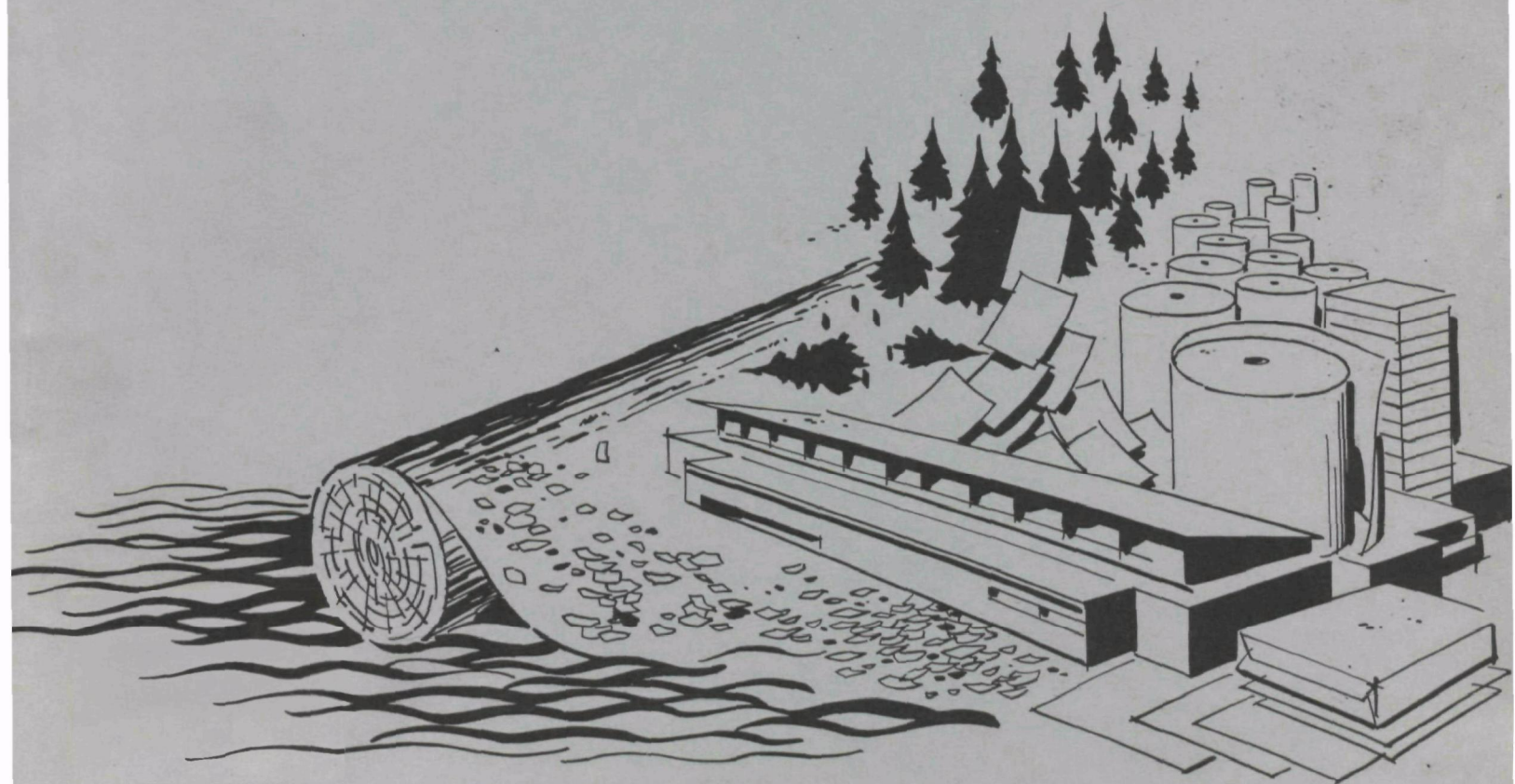# Treatment of Selected Internal Kraft Mill Wastes in a Cooling Tower

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# TREATMENT OF SELECTED INTERNAL KRAFT MILL WASTES
## IN A COOLING TOWER

BY

Georgia Kraft Company
Research and Development Center
Krannert Road
Rome, Georgia   30161

for the

ENVIRONMENTAL PROTECTION AGENCY

Program #12040EEK
Grant #WPRD 116-01-68
August, 1971

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# ABSTRACT

Pulp mill condensates, decker filtrate, and turpentine decanter underflow from an 850 ton/day kraft linerboard mill have been successfully treated in a conventional cooling tower. These waste streams, in combination with the condenser waters from a barometric type evaporator condenser, are cooled in the tower and reused. The overall accomplishments of this process are the removal of about 10,000 lbs of BOD per day and the reduction in overall mill water needs of about 8-10 MGD. Theoretical, laboratory, and pilot studies investigated the BOD removal mechanisms involved and proved that the predominant mechanism is stripping of volatile components. As a part of the laboratory studies a simple procedure called a static vapor-liquid equilibrium method was developed for collecting and analyzing low concentration volatile components in waste water. Mathematical relationships were developed which allow the translation of the findings of this study to other waste water treatment applications. The primary factors controlling BOD removal in this system are blowdown rate, liquid-gas ratio, and average temperature. For a blowdown rate of 15-20 per cent of the tower influent, average treatment efficiencies for the waste streams considered are 55-65 per cent for sixth effect condensate, 45-55 per cent for combined condensate and turpentine decanter underflow, and 25-35 per cent for decker filtrate.

The reduction in BOD of these waste streams is believed due primarily to the stripping of methanol. Some biological activity is evident in the tower, however, and the addition of nutrients results in an improvement of 5-10 per cent in BOD removal. The system has several advantages over the conventional surface condenser system used with kraft mill evaporators. Both operating and capital costs compare favorably with other waste-treatment methods.

This report was submitted in fulfillment of Project Number 12040EEK, Grant WPRD 116-01-68, under the (partial) sponsorship of the Office of Research and Monitoring, Environmental Protection Agency.


Key Words:  Sulfate pulping, pulp mills, water pollution, waste treatment, water reclamation, cooling towers, evaporators, condensers (liquefiers), biochemical oxygen demand, wastes, effluents, condensates, filtrates, methanol, stripping.

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# SECTION I

## CONCLUSIONS

Based on the theoretical and experimental results of this study, it is concluded that:

1. A cooling tower can function very effectively in providing reusable water for a barometric condenser used in connection with the evaporation cycle on a kraft pulping operation.

2. Through the use of the barometric condenser-cooling tower system a very significant reduction in water requirements for a kraft pulp mill can be accomplished (8-10 MGD for an 850 ton unbleached linerboard mill).

3. A cooling tower can achieve a 25-30 per cent reduction in the BOD discharged from a kraft mill.

4. The primary mechanism of BOD removal is physical stripping of volatile components.

5. Only minor improvement in BOD removal can be accomplished by adding supplemental nutrients to the tower feed.

6. Sixth effect condensate, combined condensate, turpentine decanter underflow, and decker filtrate can be treated in a cooling tower for BOD removal. The degree of removal will be directly related to the BOD of the volatile compounds present in the stream.

7. The cost of a cooling tower installation is essentially the same as the cost of converting from barometric condensers to surface condensers. However, when the reduced cost of subsequent waste water treatment is credited to the cooling tower, it is by far the most economical system.

8. As expected, there are emissions of reduced sulfur compounds from the tower; however, these are in the 1 to 2 ppm range and are not expected to cause any significant air pollution problem.

9. There have been no significant operating problems encountered in the operation of the cooling tower-condenser system. Minor foaming in the tower basin is easily controllable with minor additions of defoamers.

10. Preliminary studies of biological treatment of the blowdown from the cooling tower indicated that such treatment processes are not adversely affected by the concentrated waste waters.

# SECTION II

## RECOMMENDATIONS

1. The cooling tower-barometric condenser is performing a successful water pollution control demonstration. Final proof of the system's value and its comparison with other waste water treatment techniques rests in its ability to perform without significant maintenance or outages over a longer time period. Therefore, the system should be maintained in good operating condition and with normal data collection over an extended period. This will allow continued performance of a desired waste water treatment demonstration.

2. A more detailed study of the impact of this unit on air quality would provide specific answers to questions raised about its impact on odors in the mill vicinity. Additional facilities such as pre-stripping and burning devices could provide further minimization of atmospheric emissions from the system.

3. Future investigation of the optimization of this system with regard to BOD removal would allow its maximum development as a waste water treatment device.

4. Further research into relative volatilization rates of various compounds in water solutions would allow application of this process in other waste water treatment situations.

5. Better knowledge of the biological organisms and their life processes in the tower would more clearly define the role that these life forms have in the operation and maintenance function of the tower-condenser system.

