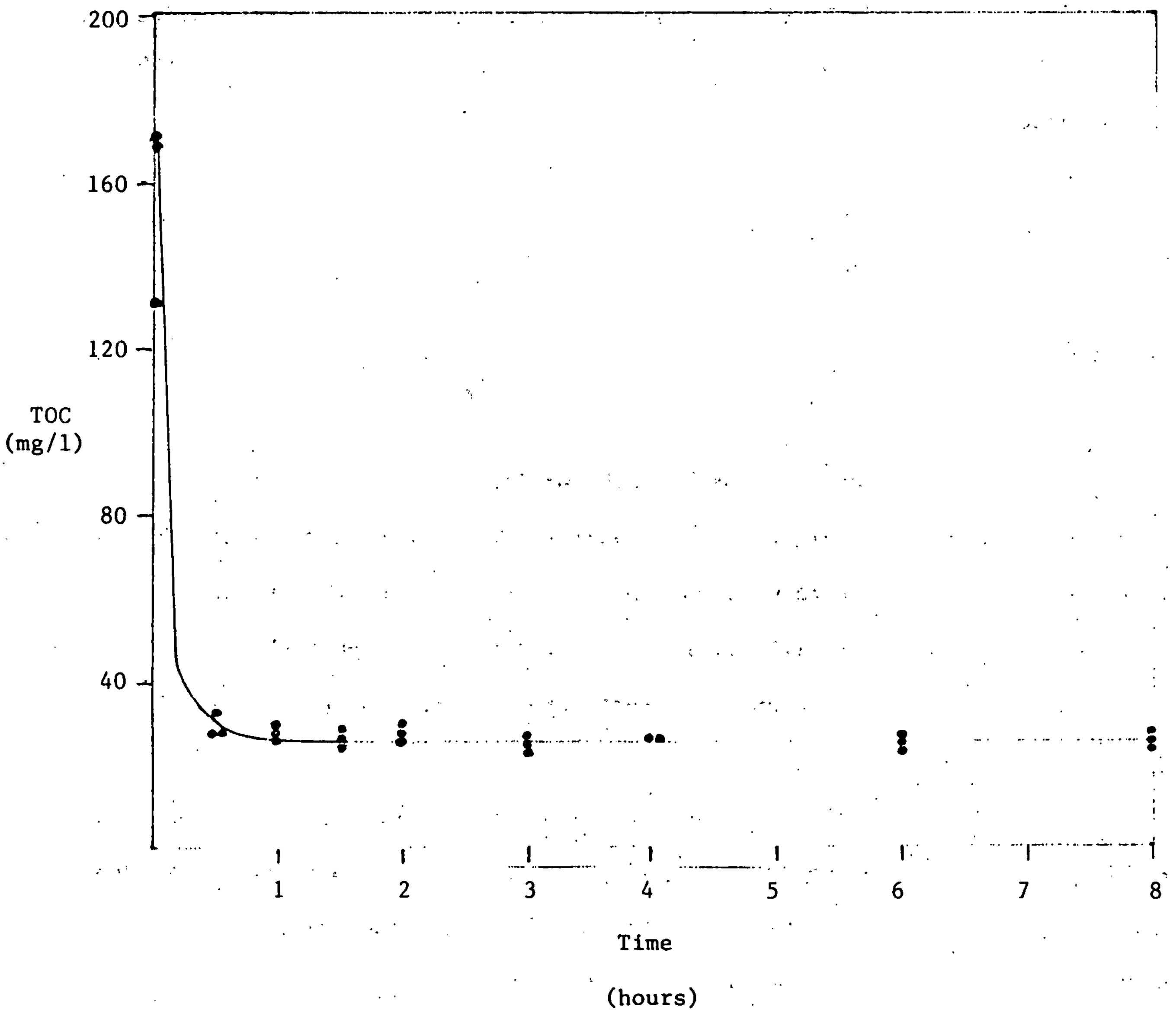


Table 42

Contact Time Equilibrium Data

Time Minutes	TOC (mg/1) Run 1	Run 2	Run 3
0	130	170	170
30	31	25	27
60	28	27	25
90	27	27	23
120	25	24	29
180	25	24	23
240	25	83	25
360	25	24	23
480	27	25	23

pH Variance Equilibrium Test

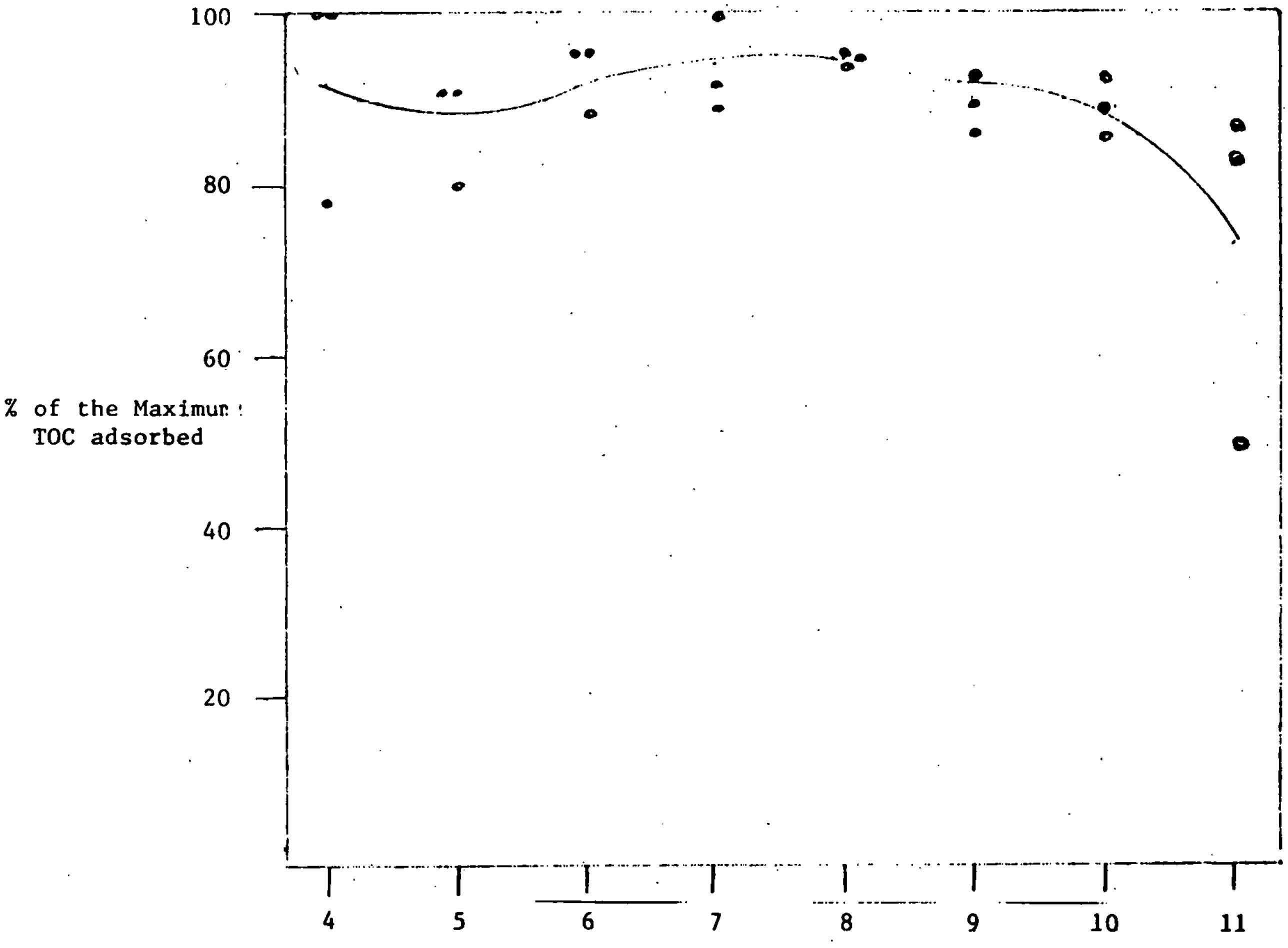
Presented in Figure 25 is a plot of the percent of the maximum TOC adsorbed versus the initial waste sample pH. Also see Table 43. From this plot it appeared that no advantage in adsorption would be gained by altering the wastewater sample pH outside of the range 6 to 8.