# SECTION III

## INTRODUCTION

### Background Developments

The pulp and paper industry is vitally involved with the mounting problems in water pollution, since water performs a key role in the pulp and papermaking processes. Current processes require an average of approximately one-hundred tons of water to produce one ton of kraft linerboard and up to 400-500 tons of water per ton of paper is required for more refined and bleached grades. With an average of over one-quarter ton of paper being consumed annually by each person in the United States, the water requirement to meet this demand places the paper industry among the foremost users of the nation's water resources. The need, therefore, is urgent to seek methods for reducing water usage and improving waste water treatment. Georgia Kraft Company recognizes this need and constantly endeavors to advance the position of the industry, as well as its own position, with regard to environmental problems. The use of cooling towers to conserve water in kraft pulping came to the attention of Company personnel in previous studies as having extensive and undeveloped potential in water conservation and waste water treatment. This investigation was conceived to pursue that potential.

Several years ago it was discovered that cooling towers potentially might be used for reducing the water usage in pulp production. Cohn and Tonn (1) uniquely applied a novel cooling tower system to the multi-effect evaporators for one kraft pulp mill and found that by cooling and reusing barometric condenser water, fresh water consumption for the condensers could possibly be reduced as much as 95 per cent. While not all mills could expect to attain the indicated reduction in water usage, many mills have a serious waste treatment problem due to the common practice of using barometric condensers in their black liquor evaporator system. This practice leads to large volumes of water being mixed with condensed evaporator vapors, thus giving rise to a high-volume, low-BOD-concentration (a reference to BOD means five-day, 20°C test) effluent. Since it is impractical to process this large volume of dilute effluent in a waste treatment plant, many mills which treat their effluent have replaced the barometric condensers with the more expensive and less efficient surface-type condenser. While preventing contamination of the cooling water, the surface condenser still requires large volumes of cooling water and transmits a significant quantity of heat to the receiving stream. This heat in some situations may be an important source of pollution.

Personnel of Georgia Kraft Company demonstrated in a pilot plant study (2) at Macon, Georgia, that aeration in the cooling tower provides BOD reduction as well as cooling, and the operation of the cooling tower

could be interconnected with other internal mill streams to give still greater reductions in water usage and in mill effluent BOD. The study showed that in the Macon mill the evaporator condensate and the decker filtrate accounted for about 40 per cent and 15 per cent of the total BOD of the mill effluent, respectively. It was estimated that if these streams could be used as makeup for the water evaporated in the cooling tower, the need for using fresh cooling water from the river would be greatly reduced. The pilot study indicated that a 45 per cent reduction of the mill's total water requirements might be expected if such a process were installed. In addition, the cooling tower treatment process would produce some reduction in the thermal load on the river.

Although the results of the pilot studies were very encouraging, several important questions still needed answering before the technical and economic feasibility of the process could be established. The more important of these were:

1. Is the BOD reduction effected by the process due to stripping of organics by the air stream or to biological action occurring in the tower?

2. Will organic vapors emitted from the tower contribute to an air pollution problem?

3. How will the efficiencies of cooling and BOD reduction be affected by the concentration of solids in the recycled stream?

4. What are the operational problems involved in a full-scale system?

5. How reliable would this process be?

6. How sensitive would the efficiency of the cooling tower be to process upsets?

7. How do the economics of the process compare with other alternates?

Further work was clearly needed before the novel cooling tower operation could become commercially dependable.

After it was found that cooling towers had potential for BOD treatment, a literature review was made to determine if cooling towers had been used for this purpose before. There was very limited published information, but two industrial companies were achieving organic waste treatment in cooling towers. The Sun Oil Company (3) had constructed cooling towers to function simultaneously as water cooling and treatment devices, and the Celanese Corporation (4) had discovered that cooling towers were effective in removing acetone from their waste waters.

If proven feasible for use in the pulping industry, this treatment method could be envisioned as having extensive application in indus-

trial waste treatment and water conservation. With over one hundred kraft mills in the United States using multiple-effect evaporators and the widespread use of evaporators in the other industries, the cooling tower treatment process could represent a major contribution to the abatement of organic and thermal pollution of the nation's water resources.

## Proposal to Study the Treatment of Kraft Mill Wastes in Cooling Towers

The proven potential for reducing BOD and water usage and the prospective wide application of cooling towers in waste water treatment made the continued development and demonstration of the technique highly desirable. To carry out further work a request for a demonstration grant from the Office of Research and Monitoring, Environmental Protection Agency was made. The proposed project was intended to evaluate fully the technical and economic feasibility of using cooling towers to reduce the BOD and heat content of certain selected kraft mill effluents and to reduce the water usage of kraft mills. The specific objectives were:

1. To determine the efficiencies of BOD reduction and cooling as functions of cooling tower operating variables (liquid and air flow rates, temperatures, and composition and concentration of feed and recycled stream components).

2. To determine if organic vapors emitted from the tower would cause air pollution problems.

3. To determine which internal process waste waters can be effectively treated by this process.

4. To determine the mechanism of BOD reduction in the tower. i.e., how much reduction is due to stripping of organics by the air stream and how much is due to biological and chemical action.

5. To determine how sensitive the cooling and BOD reduction efficiencies will be to shock loadings and other process upsets.

6. To determine how the economics of this treatment process compare with those of alternate treatment processes.

7. To determine what operational problems were involved in continuous operation of a cooling tower on kraft mill wastes.

8. To collect engineering data which could be used for future design purposes.

9. To determine how this treatment process could be integrated with mill operations and subsequent treatment steps.

## Description of Proposed Cooling Tower System

The Office of Research and Monitoring, Environmental Protection Agency, approved the project as a demonstration grant, and Georgia Kraft Company undertook an extensive study that would result in the construction and evaluation of a full-scale cooling tower at its Macon, Georgia, pulp mill. The proposed system, as it would be included in the mill operation, is pictured in Figure 1. As shown by the figure, the envisioned installation takes barometric condenser water from the hot wells, cools it, and recirculates the cooled water to the direct contact condenser and the ejector for the non-condensable gases. Barometric legs below these units produce the vacuum for the multiple effect evaporators. Makeup water to the tower compensates for blowdown, spray losses, and evaporation. Waste streams in the pulp mill from which makeup water could be derived would be combined condensate from the evaporators, decker filtrate (wash water from final washing of pulp) and turpentine decanter underflow. Sixth effect condensate furnishes some of the makeup volume but is not a separable stream as are the other wastes mentioned. Since the barometric condenser consumes large volumes of water, the use of the cooling tower would reduce greatly the intake of fresh water from the river. Further, since several highly contaminated streams could be treated and used as makeup water for the cooling tower, a very significant reduction in BOD discharged from the pulp mill was expected. The proposed study was envisioned to evaluate which of these available waste streams should be used, how much BOD removal could be achieved, how much reduction in water usage would be obtained, and how practical and economical the process would be on a commercial scale. In addition to the ultimate demonstration of the practicality of the process, basic scientific data about the process would be sought.
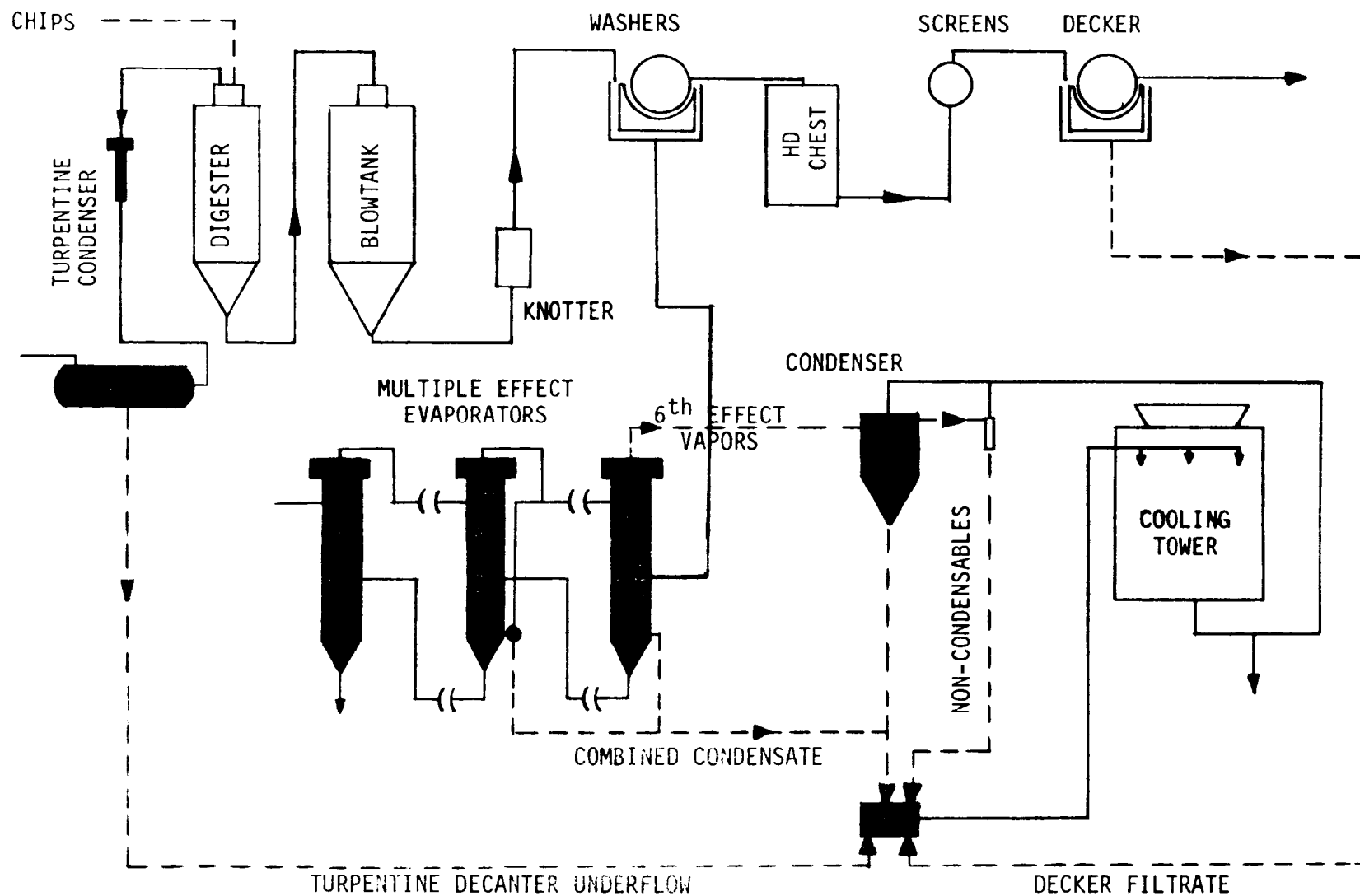
FIGURE 1: SCHEMATIC DIAGRAM OF PROPOSED FULL-SCALE COOLING TOWER SYSTEM

# SECTION IV

## ANALYSIS OF WASTE WATER STREAMS

### Standard Analysis of Waste Water Streams

To begin a fundamental study of waste water treatment in cooling towers, a thorough chemical and biochemical analysis was required. These data provided a basis for characterizing the waste waters, for evaluating treatment effectiveness, and for analyzing the treatment mechanisms involved. The characteristics usually employed for describing waste water streams include BOD, COD, solids, pH, conductivity, alkalinity, and, in this particular type of waste, sulfide content. Table 1 gives a typical description of the waste water streams investigated in this study and the range of variation in the characterizing measurements. The streams of interest were sixth effect condensate, combined condensate, decker filtrate, and turpentine decanter underflow.

The analyses given in Table 1 reveal only gross features of the nature of the waste streams. The BOD test results reveal the existence in the waste water of significant concentrations of biodegradable organic compounds. As is typical of most organic bearing waste, particularly pulp mill wastes, the COD analysis is greater than the BOD, indicating that all the oxidizable constituents were not biodegradable. Other features are that all of the streams are alkaline, essentially all of the solids in the stream are dissolved, and a sizable fraction of the dissolved solids are volatile, implying again the presence of organic materials. It should be noted that the very volatile organic constituents would escape detection in the dissolved solids test due to the nature of the test. Sulfide, though present, constitutes a very small fraction of the oxygen demand.

The results of Table 1 were derived from standard analytical tests. These tests were adopted for the duration of the study and with one exception, which is discussed in the following section, the procedures were taken from a text on standard methods for analyzing water and waste water streams (5). The exception was the sulfide ion content, and this was determined by a modified TAPPI procedure (T-625ts-64) using an Orion sulfide electrode.

### Analysis of Volatile Materials

Development of Analytical Method - While standard analytical data furnished a generalized characterization of the waste streams, a more comprehensive examination was needed to determine the composition of the volatile materials and to estimate their involvement in the air stripping processes present in cooling tower operation. From previous

## TABLE 1

### CHEMICAL COMPOSITION OF STREAMS TO BE TREATED IN TOWER

| | 6th Effect Condensate[1] | | | Combined Condensate[2] | | | Decker Filtrate[2] | | | Turpentine Decanter Underflow[3] |
|---|---|---|---|---|---|---|---|---|---|---|
| | Avg. | Max. | Min. | Avg. | Max. | Min. | Avg. | Max. | Min. | Average |
| BOD - mg/l | 1360 | 1600 | 810 | 722 | 833 | 610 | 900 | 1166 | 633 | 8180[4] |
| COD - mg/l | 4225 | 5222 | 3039 | 982 | 1192 | 771 | 1823 | 2068 | 1577 | 7100 |
| pH | 9.7 | 10.7 | 8.7 | 7.4 | 7.4 | 7.3 | 9.0 | 9.9 | 8.2 | 9.9 |
| Solids: | | | | | | | | | | |
|   Total, mg/l | 2850 | 4036 | 1492 | 388 | 480 | 276 | 1808 | 2404 | 1212 | 260 |
|   Dissolved, mg/l | 2820 | 3986 | 1540 | 280 | 384 | 176 | 1632 | 2104 | 1160 | 220 |
|   Total Volatile, mg/l | 1133 | 1348 | 736 | 224 | 244 | 204 | 1194 | 1560 | 828 | 39 |
|   Dissolved Volatile, mg/l | 1188 | 1320 | 676 | 186 | 196 | 176 | 962 | 1268 | 656 | 21 |
| Conductivity, umhos | 1600 | 2600 | 500 | 260 | 270 | 250 | 1150 | 1500 | 800 | 480 |
| Total Alkalinity, mg/l as $CaCO_3$ | 498 | 862 | 114 | 39 | 52 | 26 | 450 | 534 | 366 | 500 |
| Phenolphthalein Alkalinity, mg/l as $CaCO_3$ | 162 | 378 | 14 | 0 | 0 | 0 | 54 | 108 | 0 | 430 |
| Sulfide, mg/l | 43 | - | - | 2 | - | - | 16 | - | - | 520 |

(1)  Five sets of data from Rome plant.
(2)  Two sets of data from Macon plant.
(3)  One set of data from Rome plant.
(4)  Seven sets of data from Macon plant.

studies on the Macon pilot cooling tower, it was suspected that air-stripping was one of the major treatment mechanisms; and it became necessary to identify the strippable components. The qualitative identification, quantitative estimation, and the determination of the oxygen-demanding (BOD) characteristics of each of these volatile components was needed to establish the basis for a fundamental evaluation of the overall potential of the proposed processes. An analytical method was not directly available to achieve the required measurements; initial work, therefore, had to be devoted to the development of a suitable method of analysis.

Studies in the air pollution control field (6, 7, 8) provided some insight into analytical procedures for these volatile emissions from kraft mills. These studies were helpful in the analysis of the volatile components but did not resolve the problem of determining the concentration of such components in a waste water stream. In connection with a SEKOR (Stripping Effluents for Kraft Mill Odor Reduction) study, Hruitfiord and McCarthy (9) identified methyl mercaptan, dimethyl sulfide, acetone, methanol, ethanol, and methyl isobutyl ketone, as well as the more common hydrogen sulfide and carbon dioxide gases, in digester blow gas condensate. Bethge and Ehrenborg (10) working in Sweden confirmed this analysis of blow gas condensate; and Ruus (11), also a Swedish researcher, reported quantitative data on the concentration of hydrogen sulfide, methyl mercaptan, dimethyl sulfide, methanol, ethanol, and acetone found in various effluent and condensate streams from kraft pulp mills in his country.

For the purpose of this study several methods of analysis had to be evaluated to develop a suitable analytical procedure. Since the gas concentrations were very low, the gas chromatograph was particularly suited for a test method and was used in all cases. A Perkin-Elmer Model 881 gas chromatograph, equipped with a flame ionization detector, a recorder, and an Infotronics CRS-104 Integrator served as the analytical instruments. Separations were made on a 6 ft, 1/8 in. column of 15 per cent Carbowax 20M on 100-120 mesh Chromosorb W operated at 70°C with a helium flow of 30 cc/minute.

The search for an analytical method began with an attempt to analyze cooling tower off gases directly. This proved unsuccessful because the high degree of dilution brought about by the large volumes of air necessary for operation of the cooling tower produced concentrations below the detectable limits of the gas chromatograph.

In the next method considered, stripping action of the cooling tower was simulated in a bench-scale apparatus. With this unit, a gas (air or nitrogen) was sparged slowly into a fixed volume of condensate which was maintained at constant temperature. The off gases were conducted directly to the gas sampling loop of the gas chromatograph. This method was quite satisfactory for qualitative work; however, concentrations of some components in the discharged gases changed

very rapidly upon initial stripping, and it was impossible to relate vapor concentrations to the concentrations in the liquid phase.

To circumvent the problem of the changing vapor concentrations, an attempt was made to condense and to collect all the stripped vapors by freezing in a dry ice-acetone mixture. It was intended that the collected materials would be subjected to further analysis by gas chromatography. But this procedure was also regarded as unsatisfactory because the cold trap was not sufficiently chilled with dry ice and acetone to collect all of the stripped organic vapors. Perhaps this method could be improved by the use of liquid nitrogen in the cold trap.