As anticipated, above pH 9 the percentage of adsorbate adsorbed dropped. This result was thought to be due to the formation of anionic complexes which were repelled by the slight negative electrostatic charge on the carbon particles.

It should be noted that the anticipated competition for adsorption sites between hydronium ions and adsorbate in the acidic samples was marginal, possibly due to the acidic composition of the adsorbate (including carboxylic acids, alcohols, and other substances).

Figure 25

Equilibrium pH Variance Plot



(prior to treatment)

Table 43

Equilibrium pH Variance Test Data

	TOC (mg/l)		
pH	Run 1	Run 2	Run 3
Blank	100	100	140
4	10	10	42
5	18	28	26
6	14	13	30
7	20	17	15
8	14	15	21
9	20	23	23
10	20	23	24
11	25	56	31

Carbon Dosage Test

The Freundlich equation is as follows:

Equation 1: $\frac{X}{M} = K\ (C_e{}^{1/N})$

Where $\frac{X}{m}$ represents the weight of adsorbate adsorbed per unit weight of carbon, C_e is the equilibrium adsorbate concentration in the reacted sample, and K and N are experimentally determined constants. By taking logarithms of both sides of Equation 1, a linear relationship may be obtained:

Equation 2: $\text{Log}\ \left(\frac{X}{M}\right) = 1/n\ (\log C_e) + \log K$

Figure 26 illustrates the Freundlich plot of the carbon dosage data. Also see Table 44. The data are somewhat clustered but do indicate a linear relationship.

Figure 26

Logarithmic Adsorption Isotherm Plot

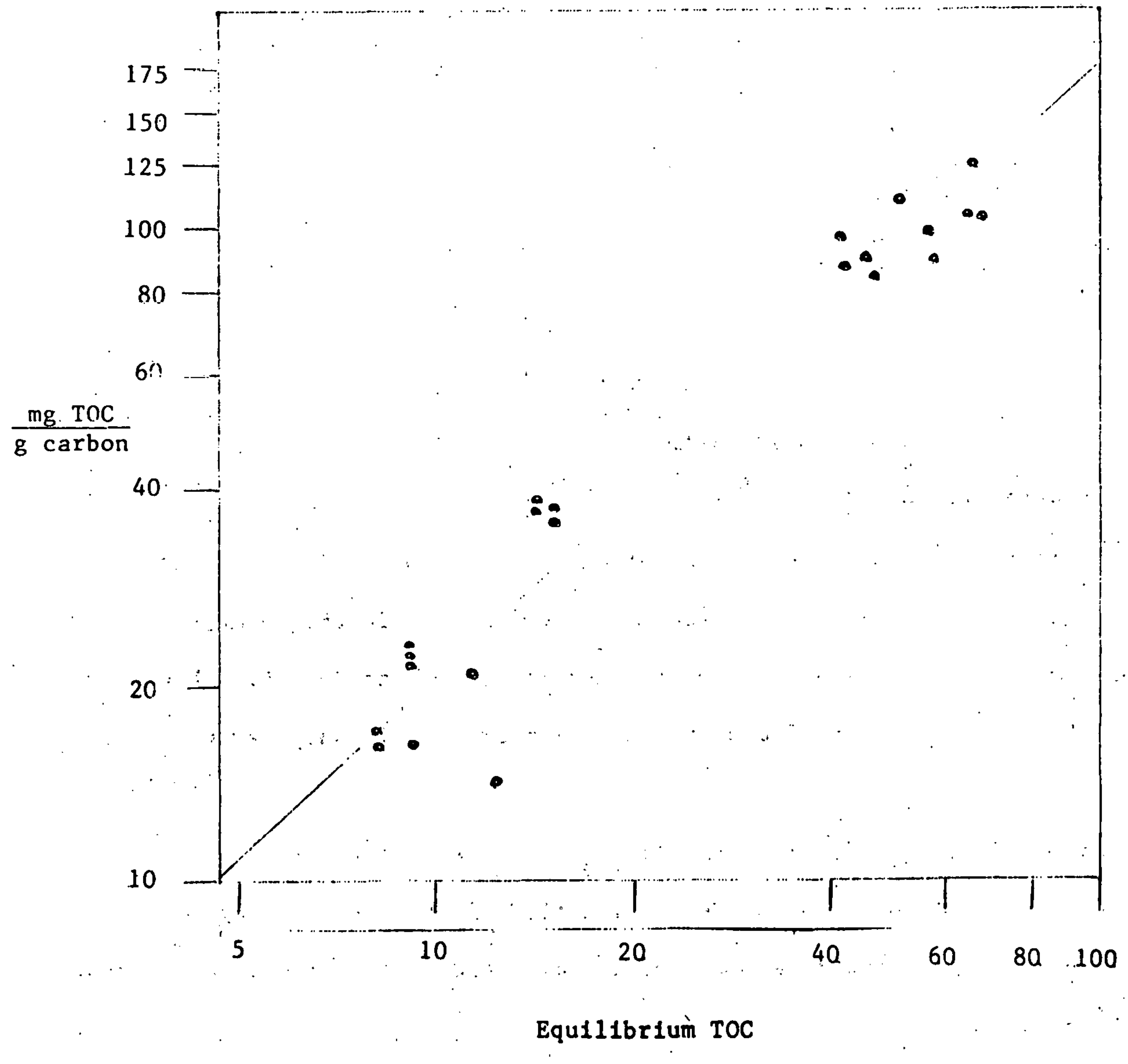


Table 44

Equilibrium Carbon Dosage Tests Data

	Carbon Wt. (g)	TOC (mg/l) Equilibrium	mg TOC/gc
Run 1	Blank	88	-
	0.0707	56	90.5
	0.1005	45	85.6
	0.3998	14	37.02
	0.7003	9	22.56
	1.0004	8	15.9
Run 2	Blank	89	-
	0.0397	68	105.79
	0.0700	50	111.43
	0.1003	44	89.73
	0.4008	15	36.93
	0.7001	9	22.85
	0.9999	8	16.20
Run 3	Blank	90	-
	0.0399	65	125.31
	0.0700	55	100.00
	0.1010	41	97.03
	0.3995	14	38.05
	0.7007	9	23.12
	0.9990	9	16.22
Run 4	Blank	85	-
	0.0403	64	104.22
	0.0998	41	88.18
	0.4005	15	34.96
	0.7000	11	21.14
	1.0000	12	14.60

For all four (4) runs combined:

$N = 22$
$r = 0.97$
$t\text{-test}_r = 17.91$ (for $N-1 = 21$)
$\log K = $ y-intercept $= 0.4270$, $K = 2.67$
$1/N = $ slope $= 0.9143$, $n - 1.09$

Equation is:

$$\frac{mg\ TOC}{gc} = 2.673\ (TOC_e)^{(0.914)}$$

$$\frac{X}{M} = K\ (C)^{1/n}$$

Linear regression was performed on the data and a correlation coefficient of 0.97 was calculated, with a t-score = 17.9 indicating a high ($>$99%, N - 1 = 21) level of certainty associated with the estimate for the correlation coefficient.

To estimate K and N, least squares analysis was performed. The calculated values were K = 2.67 and N = 1.09, thus Equation 1 becomes:

$$\text{Equation 3:} \quad \left(\frac{\text{mg TOC adsorbed}}{\text{gram carbon}}\right) = 2.67\ (\text{TOC}_e)^{1/1.09}$$

By substituting the initial sample TOC for TOC_e, an estimate of the equilibrium adsorption capacity is obtained. The initial TOC of 95 mg/l gives an equilibrium adsorption capacity of 174 mg TOC adsorbed per gram of carbon. Since the initial TOC was 95 mg/l and 200 ml of sample were treated, for complete adsorbate removal, one gram of carbon will remove all the TOC, theoretically, in 366 ml of waste sample. Therefore, 0.273 pounds of carbon are needed to treat 100 pounds of waste sample.

Chapter 8

Discussion

Untreated Wastewater

As already noted, the quantity of excess wastewater, requiring disposal, was estimated as:

Amount evaporated:	685 gal/day
Amount removed with grease and oil:	485 gal/day
Total	1,170 gal/day

The amount evaporated is estimated to vary plus or minus 50% (343 gal/day) depending on the season. The amount removed with grease and oil has a standard deviation calculated at 9.8% of the mean (48 gal/day). Thus, the standard deviation of the total flow may be estimated at 346 gal/day. The 95% confidence interval for the mean flow then would be 502 to 1,848 gal/day. Although these values are considered to be a reasonable representation of the wastewater produced at the Holston facility, they are only approximate.

The mean flow noted above corresponds to the following unit production of wastewater:

53 gal/ton coal (as received)
366 gal/million cubic feet of product gas

This quantity of wastewater corresponds to 91,500 gal/day for a coal gasification plant producing 250 million cubic feet/day of product gas. Although this is far lower than estimates for modern plants (26,74), several factors should be emphasized:

1. The Holston facility, with total flow estimated as 1,094,000 gal/day, recycles (mainly for scrubbing and cooling product gas) all except 0.11%, which is the express wastewater requiring disposal.
2. Data on quantity of wastewater are necessarily incomplete, since quantification was not possible for various additions of liquid (such as

from reactions in the gasifiers) and losses (such as from absorption in residue and evaporation).

3. The plant studied apparently represents old technology.

The following summarizes data on concentrations of pollutants in the untreated wastewater:

Pollutant	Mean Concentration (mg/l)	S.D. (mg/l)	95% C.I. (mg/l)	Total Lb/day	Lb Per Ton Coal
Alkalinity	1,631	153	1,331 - 1,931	15.9	0.72
BOD(pretreated)	7,581	2,561	2,561 - 12,601	74.0	3.36
Ammonia nitrogen	3,201	1,470	320 - 6,082	31.2	3.24
TOC	32,777	33,102	0 - 162,500	319.8	14.54
COD	30,009	14,206	2,518 - 57,500	292.8	13.31
Total solids	19,060	5,733	7,823 - 30,297	186.0	8.45
Total volatile solids	18,750	6,953	5,128 - 32,372	183.0	8.32
Suspended solids	140	64.4	14 - 266	1.4	0.064
Volatile suspended solids	92.5	45.7	2.9 - 182.1	0.9	0.041
Sulfide	5,376	3,784	0 - 12,793	52.5	2.39
Thiocyanate	613	251	121 - 1,105	6.0	0.27
Grease & Oil	2,537	2,059	0 - 6,573	24.8	1.13
Phenols	1,924	272	1,391 - 2,457	18.8	0.85
Cyanide	1.3	1.3	0 - 3.8	0.013	0.00059

Generally, the values noted for mean concentrations are reasonable (22, 70, 74). Although TOC and COD values noted in this study are high, it must be noted that the concentrations of these parameters was not well determined here. Concentrations of sulfide and thiocyanate found in the present study also are higher than those previously reported. Part of the explanation might be that improved analytical methods were developed for these substances in the present study. In the case of sulfide, however, the improved method has not been fully validated.

Possible effects of the high degree of recirculation should be noted. It is likely that some materials were being volatilized, which would be one explanation for the moderate levels of ammonia nitrogen that were found. Conversely, some materials would be concentrated to quite high levels, providing an explanation for the indication of extremely high levels of chloride.

Variation in Concentration

That there is considerable variation in concentration is indicated by the high value of the standard deviation in comparison to the mean in numerous cases. The seeming relation between some variation in concentration and operation of the gasifiers (placing in service, removing from service, and practicing burn-out), has already been described (89). However, wide variation in concentration is undesirable for treatment by certain activated sludge processes. Possibilities for equalization of concentration include:

1. Use of an equalization tank - The volume required would have to be sufficient to store high concentration flows so that they could be mixed with lower concentration waste, or drained into the activated sludge facility gradually. In order to maintain constant the level of biochemical oxygen demand in the pretreated waste, an equalization tank with capacity equal to 19 days flow would be required. Since the analysis which produced this estimate considered variation in level of the pollu-

tant parameter, but could not consider variation in flow, in actuality a larger equalization tank than this would be needed.