Another possible means of collecting off gases was to absorb them on activated carbon and then extract with a solvent. The carbon readily absorbed all of the vapors; however, the solvents generally used, e.g., chloroform, ethyl ether, and petroleum ether, interferred with analysis on the gas chromatograph. The relatively large amount of solvent present tended to hide the characteristic peaks of most of the compounds of interest on the gas chromatogram. The change to a high boiling point solvent may have solved the interference problem; but it would have increased the time for gas chromatographic analysis by as much as two to three times or would have been retained on the column to be eluded slowly giving poor baseline stability. Further consideration might have been given to the use of carbon disulfide as an extraction medium as this solvent reportedly does not show up on a flame ionization detector.

After these several attempts failed to provide completely satisfactory results, a scheme--referred to as the static vapor-liquid equilibrium method--was developed. The liquid sample was placed in a 500 ml flask, the flask was sealed with a serum cap, and then the flask with contents was placed in a constant temperature bath at 55°C. After sufficient time was allowed for vapor-liquid equilibrium to be established, usually 30 to 60 minutes being required, a vapor sample was removed by inserting a syringe needle through the cap, and the vapor sample was injected into the chromatograph. The method gave very reproducible results.

A second method which was found satisfactory for quantitative analysis of the more concentrated components involved direct injection of a known volume of the liquid condensate sample into the gas chromatograph. Concentrations of the gaseous components could be determined by comparing the measured peak used on the chromatogram to a previously determined calibration curve.

Compound Identifications - Once a method was available which would give reproducible results and could be relied upon to show small changes in the composition of condensates, the problem of identifying and quantify-

ing the gas chromatographic peaks required solving. Figure 2 represents a typical chromatogram.

To identify the peaks on the chromatograms of condensate samples, a series of dilute water solutions of pure compounds were prepared. Chromatograms of these pure compounds were made using the static vapor-liquid equilibrium method. The retention times of the known compounds were then compared with those of the unknown peaks of the condensate sample. In the earlier work in which stripped vapors were condensed in a cold trap, it was possible to obtain enough concentrated condensed vapors for infrared analysis, and this analysis strongly suggested that acetone and methyl alcohol were present. Thus, retention times were determined for these compounds along with many others suggested by the literature and some which were used simply to satisfy scientific curiosity. The known compounds tested, in addition to methyl alcohol and acetone, were ethyl alcohol, methyl mercaptan, methyl sulfide, dimethyl sulfide, formaldehyde, acetic acid, ethyl sulfide, α-pinene, β-pinene, isopropyl alcohol, acetaldehyde, ethyl mercaptan, and ethyl ether. A study of the retention times of these compounds indicated that ethyl alcohol, formaldehyde, acetic acid, ethyl sulfide, β-pinene, isopropyl alcohol, formaldehyde, ethyl mercaptan, and ethyl ether could be eliminated as the major components of the evaporator condensate samples.

A further step was taken to tie the analysis down more closely. A sample of the condensate was prepared and subjected to the static vapor-liquid equilibrium method for determining the gas chromatogram. Then a small amount of the suspected pure compound was added to the sample, and after establishment of the new equilibrium, another chromatogram was obtained. Addition of a pure compound amplified one of the peaks without any evidence of peak splitting. This method was used to confirm six of the typical peaks as methyl mercaptan, methyl sulfide, acetone, methanol, α-pinene, and methyl disulfide. The others were eliminated as possible components when it was determined that their peaks were not exactly coincident with those of the unknown sample.

It was recognized that the identification procedure as outlined did not constitute complete proof of identity; it was, however, regarded as very substantial evidence, particularly since previous investigators had found the named compounds in their work which was similar. Further proof of these assignments would have required the collection of sufficient amounts of the separated components using a preparative gas chromatograph followed by infrared or possibly NMR analysis.

For quantitative analyses, the static vapor-liquid equilibrium method was used to prepare calibration curves for the six identified compounds. With the pure compounds, solutions of known strength were prepared and curves of concentrations versus the peak areas as determined by the integrator were plotted. The pH of the standard solution had to be adjusted to approximately the same value as the samples to be

A. UNKNOWN
B. METHYL MERCAPTAN
C. METHYL SULFIDE
D. ACETONE
E. METHYL ALCOHOL
F. α-PINENE
G. METHYL DISULFIDE
H. UNKNOWN
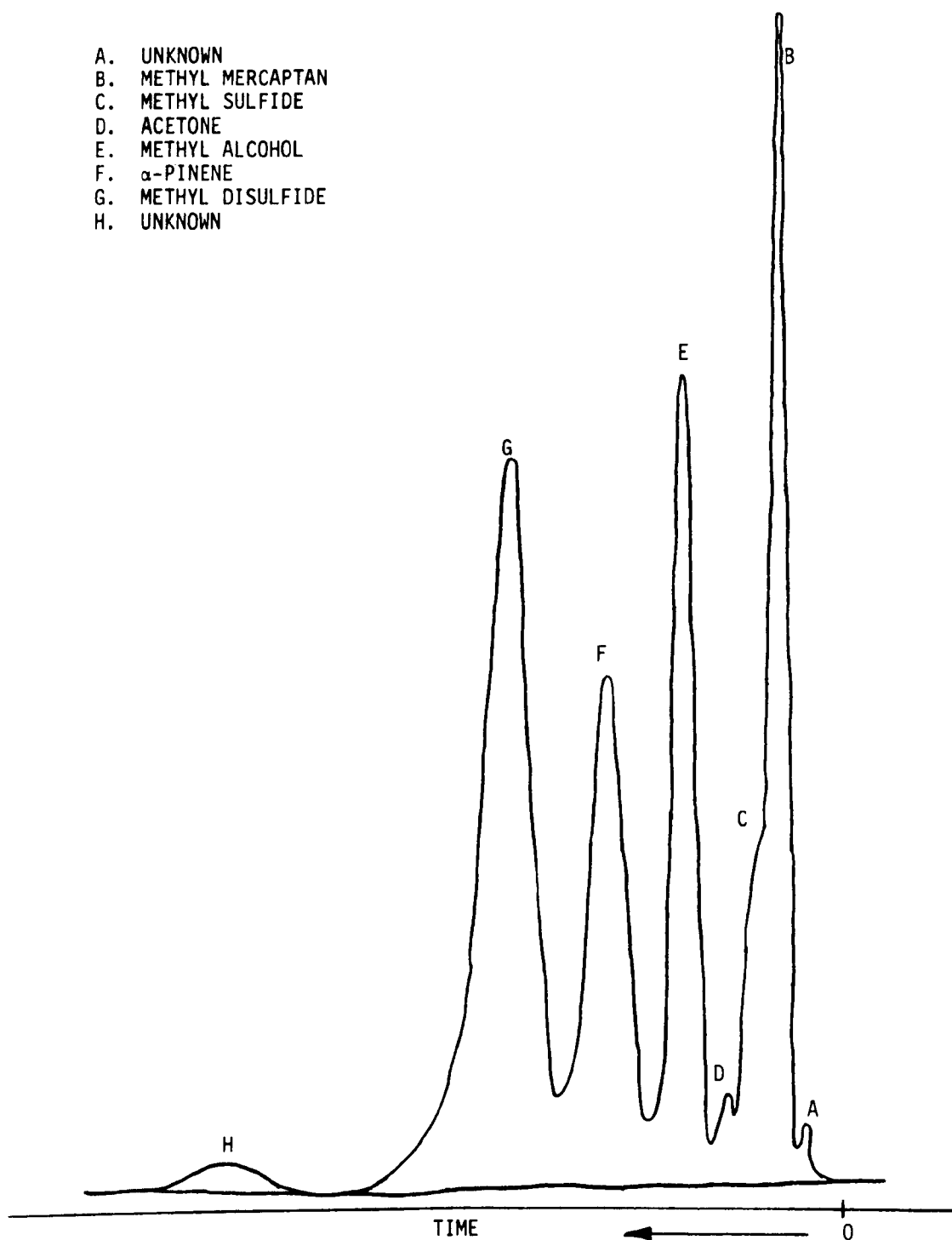


FIGURE 2: TYPICAL GAS CHROMATOGRAPH TRACE FOR EVAPORATOR CONDENSATES

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analyzed. The effect of pH was dependent upon the substance; for example, if pH were not adjusted, an error as low as 1 per cent/pH unit variation would be introduced for acetone and as high as 30 per cent/pH unit variation for methyl mercaptan. The samples in this study were constantly within 1/2 pH unit and no adjustment was made.

With the described analytical method, a number of samples of evaporator condensates from each of the Georgia Kraft Company mills were analyzed. The results are given in Table 2. Methanol appears to be the major organic component of evaporator condensates with only minor amounts of other compounds present.

## TABLE 2

### SUMMARY OF VOLATILE COMPOUNDS IN KRAFT MILL EVAPORATOR CONDENSATES

| Sample | No. Sample | Methyl Mercaptan (ppm) Avg. | Max. | Min. | Methyl Sulfide (ppm) Avg. | Max. | Min. | Acetone (ppm) Avg. | Max. | Min. | Methyl Alcohol (ppm) Avg. | Max. | Min. | α-Pinene (ppm) Avg. | Max. | Min. | Methyl Disulfide (ppm) Avg. | Max. | Min. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6th Effect Condensate Krannert | 4 | T | T | T | .2 | .2 | .1 | 3 | 4 | 2.5 | 1100 | 1350 | 950 | 1.4 | 2.0 | T | 6.5 | 13.9 | 2.6 |
| Combined Condensate Krannert | 10 | T | T | T | .5 | .6 | .1 | 2.0 | 2.2 | T | 400 | 500 | 310 | .2 | .4 | T | 5.2 | 6.5 | 2.5 |
| 6th Effect Condensate Macon | 4 | 1.8 | 6.6 | T | T | T | T | 1.8 | 3.0 | 1.0 | 950 | 1300 | 350 | T | T | T | .7 | 2.8 | 1.2 |
| Combined Condensate Macon | 20 | 3.0 | 10.7 | T | T | .1 | T | 1.3 | 4.5 | .1 | 245 | 490 | 100 | T | T | T | .1 | .8 | T |
| Combined Condensate Mahrt | 2 | 6.2 | 11.0 | T | T | .2 | T | 4.0 | 7.0 | 1.6 | 670 | 710 | 620 | T | T | T | 5.2 | 6.0 | 1.0 |
| Turpentine Decanter Underflow - Macon | 7 | 1934 | 10000 | 23 | 224 | 900 | 3 | 150 | 210 | 0 | 4386 | 6500 | 2575 | 148 | 363 | 18 | 284 | 490 | 155 |
| Cooling Tower Feed | 10 | 1.0 | 3.6 | T | .1 | .2 | T | .5 | .9 | T | 120 | 190 | 50 | T | T | T | .8 | 2.0 | T |
| Cooling Tower Blowdown | 10 | .7 | 3.1 | T | .1 | .3 | T | .3 | .6 | T | 80 | 125 | 33 | T | T | T | .2 | .4 | T |

T = Trace

# SECTION V

## MECHANISM OF BOD REMOVAL

### Possible Mechanisms

The identification and quantitative description of the BOD removal
mechanisms were among the primary objectives in the investigation of
waste water treatment in cooling towers, and considerable effort was
expended on this phase of the project. From the beginning it was ap-
parent that air stripping of volatile compounds was very likely a major
treatment mechanism; but it was important that all mechanisms be
thoroughly investigated. A careful evaluation of all the basic pro-
cesses operating in a cooling tower and a review of past experience
in treating waste waters suggested three possible mechanisms. These
were: air stripping of volatile compounds, biological action, and
chemical oxidation. Experimental results from the Macon pilot cooling
tower and the more recent study of volatile compounds in kraft mill
waste waters suggested that treatment was, to a great extent, due to
the stripping of volatile organic materials from waste water by atmos-
pheric air. Further, from previous experience with trickle filters in
treating kraft mill effluent (12), it was known that waste water,
raining through a high void packing in a manner very similar to water
falling through a cooling tower, is reduced in BOD when bacteria are
caused to grow on the packing surfaces by the addition of suitable
nutrients. Finally, because of the intimate contact of the waste water
with atmospheric air, there was some possibility that chemical oxida-
tion could occur. A series of experiments was designed and conducted
to test for the presence and the relative effects of the three postu-
lated mechanisms.

### Laboratory Sparging Studies

Comparison of Chemical Oxidation and Air Stripping - Chemical oxidation
and air stripping could be separated and their relative effectiveness
determined by sparging a small amount of liquid with nitrogen and with
air. Sparging with nitrogen would produce only stripping, while air
sparging would produce both stripping and oxidation. No biological
action would be present if the system were kept sterile and no nutri-
ents were added to support biological growth. Experiments of this type
were conducted in a sparging unit consisting of two four-liter flasks
with appropriate connections being provided for the introduction and
release of the sparging gases. The gases were released into the waste
water through a sintered glass diffuser located near the center and at
the bottom of the flask. The gases in the form of small bubbles rising
rapidly in the vicinity of the diffuser provided a continuous mixing of
the liquid contents. The flasks were immersed in a constant tempera-
ture bath to provide temperature control.

So that the results of the bench experiment would be indicative of the cooling tower processes, the gas rates and amount of liquid used were determined from the operating parameters used in previous studies with the pilot cooling tower. It resulted that two liters of liquid should be sparged for 62.6 hours at a gas rate of 400 cc/min. These conditions were estimated to be equivalent to a tower air flow rate of 400 ft/min, a liquid flow rate of 4 gal./min/ft$^2$. The data from these experiments (shown in Table 3 and Appendix A) revealed that the treatment by chemical oxidation was small. The study showed that stripping with air resulted in only slightly greater treatment than that obtained by the stripping action of pure, inert nitrogen alone. Also, it appeared from the measurements that the stripping of organic constituents was dominantly the only significant BOD removal mechanism.

Comparison of Biological Action and Air Stripping - The sparging experiments, as described for air and nitrogen, were conducted for periods up to three days and were not suitable for investigating biological action. Other more lengthy sparging experiments were performed for periods up to a month in a "Bio-oxidation Unit".[1] The longer period of operation was required to allow the biological action to establish itself and become operative. The unit was operated as a completely mixed system similar to an aerated lagoon. The experimental apparatus consisted simply of a small (about 9 liters) rectangular chamber through which waste water fortified with biological nutrients was passed. The unit was started by seeding with biological growth from the trickling filter in the Rome mill waste treatment plant. The unit was then fed sixth effect condensate from the Rome mill with nutrients added. The nutrients consisted of ammonium nitrate and phosphoric acid added in the ratio of 100:5:1 for BOD, nitrogen, and phosphorus, respectively. The liquid feed rate was from 1 to 7 mls per minute, and the air rate was adjusted as low as would maintain some oxygen content in the liquid. The use of different feed rates gave different liquid retention times in the treatment process. The unit was operated at room temperature.

Visual observation of the activity inside the unit revealed that the biological organisms immediately attached themselves to all surfaces exposed to the waste water; however, there seemed to be considerable suspended solids also. The attaching phenomenon was not surprising considering the source of the micro-organisms. As time passed with continued feeding, an increase in suspended solids and a gradual decrease in quantity of attached organisms were noted.

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(1)  A standard laboratory apparatus purchased from BioDevelopment Associates, P. O. Box 1752, Austin, Texas  78767, for investigating biological oxidation.

## TABLE 3

### COMPARISON OF AIR SPARGING AND NITROGEN SPARGING TO TREAT SIXTH EFFECT CONDENSATE

| Experiment | Sparging Time (hrs) | BOD Removal* | | | COD Removal* | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | Initial $BOD_5$ (mg/l) | After Sparging With Nitrogen (mg/l) | Air (mg/l) | Initial COD (mg/l) | After Sparging With Nitrogen (mg/l) | Air (mg/l) |
| 1 | 48.0 | 1600 | 1460 | 1210 | 5080 | 4039 | 3794 |
| 2 | 51.0 | 1380 | - | - | 5222 | 4769 | 4731 |
| 3 | 22.0 | 1400 | 1166 | 966 | 4019 | 3541 | 3618 |
| 4 | 71.5 | 1366 | 1033 | 900 | 3704 | 3136 | 2744 |
| 5 | 29.0 | 810 | 770 | 600 | 3039 | 2115 | 2404 |
| 6 | 62.0 | 843 | 850 | 800 | 1830 | 1675 | 1618 |

(*)  Experimental Conditions:  $135^{O}F$, 400 cc/min gas flow, liquid volume 2 liters; detailed data given in Appendix A.

The bio-oxidation unit was operated for approximately one month. Table 4 summarizes the BOD reduction experienced at various liquid retention times. These results showed that waste water would sustain and propagate the growth of micro-organisms which in turn remove the dissolved organic constituents. The high percentages of removals of 96.4 and 98.0 per cent were achieved by a combination of air stripping and biological oxidation. With the short retention time the BOD removals were only 14.5 and 49.3 per cent. Since the liquid residence time in a cooling tower operation is short, biological action would appear not to be a very effective removal mechanism.

## TABLE 4

### EFFECT OF ADDING NUTRIENTS TO AIR SPARGING OF SIXTH EFFECT CONDENSATE IN "BIO-OXIDATION" UNIT

| Experiment | Liquid Retention Time (hrs) | Feed BOD (ppm) | Effluent BOD* (ppm) | BOD Removal* (%) |
|---|---|---|---|---|
| 1 | 96.0 | 990 | 19.8 | 98.0 |
| 2 | 36.5 | 641 | 23.3 | 96.4 |
| 3 | 16.2 | 1214 | 616 | 49.3 |
| 4 | 18.2 | 1000 | 863 | 14.5 |

*For experimental conditions, see text.