2. Recycle - A high recycle rate makes any change in waste concentration less substantial in terms of apparent increase in actual concentration reaching the activated sludge facility.

Potential for Recovery

An important finding of this study is that wastewater was recycled successfully at the Holston plant for scrubbing and cooling product gas, with only minimal treatment ("settling" in the decanter). Potential for recovery of chemical substances probably is limited by the quantities involved. At Holston, ammonia nitrogen amounted to only some 30 lb/day, and phenols to only 20 lb/day. For a plant producing 250 million cubic feet per day of product gas, this would be approximately 2,400 lb/day of ammonia nitrogen, and 1,500 lb/day of phenols. The value of the product, doubtlessly collected in an impure state, would need to be compared with the cost of production. In the case of ammonia, especially, recovery doubtlessly will be necessary for reasons of air pollution control. Such recovery, perhaps by absorption in acid solution, may be useful, even if production of low-grade fertilizer with limited use is all that is possible, and even if the recovery is not profitable.

Pretreatment

The equation describing the removal of ammonia nitrogen, as reported last year, was found to describe stripping effectiveness in the relatively large batches of wastewater that were treated. Nevertheless, this equation is limited in that it was totally empirical, not being based on fundamental, theoretical considerations. Another problem is that the equation, as presented, was developed from data gathered in the stripping of batches of wastewater. By contrast, a full scale coal gasification plant doubtlessly would utilize a continuous-flow facility, such as a packed tower.

Limited data were gathered from small scale batch studies of the removal of grease and oil. Linear regression was used to develop an equation that related the degree of removal of grease and oil to treatment conditions, but the result was a formula that was only approximate. An alternate formula, developed from linear regression with the data from the treatment of large batches of wastewater, was as follows:

$$y = 16.5x, -0.0360x_2 + 6.75x_3 + 11.9$$

y = percent removal of grease and oil, x_1= pH, x_2 = treatment time (minutes), and x_3 = aeration rate (liters per minute per liter of sample). The correlation coefficient was 0.80, which is significant at the 99% confidence level.

This equation, also,is totally empirical.

Another benefit to the pretreatment scheme used in this study was that other substances also were removed from the waste. The most notable example was that most of the sulfide was removed, with this occurring mainly in stripping. However, pretreatment also brought substantial removal, some 25% to 50%, of phenols, biochemical oxygen demand, alkalinity, and, doubtlessly, other substances. Interestingly, the concentration of thiocyanate increased on many occasions, during pretreatment.

One notable feature of pretreatment was the substantial decrease in volume which occurred. The mean decrease in volume was 18.9%, with a 95% confidence interval of 0% to 42.8%. Of the decrease in volume, most (46.9%) took place during the stripping. The balance occurred during the removal of grease and oil (16.8%) and neutralization (36.3%). The volume reductions during grease and oil removal,and during neutralization, probably were mainly sludge, and amounted to a mean of about 10% of the volume of the wastewater. This large volume of sludge would present a considerable problem in handling and disposal in a full scale coal gasification plant.

The dose of reagents used in pretreatment in two recent occurrences was as follows:

Date:	5/23/80	7/2/80
Stripping:		
NaOH(mg/l)	40,500	31,500
Grease and Oil:		
H_3PO_4(mg/l)	2,090	2,610
H_2SO_4(mg/l)	10,300	12,900
Neutralization:		
NaOH(mg/l)	1,530	1,820

These are extremely high doses by ordinary standards for dosing reagent. However, the quantity of wastewater produced in coal gasification is relatively small. An additional factor is that these values are only approximate indicators of the required doses. Nevertheless, on the basis of the data of 7/2/80, the following amounts of these reagents would be required each day:

	Holston Plant	250 CF per day Plant
NaOH	139. kg	10,900 kg
H_3PO_4	11.6	906
H_2SO_4	57.1	4,460
NaOH (for neutralization)	8.06	630

Biological Treatment

The study of biological processes generally showed that successful treatment could be obtained by all of the alternatives considered. General effectiveness of treatment was as follows:

Biochemical oxygen demand: Reduction averaged at least 60% for all alternatives studied, but frequently was much higher, even over 90%.

Total organic carbon: Reasonable reductions were obtained, typically about 40% to 50%.

Phenols: After initial operation, very high degree reduction was found, often well over 90%, and even greater than 99%.

Ammonia nitrogen: Although pretreatment was shown to be quite effective in removing ammonia, activated sludge generally was poor. An actual increase in ammonia nitrogen concentration was recorded in most tests, with reduction, at best, being low (generally 30% or less). A notable exception to this was joint treatment with municipal sewage, where the ammonia nitrogen was nearly totally removed.

Thiocyanates: Reductions were variable, ranging from an actual increase during the treatment process, to approximately 70%.

In order to further compare the several alternatives for biological treatment, the following gives effectiveness in reduction of biochemical oxygen demand:

Process	Mean Reduction (%)	S.D. (%)	n	95% Confidence Interval
Activated sludge,without modification (Unit 1, first year of study).	64.4	20.6	14	53.6-75.2
Activated sludge, with stabilized influent concentration of BOD (Unit 2, 6/7/79-12/31/79).	66.5	13.4	15	59.7-73.3
Activated sludge, with preceding aerated waste stabilization pond (Unit 1, 6/7/79-1/16/80).	77.8	8.8	11	72.6-83.0
Activated sludge, with preceding aerated waste stabilization pond, and chemical precipitation in aeration tank (Unit 1, 1/17/80-6/30/80).	82.1	12.5	18	76.3-87.9
Joint treatment with municipal sewage	73.5	19.9	14	63.1-83.9

It must be noted that numerous factors enter into the degree of treatment provided, factors in addition to the type of biological treatment provided. These would include the characteristics of the waste, the pretreatment, the load on the biological treatment, and more. Nevertheless, the data suggested that activated sludge without modification produced only moderate treatment, and that the treatment effectiveness that resulted was relatively variable. Stabilizing the influent concentration of BOD apparently yielded only a small improvement in treatment effectiveness, though it may have stabilized the degree of treatment. The addition of a preceding aeration pond may have provided significant improvement, both in treatment effectiveness (especially when coagulant was dosed in the aeration tanks) and stability of treatment. Emphasis must be placed on the need to utilize more controlled studies to verify these results.

The aerated waste stabilization pond preceding the activated sludge unit appeared to enhance treatment considerably. Not only was reduction in BOD rather high and stable, but reduction in phenol was excellent (mean of 99.69%, standard deviation of 0.33%), and reduction in TOC was better (mean of 48.8%, versus 39.7% without the aerated pond). Nevertheless, several points should be noted. The aerated pond greatly reduced the load on the activated sludge treatment units, possibly preventing efficient utilization. Further, the aerated pond in itself, produced substantial treatment, as exemplified by the following:

Parameter	% Reduction Mean	S.D.
BOD	63.1	19.1
TOC	46.7	12.7
Phenols	89.6	9.9

These results are comparable to those obtained for activated sludge without modification, or even slightly better. The data could be interpreted as showing that aerated waste stabilization ponds are an effective alternative to activated sludge, for the biological treatment portion of an integrated treatment scheme. Certainly, it merits further evaluation in this regard.

An important group of problems was found associated with solids concentrations. Generally, levels of suspended solids in the effluents were relatively high, preventing the attainment and maintenance of high mixed liquor suspended solids concentrations. This condition limited cell detention to relatively low levels. Thus,loads on the treatment units also were limited and high dilution of pretreated wastewater was required. At this point, it is not certain that this is an inherent limitation. If effluent solids can be controlled, higher levels of mixed liquor suspended solids maintained and cell detention kept satisfactorily high, then considerably greater loads may be possible. Efforts to control solids levels in the biological effluent included improved settling (totally unsuccessful), chemical precipitation in the aeration tank (no improvement noted), and effluent chemical precipitation (highly successful). The last approach may be the most useful. However, high doses of coagulant were required (250 mg/l of $FeCl_3$), and the viability of microorganisms in the precipitated sludge remains to be established.

Joint treatment with municipal sewage was rather successful. Ammonia nitrogen was removed essentially entirely, BOD was reduced by more than 80% (and often by more than 90%) after the process had stabilized, phenols were greatly reduced, and the effluent was high in products of oxidation (sulfates and nitrates). However, a maximum of only 0.3% by volume of coal gasification wastewater was included in the influent. Load was 0.28 mg BOD/day/mg MLVSS. The only negative feature noted was an increase in the discoloration of the effluent. Thus, the alternative of joint treatment was relatively successful, and merits further study.

Attempts to study the biological reaction kinetics were restricted by poor ability to control cell detention. Thus, the values which were estimated for the parameters of reaction kinetics have much less significance than desired, and should be regarded only as general indicators.

Tertiary Treatment

The results for tertiary treatment of the biological effluent by granular activated carbon already have been presented and discussed. Generally, reasonable results were obtained. The carbon dosage test showed that, in theory, 0.273 pounds of activated carbon would treat 100 pounds of wastewater. Incidental information from this phase of the study was that the TOC could be reduced to a value of approximately 10 mg/l. Note, however, that "breakthrough" studies have not been completed with this wastewater.

An Integrated Treatment Scheme

Although numerous alternatives are possible for the management of the wastewater from a coal gasification plant, this study included only those presumed to have the greatest potential for success. The following integrated management and treatment scheme is offered as worthy of further development, based on the present study:

Process	Comment
Recycling of wastewater for cleaning and cooling product gas.	An important advantage of this is reducing the amount of wastewater requiring treatment. At Holston, a simple decanter to reduce grease and oil appeared sufficient.
Stripping to reduce ammonia nitrogen.	A stripping tower probably would be used to remove as much ammonia nitrogen as possible, leaving enough for nutrient for biological treatment.
Recovery of ammonia nitrogen as a by-product by absorption in an acid solution.	This may be the best possibility for by-product recovery.
Removal of grease and oil by suppression of pH, light aeration, and settling.	This is a very needful step in pretreatment.
Neutralization	Settling to remove sludge will be necessary in conjunction with neutralization.
Combination equalization tank and aerated waste stabilization pond.	The purposes of this are dampening variations in levels of pollutants, and stabilizing treatment effectiveness in an activated sludge process.
Activated sludge.	This must include aeration and subsequent settling, plus operation with a sludge reserve. The latter might be an aerobic sludge digester.
Chemical precipitation of effluent.	Coagulation of the biological effluent may be necessary to avoid high effluent solids, and should be operated as necessary to maintain satisfactory cell retention.
Adsorption in columns with granular activated carbon.	

Limitations

This study had numerous limitations, which severely limit interpretation of results. Particular problems include:

1. Poor control over confounding factors means that various results of this study must be verified. That is, additional studies with careful controls are required.

2. This study considered only the wastewater from the Holston Coal Gasification Plant. It is unclear to what extent wastewater characteristics and other conditions appropriate to this facility may be applicable elsewhere. In fact, since Holston utilized old technology, much found in this study probably has only limited applicability elsewhere.

3. The present study was based on the use of laboratory-scale treatment units, and small scale studies. The applicability of the data which were thus derived to full size facilities is highly questionable. Thus, scale-up requires study.

Chapter 9

Summary and Conclusions

Under contract with the U.S. Department of Energy, Pittsburgh Energy Technology Center, study was performed on the wastewater from the coal gasification plant serving the Holston Army Ammunition Plant. Study of this sort has become of considerable interest, due to the mushrooming of coal conversion projects in this region and the nation. Projects now are planned by the Tennessee Eastman Company, in Kingsport, by the Tennessee Valley Authority, in Memphis and in North Alabama, and by others. The general objectives of the study were two, to characterize the wastewater, and to evaluate control technology.

The characterization was performed by analysis of some 40 samples of untreated waste collected during the two years of the study. The evaluation of control technology centered on gathering data from laboratory scale wastewater treatment units, especially two unitized activated sludge plants. It is fundamental that research builds upon the results of other workers, including, especially, in this case, some at the Pittsburgh Energy Technology Center. Additionally, analytical methods had to be adapted for the particular wastewater that was studied, and various procedures developed.

Conclusions reached in this study included:

1. At the Holston gasification plant, wastewater after treatment in a decanter, was satisfactorily recycled for cleaning and cooling the product gas.

2. Wastewater requiring disposal at Holston was only a small fraction of that present in the system, with a mean of some 1,170 gallons per day, but varying considerably with season of the year. This amounted to 53 gallons per ton of coal, or 366 gallons per million cubic feet of product gas.

3. The wastewater was highly contaminated, but variable in levels of pollutants. Important pollutants included organic material (mean BOD of pretreated waste was 7,581 mg/l, standard deviation was 2,561 mg/l), ammonia nitrogen (mean was 3,201 mg/l, standard deviation 1,470 mg/l), volatile solids (mean was 18,750 mg/l, standard deviation was 6,953 mg/l), sulfide (mean was 5,376 mg/l, standard deviation was 3,784 mg/l), thiocyanate (mean was 613 mg/l, standard deviation was 251 mg/l), grease and oil (mean was 2,537 mg/l, standard deviation was 2,059 mg/l), phenols (mean was 1,924 mg/l, standard deviation was 272 mg/l), and other substances.

The variability in levels of pollutants appeared to be related to aspects of operation of the production facility. Sulfide and thiocyanate levels frequently were higher in the wastewater studied than reported by other workers.

4. An equalization tank would be desirable to stabilize concentrations of pollutants, and would need sufficient capacity to contain at least several weeks of flow.

5. Stripping was capable of removing essentially any desired fraction of the ammonia nitrogen in the raw waste, and could be described by an empirical equation that was developed. Air pollution control requirements would generally necessitate removal of ammonia from emissions, which could provide additional incentive for recovering ammonia as a by-product.