## Mechanism Investigations in Laboratory Cooling Towers

Comparison of Chemical Oxidation and Air Stripping - While the basic laboratory sparging experiments had shown that air stripping was the major reduction mechanism and that biological action and chemical oxidation were essentially insignificant, it was desirable that these mechanisms be investigated further under conditions more nearly like those found in a full-sized cooling tower. For this purpose a laboratory cooling tower was designed large enough to retain the principle features of a typical industrial installation, yet small enough to allow the processing of the air and liquid streams with conventional laboratory devices. The tower was constructed as described in Appendix "B" and had features similar to a conventional counterflow cooling tower.

Again, experiments were conducted to evaluate the effects of operating with air and with nitrogen, and the experimental technique was a batch operation very similar to the previous laboratory sparging experiments. A known volume of waste water was added to the basin of the cooling tower and recirculated through the tower as shown in Figure 3. The falling of the liquid through the tower packing was a better simulation of the actual tower operation than air sparging. So that a comparison could be made of chemical oxidation and air stripping, the tower was operated first with compressed air and then in a subsequent experiment with nitrogen. It was necessary to operate the tower in a forced draft fashion rather than an induced draft because nitrogen was furnished by commercial compressed gas cylinders and pressure feeding was the better method of supplying the gas to the tower. Compressed air was used for the experiment complementary to the nitrogen test so that the results from both operations would be comparable. Two sets of experimental data were obtained and treatment was determined both as BOD removal and as methanol removal. These data plotted in Figure 4 provide dramatic evidence of the low contribution of chemical oxidation. It was concluded that chemical oxidation for all practical considerations was nonexistent.

Comparison of Biological Action and Air Stripping - To provide proof that biological action also was a very minor treatment mechanism, actual evaluations were made in the laboratory cooling tower. In these experiments, it was necessary to employ two identical cooling towers (Figure 5) constructed according to specifications in Appendix "B" to separate biological action from the other mechanisms. Operation with two identical towers provided for one tower to operate on air stripping alone and the other, being seeded with bacteria and fed with nutrients, to operate on air stripping and biological action. If it could be assumed, as was done in other mechanism studies, that no synergistic effects were produced, the treatment due to the effect of biological action could be derived from the difference in performance of the two towers.

In the tower operating with biological growth it was necessary to operate this system continuously for about one month to prepare a well developed biological culture within the tower. Experiments were performed when the bacterial growth had covered the tower packing surface to the extent that portions of growth would slough off and fall into the basin.