6. The removal of grease and oil could be readily accomplished, mainly by suppression of pH, supplemented by aeration for flotation.

7. The pretreatment procedure which was used also provided substantial reductions sulfides, phenols, BOD, and alkalinity.

8. Problems with the pretreatment procedure included the requirement for high doses of reagents, and production of large volumes of sludge.

9. Biological treatment by an activated sludge process, without modification, was found capable of providing substantial treatment, although results were variable,with frequent process upsets, possibly related to variation in characteristics of the wastewater. Although organic materials, and especially phenols, were removed well, the reduction of ammonia nitrogen and thiocyanates was poor.

10. Diluting wastewater so as to provide a nearly constant influent concentration of BOD had little value in raising the treatment effectiveness, but appeared to yield a more stable degree of treatment.

11. The provision of an aerated waste stabilization pond prior to the activated sludge unit appeared to improve both the efficiency and stability of treatment. However, the pond probably reduced the effectiveness of utilization of the activated sludge units.

12. Aerated waste stabilization ponds should be evaluated as an alternative to activated sludge in providing biological treatment of coal gasification wastewater.

13. Chemical precipitation in the aeration tank apparently improved and stabilized treatment, but was not effective in controlling the high levels of suspended solids in the biological effluent.

14. Joint treatment with municipal seawage provided effective treatment, including reduction in ammonia nitrogen. A problem with this alternative was discoloration of the effluent.

15. Chemical precipitation with $FeCl_3$ was effective in reducing the high levels of suspended solids in the biological effluent, and was considered to have potential for controlling cell retention.

16. Limited study indicated that adsorption of granular activated carbon was both effective and practical for tertiary treatment of the wastewater.

17. An integrated management and treatment scheme, as proposed, can provide effective control of the wastewater that was studied.

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APPENDIX A

Contract Between East Tennessee State University and The U.S. Department of Energy

CONTRACT BETWEEN
EAST TENNESSEE STATE UNIVERSITY
AND
THE U. S. DEPARTMENT OF ENERGY

THIS AGREEMENT is effective the 15th day of July, 1978, between the UNITED STATES OF AMERICA (hereinafter referred to as the "Government"), acting through the DEPARTMENT OF ENERGY (hereinafter referred to as "DOE"), and the EAST TENNESSEE STATE UNIVERSITY, a corporation duly organized and existing under the laws of the STATE OF TENNESSEE with its principal office in JOHNSON CITY, TENNESSEE (hereinafter referred to as the "Contractor").

WITNESSETH THAT:

WHEREAS, DOE wishes to have the Contractor perform certain research work, as hereinafter provided; and

WHEREAS, this agreement is authorized by the Department of Energy Organization Act and other applicable law;

NOW, THEREFORE, the parties hereto agree as follows:

ARTICLE I - THE RESEARCH TO BE PERFORMED

(a) The Contractor shall, to the best of its ability, furnish personnel, facilities, equipment, materials, supplies, and services, except such as are furnished by the Government, necessary for the performance of the research provided for in Appendix A and shall perform the research and report thereon pursuant to the provisions of the contract. It is understood that Appendix A, a guide to the performance of this contract, may be deviated from by the Contractor subject to the specific requirements of this contract.

(b) This work shall be conducted under the direction of Dr. Albert F. Iglar or such other member of the Contractor's staff as may be mutually satisfactory to the parties.

ARTICLE II - THE PERIOD OF PERFORMANCE

The period of performance under this contract shall commence on July 15, 1978 and expire on July 14, 1980. Performance may be extended for additional periods by the mutual written agreement of the parties.

ARTICLE III - CONSIDERATION

(a) In full consideration of the Contractor's performance hereunder, DOE shall furnish the equipment, supplies, materials, and services, if any, listed in Article A-II(b) and pay the Contractor the sum of $35,690.00, hereinafter called the "Support Ceiling" which sum shall be subject to adjustment as hereinafter provided.

(b) Payments to the Contractor shall equal the "Cumulative Support Cost" of the performance of this contract, as the term "Cumulative Support Cost" is defined in Article B-XXVIII; provided, however, and notwithstanding any other provision of this contract, that the Government's monetary liability under this contract shall not exceed the Support Ceiling specified in (a) above. DOE shall not pay more than the Support Ceiling or an amount equal to the Cumulative Support Cost, whichever is less.

(c) Whenever the Contractor has reason to believe that the amount of funds obligated under this contract will be insufficient to permit the Contractor to continue to perform for more than 30 days (or such other period as DOE may from time to time time establish by notice to the Contractor), the Contractor shall promptly notify DOE to that effect. The Contractor shall be required to perform under this contract throughout the agreed-upon period of performance, and to bear all costs which DOE has not agreed to pay; provided, however, that the Contractor shall have the right to cease to perform the research provided for in this contract, upon written notice to DOE to that effect, at any time when or after the Cumulative Support Cost equals or exceeds the Support Ceiling.

(d) The Support Ceiling specified in (a) above may be increased unilaterally by DOE by written notice to the Contractor and may be increased or decreased by written agreement of the parties (whether or not by formal modification to this contract). In the event the stated period of contract performance is extended, the Support Ceiling will be revised to reflect any increased DOE support for the extended period or periods.

(e) Upon termination, or expiration of the total period of performance, the Contractor shall promptly refund to DOE (or make such disposition as DOE may in writing direct) any sums paid by DOE to the Contractor under this contract, through direct payment or under letter of credit, in excess of the Cumulative Support Cost incurred in performance under the contract.

ARTICLE IV - GOVERNMENT PROPERTY

The following items of property procured or fabricated by the Contractor are hereby listed as "Government property":

NONE

ARTICLE V - APPENDICES

Appendix A, Appendix B - General Provisions, Appendix C - Statement of Costs, and Appendix D - Intellectual Property Provisions, are hereby attached to and made a part of this contract.

ARTICLE VI - CIVIL RIGHTS ACT OF 1964

Contractor agrees to comply with DOE's Regulation (Part 704 of Chapter III, Title 10, Code of Federal Regulations), as amended, effectuating the provisions of Title VI of the Civil Rights Act of 1964.

IN WITNESS WHEREOF, the parties have executed this document.

UNITED STATES OF AMERICA
BY: Michael Hogan
Contract Administrator
(title)

Pittsburgh Energy Technology Center
Department of Energy

EAST TENNESSEE STATE UNIVERSITY
BY: Arthur H. DeRosier Jr.
Arthur H. DeRosier, Jr.
~~President~~
(title)

by Christopher L. Bramlett
Vice-President for Academic Affairs

David L. Kite, certify that I am the
(attester)

Director of Business Affairs of the Contractor named
(title)

under this document; that Christopher L. Bramlett
(signatory)

who signed this document on behalf of said Contractor was then

Vice-President for Academic Affairs and
Authorized to sign for the President. of said Contractor; that
(title)

this document was duly signed for and on behalf of said Contractor by authority

of its governing body and is within scope of its legal powers.

IN WITNESS WHEREOF, I have hereunto affixed my hand and the seal of said Contractor.

(SEAL)

APPENDIX A

For the Contract Period July 15, 1978 through July 14, 1980.

Article A-I RESEARCH TO BE PERFORMED BY CONTRACTOR

(a) The scope of work under this contract is unclassified and shall consist of a study to evaluate methods of treating coal gasification process wastewater, with regard to meeting requirements for water pollution control. Detailed study will focus on the coal gasification facility at the Holston Army Ammunition Plant in Kingsport, Tennessee. Characterization will be conducted on the wastewater to evaluate flow, chemical characteristics, and physical characteristics. While the study will somewhat consider pretreatment, by-product recovery, and other matters, it will focus on possibilities for biological treatment, especially by the activated sludge process. The highly contaminated nature of this wastewater will necessitate investigation of specialized techniques, such as joint treatment with municipal sewage, biological contact media, and other possibilities. In the actual treatability studies, levels of major pollution parameters will be determined both before and after treatment. Various loading and design parameters will be evaluated, together with appropriate investigation of treatment kinetics.

(b) The scope of work shall include such other studies, investigations and services as may be mutually agreed upon.

(c) The Principal Investigator(s) expects to devote the following approximate amount(s) of time to the contract work: 100% of his time for 3 months.

Article A-II WAYS AND MEANS OF PERFORMANCE

(a) Items for which support will be provided as indicated in A-III, below:

(1) Salaries and Wages	$ 21,755.00
(2) Equipment to be purchased or fabricated by the Contractor	$ 14,600.00
(i) Item(s) expected to cost $1,000.00 or more.	
1. Total Organic Carbon Analyzer	
2. 2 Bench-Scale Activated Sludge Units	
3. Compositing Sampler	
(3) Travel	
(i) Domestic	$ 1,350.00
(ii) Foreign	$ -0-
(4) Other direct costs	

(5) Indirect costs for the period July 15, 1978 through July 14, 1979 shall be based on a predetermined rate of 51.1 percent applicable to salary and wages, excluding vacations, holidays, sick pay and other fringe benefits.

Indirect costs for the period July 15, 1979 through July 14, 1980 shall be based on a predetermined rate, together with its applicable base shall be agreed to in writing, by the parties prior to the initiation of any work during said period. Said agreement shall not be construed to increase the Support Ceiling specified in Article III of this contract.

(b) Items, if any, significant to the performance of this contract, but excluded from computation of Support Cost and from consideration in proportioning costs:

NONE

(c) Time or effort of Principal Investigator(s) including indirect costs and fringe benefits contributed by Contractor but excluded from computation of Support Cost and from consideration in proportioning costs:

100% of 2.2 months

Article A-III

The total estimated cost of items under A-II(a) above for the contract period stated in this Appendix A is $57,997.00; DOE will pay 100 percent of the actual costs of these items incurred during the contract period stated in this Appendix A, subject to the provisions of Article III and Article B-XXVIII. The estimated DOE Support Cost for the contract period stated in this Appendix A is $57,997.00.

Funding for the estimated DOE Support Cost will be as follows:

(a) Estimated unexpended balance from prior period(s)	$ -0-
(b) New funds for the current period	$ 35,690.00
(c) Subject to their availability, additional funds anticipated for the current period	$ 22,307.00

APPENDIX B

Sulfide Determination in Coal Gasification Wastewater

SULFIDE DETERMINATION IN COAL GASIFICATION WASTEWATER

1. Sampling

Raw samples:

In BOD bottle, place 3 ml 2N $Zn(CH_3COO)_2$, fill with sample water, and then add 6 drops of 10N NaOH. Stopper with no air bubbles, and mix by rotating back and forth about transverse axis. Then place the bottle in ice bath to preserve.

Pretreated samples:

In BOD bottle, place 5 ml 2N $Zn(CH_3COO)_2$, fill with sample water, and then add 4 drops of 1 ON NaOH. Stopper with no air bubbles, and mix by rotating back and forth about transverse axis.

Adding more NaOH in raw sample is explainable by the high concentration of ammonia present there, which may act as a pH buffer. In pretreated sample, more $Zn(CH_3COO)_2$ is added because of the presence of high concentrations of phosphate which can form $Zn(H_2PO_4)_2$, $ZnHPO_4$, and $Zn_3(PO_4)_2$.

2. Determination

Raw samples:

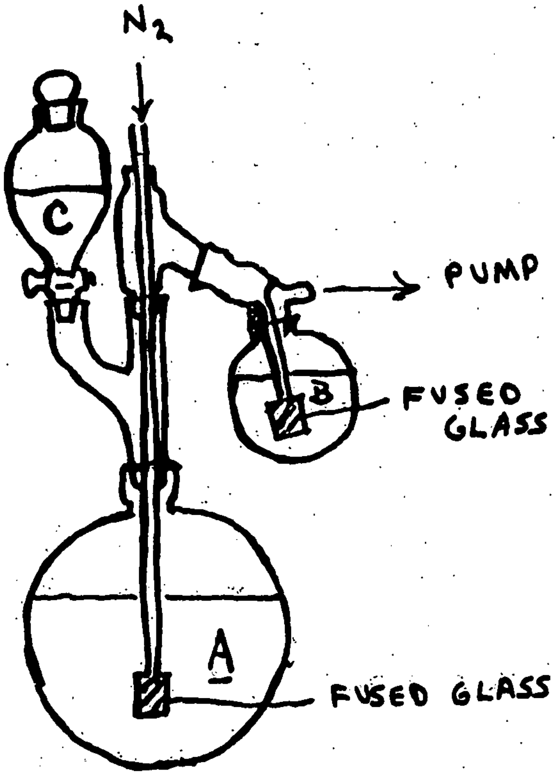
Carefully remove the supernatant from the upper layer of solution in BOD bottle. Add 50 ml acetone to the bottle. Mix and allow to settle for 2 minutes. Pour solution through glass fiber filter. Then use another 20 ml of acetone, wash the bottle with this, and pass the liquid through the filter. Wash the filter paper with an additional 50 ml of acetone to insure that organic matter has been removed. Air dry the filter paper.

Pretreated samples:

With care, remove the supernatant from the upper layer of the solution in the BOD bottle. Add 75 ml of 1.27% ammonia solution (5 ml of ammonium hydroxide with 28.2% NH_3, specific gravity 0.897 at 60°F, diluted to 100 ml with water). Stir for 2 minutes and then filter through glass fiber filter, followed by washing with an additional 25 ml of ammonium hydroxide solution. Then use 50 ml of water to wash the residue on the filter.