Figure 6 presents a summary of the experimental results, showing treatment as a function of liquid-to-gas ratio, which was the controlling independent variable for the experimental conditions. Blowdown flow rate was also a significant variable and changed from a low value of 50 mls per minute at the low liquid-to-gas ratio to a high value of 400 mls per minute at the high liquid-to-gas ratio. The direct correspondence between these two variables made it possible to study the
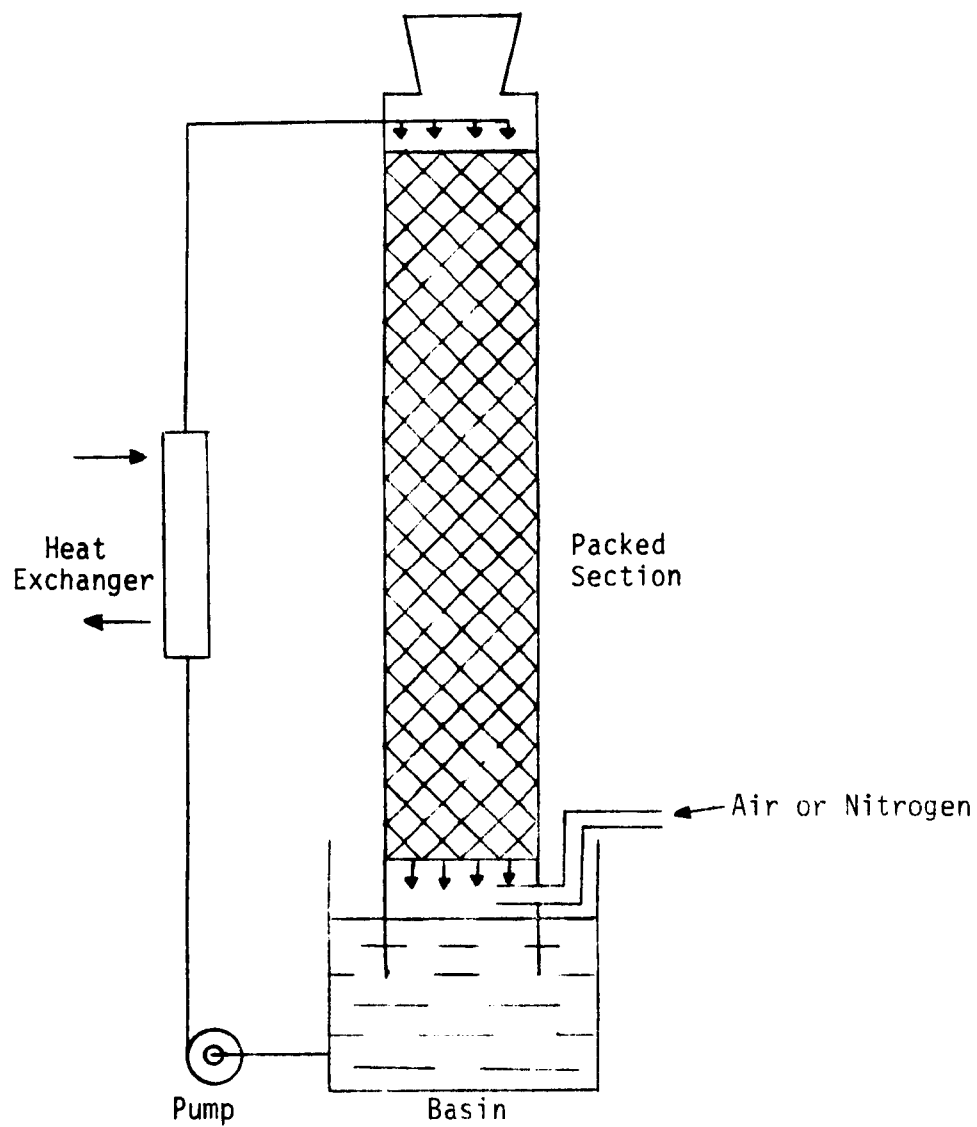
FIGURE 3:  PILOT COOLING TOWER FOR BATCH STRIPPING EXPERIMENT
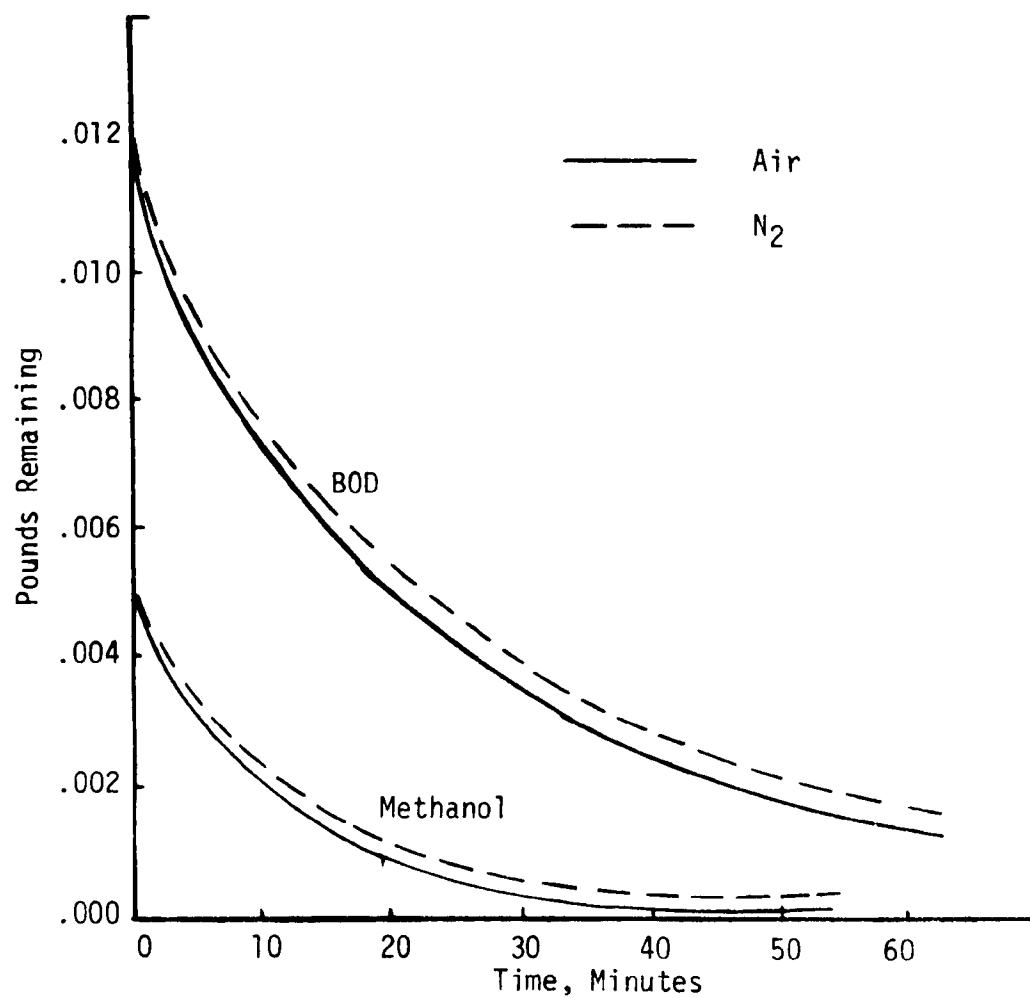
FIGURE 4: COMPARISON OF STRIPPING WITH NITROGEN AND AIR
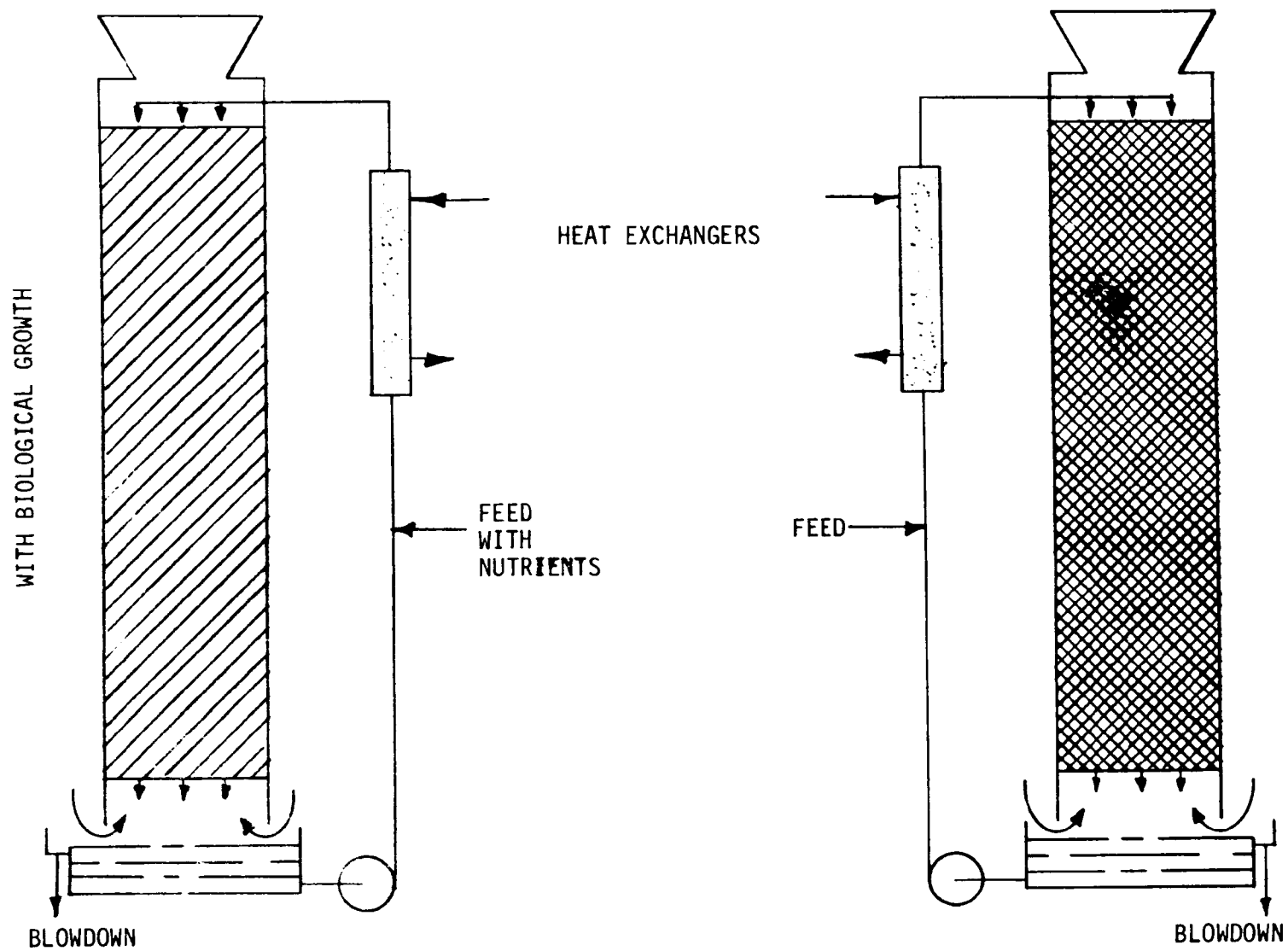
FIGURE 5: PILOT COOLING TOWERS FOR COMPARISON OF STRIPPING AND BIOLOGICAL TREATMENT
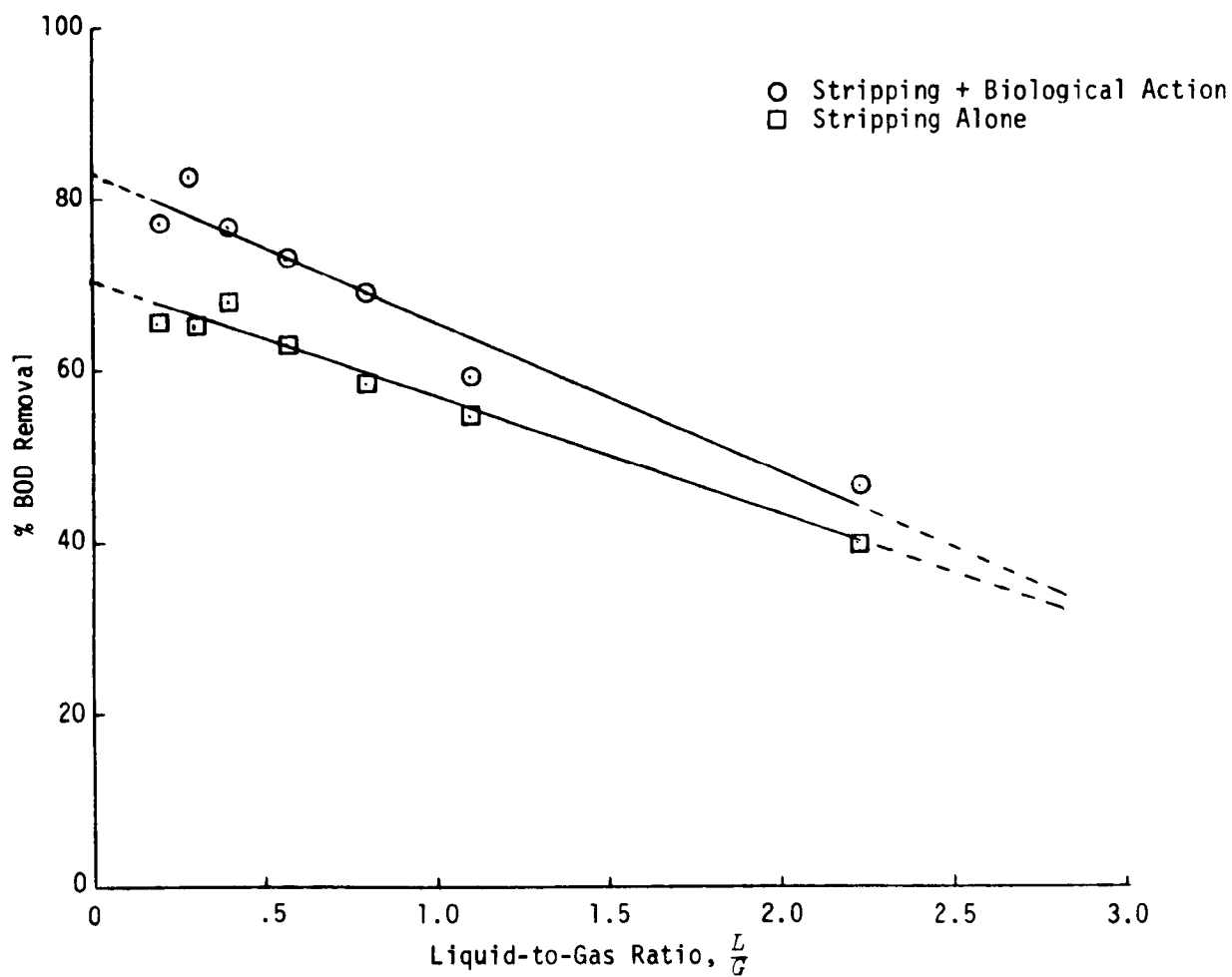
FIGURE 6: COMPARISON OF BOD REMOVAL BY STRIPPING AND
BIOLOGICAL MECHANISMS IN PILOT TOWER

degree of treatment as a function of either blowdown or liquid-to-gas ratio. The relation derived in Figure 5, therefore, distinguished between stripping and biological action, but did not represent treatment as a pure function of liquid-to-gas ratio. The experimental points represented averages of all data for a particular liquid-to-gas ratio. The complete experimental data are given in Appendix "C".