Further removing of interference:

Set up distillation apparatus as shown:



Place the sample into A, apply a negative pressure, then add 3N HNO_3 to A by opening the valve on C. After acid in C has completely gone into A stop the pump. Then conduct N_2 to the system. The acid reduces the solubility of sulfide:

$$2H^+ + S^{-2} \longrightarrow H_2S_{(g)}$$

H_2S is carried out by the N_2 and absorbed by 1.25N NaOH in B. The purpose of the N_2 is to prevent the oxidation of sulfide:

$$S^{-2} + 2H^+ + O_2 \longrightarrow S_{(s)} + H_2O$$

which was experienced in previous experiments.

The samples from this method contain a high concentration of NO_3^-, which will cause negative interference in the iodometric method.

In the iodometric method:

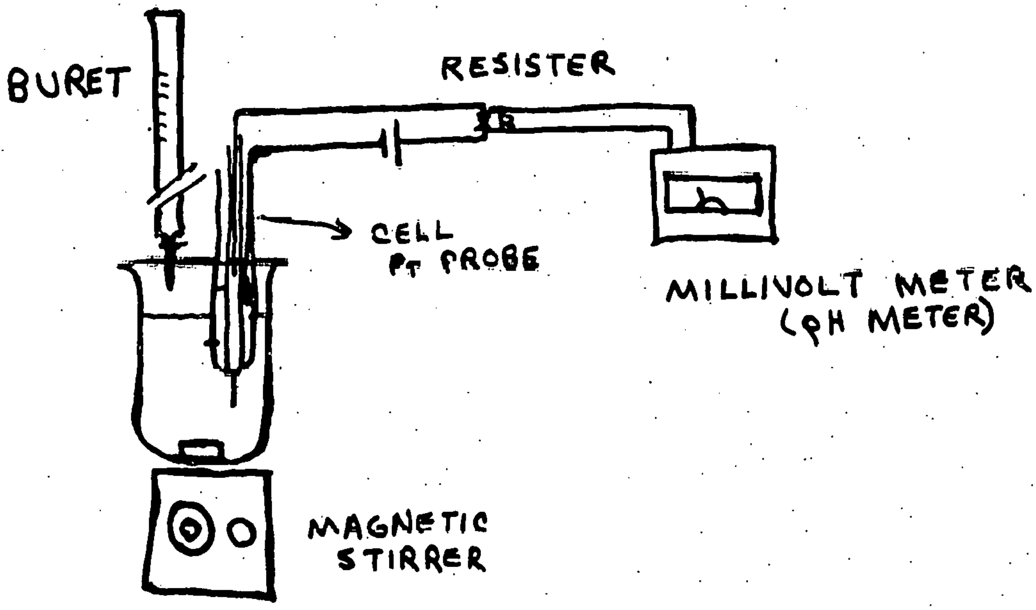
$$I_2 + S^{-2} \longrightarrow 2I^- + 2S$$

The NO_3^- in the solution will react with I^-:

$$4\,H^+ + NO_3^- + 3\,I^- \longrightarrow NOI + 2H_2O + I_2$$

Therefore, other methods should be applied; in this case we use the amperometric method.

The amperometric method of determining sulfide in the sample involves the apparatus shown:



In the titration excess $Pb(NO_3)_2$ was used to react with the sulfide:

$$Pb^{+2} + S^{-2} \longrightarrow PbS_{(s)}$$

$$Pb^{+2} + CrO_4^{-2} \longrightarrow PbCrO_4$$

The end point was determined by plotting the ml of titrant added against mv.

APPENDIX C

Method For Determination of Thiocyanate in Coal Gasification Wastewater Using a Modified Ferric Thiocyanate Spectrophotometric Technique (9)

Modified Ferric Thiocyanate Spectrophotometric Technique

REAGENTS:

(1) <u>1:1 HNO_3</u> - to 100 ml distilled water slowly add 100 ml concentrated HNO_3.

(2) <u>Ferric Nitrate Solution</u> - Dissolve 50 g of $Fe(NO_3)_3$ in 400 ml distilled water. Add 25 ml concentrated HNO_3 and dilute to 1 liter.

(3) <u>Standard Thiocyanate Solution</u> - Weigh 1.3956 g of NaSCN and dissolve in 500 ml distilled water. Dilute to 1 liter. One ml of of this solution contains 1 mg SCN^-. Standardize by Volhard's Method.

TECHNIQUE:

(1) Place a sample (which will yield 1-10 mg/1 SCN^- upon dilution) in a volumetric flask.

(2) Acidify using 1:1 HNO_3.

(3) Dilute to the mark with distilled water. If there is apparent turbidity, filter through S&S 589 (or equivalent) paper.

(4) Read absorbence of the "color" at 480 nm using distilled water at zero blank.

(5) To 45 ml diluted sample add 5 ml ferric nitrate reagent.

(6) Read absorbence at 480 nm using a reagent blank for zero absorbence.

(7) Use the following formula:

$$\frac{(A - B)\left(\frac{C}{D}\right) - E}{m} = \text{mg/1 } SCN^-$$

where: A = absorbence from Step 6

B = absorbence from Step 4

C = original sample volume (from Step 1)

D = final volume of diluted sample (from Step 3)

E = Y-intercept (from the calibration curve equation)

m = slope (from the calibration curve equation)

Prepare the calibration curve as for the modified Standard Methods procedure.

NOTES:

A series of eight determinations using this method took about 20 minutes to perform.

This method presupposes that the analyst knows the approximate volume of acid solution needed per sample aliquot and the approximate dilution needed to obtain an acceptable optical density reading.

APPENDIX D

Studies of Chloride Levels
in
Coal Gasification Wastewater

The analysis of the chlorides in the coal gasification waste liquor was complicated by various interferring ions, which were to be removed by following a procedure outlined by Luthy. This consisted of raising and lowering the pH, as well as oxidation with hydrogen peroxide and boiling to remove the then volatile substances. Results were inconsistent, with considerable variation in replicate determinations on the same sample. As an example, three runs were made with the same sample on 2/5/80. The results varied by 15.32 PPT. Compared with the generally permissible variation of 5 PPT, the results were unacceptable. Several other attempts were made, but were unsuccessful due to evident poisoning of the electrode.

After the electrode method failed, an attempt was made to use colorimetric reactions with potassium permanganate. Again, interferences made the end point undetectable. The interfering ions reacted with the permanganate, and no color change occurred, even with great excess of silver nitrate titrant.

The last method tried was to raise the pH with NaOH to about 10, and then dry the sample in an oven. The dried sample was then placed in a furnace and fired so as to remove all organics. It was felt that any chlorides would be left in the resulting ash. If consistent results could be obtained, standards would then be run to determine the amount of chloride lost in the process. Highly inconsistent results were obtained, and the process was discarded. One sample indicated a value of 37.9 grams/liter, while a similar sample, when titrated, showed 12.4 grams/liter. It is doubted that the samples could vary so much.

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