The basic significance of the experimental findings was that biological action produced from 4 to 12 per cent more BOD removal than did stripping alone. The effect of biological action was dependent on the liquid-to-gas ratio and appeared to increase with decreasing liquid-to-gas ratio, as would be theoretically expected. Similarly, with stripping alone, a decreasing liquid-to-gas ratio increased BOD removal, and this removal approached the maximum as the liquid-to-gas ratio decreased to zero. This maximum was the volatile BOD content of the waste water system. Biological action in simultaneous operation with stripping could produce greater BOD removal since the biological reactions could attack the non-volatile portion of the BOD-producing compounds. While this additional treatment was an advantage, the amount of increased treatment would not appear to justify the additional operational costs encountered to achieve it.

SECTION VI

ANALYSIS OF STRIPPING

## Theoretical Developments

Exploratory experimentation found extensive proof that air stripping was the predominant treatment mechanism and the treatment process was further elucidated by the successful identification of the volatile materials involved and the explanation of their apparent removal from the aqueous phase during passage through the cooling tower. It still remained, however, to relate the stripping process quantitatively to the operating variables of the cooling tower. Hence a mathematical description of the process was sought.

A mathematical framework was developed by first determining the variables that define the stripping produced in a cooling tower. The functional dependence was expressed by the notation:

$$R = f(x, B, G, L, t_1, t_{wb})$$ (1)

where $R$ = Fraction removal of volatile component in feed water to the cooling tower

$x$ = Concentration of volatile component in liquid phase

$B$ = Blowdown rate

$G$ = Gas rate

$L$ = Total liquid rate to tower (feed plus recirculation)

$t_1$ = Inlet temperature of water in tower

$t_{wb}$ = Wet bulb temperature of entering air

These variables were believed to be both necessary and sufficient to describe the cooling tower system, and with them it should be possible to determine uniquely the treatment due to stripping. The problem then encompassed finding the specific relationship represented by the functional notation.

As in all mass transfer processes, the composition of the transferrable materials in the interacting phases was of prime importance. Fortunately, in this analysis the description of the mass transfer process

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could be considerably simplified due to the low concentration of vola-
tile materials involved. Under these conditions, Henry's Law was valid
and for a gas-liquid equilibrium system the concentration of a gas
phase, volatile component $(y)$ could be described as being directly pro-
portional to the liquid phase concentration $(x)$. Thus,

$$y = k_h x \qquad (2)$$

In the cooling tower, equilibrium was not attained between the contact-
ing gas and liquid phases, but equilibrium was approached to approxi-
mately the same degree at all points along the height of the cooling
tower. With this background, it was envisioned that a small volume of
liquid progressing through the tower would not be in equilibrium with
the surrounding gas phase, but the gas phase composition of the trans-
ferring component at any height, $z$, in the column would be

$$y_Z = k \cdot k_h x_{LZ} \qquad (3)$$

This led to the assumption that under constant operating conditions the
amount of volatile material removed by the system $(Tx_T)$ was a constant
fraction of that entering the tower $(Lx_{L1})$, hence

$$Tx_T = KLx_{L1} \qquad (4)$$

The constant, $K$, was defined as the stripping constant and proved to be
a very satisfactory parameter for describing the fundamental mass trans-
fer process. By work that is described later in this report and by
other theoretical work (Appendix G), it was shown that $K$ was independent
of the concentration level of the volatile BOD-producing materials in
the waste water being treated. The constant was dependent, however, on
variations of the chemical makeup of the volatile compounds, on the
tower packing material, and also on temperature and the gas-to-liquid
ratio.

The constant, $K$, as defined, represented the transfer of volatile
materials to the air from a fixed volume of liquid as it passed once
through the tower. The treatment derived from the tower then had to
be a function of the recirculation rate of waste water through the
cooling tower; and recirculation, in turn, was determined by the un-
treated water feed to the tower and blowdown from the tower. Increased
recirculation of waste water through the tower would increase the num-
ber of times a given volume of waste water would pass through the tower
and would, therefore, affect the ultimate treatment accomplished on

this volume of liquid. A series of material balances on the major streams depicted in Figure 7 showed that treatment in the tower could be described with the relationship,

$$R = \frac{K(1 + \frac{B}{L_1})}{K + \frac{B}{L_1}} \tag{5}$$

and $K$ could be evaluated from the equation,

$$K = (1 - \frac{x_{L1}}{x_{L2}}) \tag{6}$$

Up to this point, the theoretical developments were based on the definition of the stripping constant, $K$. The heat and mass transfer processes, however, could be analyzed by starting with the first principles of classical theory, such as described by Treybal (13) or Bird et al. (14). The classical differential equations in a packed tower were

$$dh = \frac{dz}{HTU_H} (h^* - h) \tag{7}$$

and

$$dy = \frac{dt}{HTU_M} (y^* - y) \tag{8}$$

which could be transformed with the aid of heat and material balances over a section of the tower to

$$dt = \frac{dz}{HTU_H} \cdot \frac{1}{(\frac{L}{G})} \left[ h^* - \frac{L}{G} (t - t_1) + h_1 \right] \tag{9}$$

$$dx = \frac{dz}{HTU_M} \cdot \frac{1}{(\frac{L}{G})} \left[ y^* - (\frac{L}{G}) (x - x_1) \right] \tag{10}$$

These equations had to be solved simultaneously because $y^*$ was very temperature-dependent for volatile compounds such as methanol, which constituted a large portion of the volatile BOD-producing materials.

$G$ = Lbs dry air/hr
$y$ = Lbs Volatile mat'l./lb. dry air
$T$ = Lbs water vapor/hour; = 1
$x_T$ = Comp. of volatiles expressed as lbs volatile/lb $H_2O$
$t_{1,db}$ = °F
$t_{1,wb}$ = °F

Exhaust Air

Tower Water Feed
$L_1$, lbs/hr
$X_1$, Comp
$t_1$, °F

Packed Section

Feed Water
$F$, lbs/hr
$x_F$, Comp.

$dz$ Height $z$ ft

Recirculating Water
$N$, lbs/hr
$x_2$ Comp.

Treated Water
$L_2$=Lbs/hr
$x_2$ Comp.
$T_2$ °F

Inlet Air

$G$ = Lbs dry air/hr
$y_2$ = Lbs Volatiles/hr = 0
$t_{2,db}$ = °F
$t_{2,wb}$ = °F

Basin

NOTES:
1. $x_{comp}$ denotes composition of treatable materials or treatable BOD.
2. Average tower temperature = $\dfrac{t_1 + t_2}{2}$

Blowdown
B = Lbs/hr
$x_2$= Comp.
$t_2$= °F

FIGURE 7: SCHEMATIC DIAGRAM FOR USE IN MATHEMATICAL DEVELOPMENTS

The analysis of a set of data with these equations began with the determination of $HTU_H$ and $HTU_M$ from experimental data. Then, after $HTU_H$ and $HTU_M$ had been determined for a given tower configuration, it was possible to use the fundamental equations to evaluate the effects of entering liquid temperature, liquid and air flows, and wet bulb temperature on the removal of volatile components. Due to the complexity of these relationships, it was found advisable to use a numerical procedure with a digital computer to accomplish the required computations.

The determination of $HTU_H$ and $HTU_M$ began with the assumption of a value for $HTU_H$. Equation (9) was then employed in a numerical procedure to calculate the temperature profile along the column height. Upon reaching the top of the tower, the calculated water temperature was compared with the actual, experimental temperature. If there was a discrepancy, the assumed $HTU_H$ was corrected and the calculation repeated until agreement was obtained. After the temperature profile was established, it was possible to construct the profile for $y^*$ versus $z$. Then by using Equation (10), $HTU_M$ could be calculated by trial and error in a way similar to that employed for $HTU_H$. The test for a current solution was the agreement of $x_2/x_1$ and the calculated $x_2/x_1$.

Once the constants $HTU_H$ and $HTU_M$ have been established, the heat and mass transfer characteristics of the tower under study were completely determined and a set of conditions could be examined. Thus for any initial condition of inlet wet and dry bulb temperatures, inlet liquid temperature, and liquid-to-gas ratio, the terminal conditions of the air and liquid streams could be evaluated.

In performing the calculations as outlined, it was learned that $x_2/x_1$, and thus $K$, was independent of the absolute concentration of dilute volatile materials of interest in this study. The result was regarded highly significant in validating the assumptions used in defining $K$, and also in applying $K$ in design calculations. The theory was applied only to methanol rather than to all the BOD-producing compounds; but, since methanol was the major contributor to the volatile BOD content, it should be an excellent indicator of the overall process. The analysis in Appendix "G" verifies the relationship.

The primary application of the theoretical work was to determine what degree of treatment could be expected from conventional cooling tower equipment when operated on waste water as was done in this study. The theory is applied to the data described in the following section.

## Experimental Developments

Experimental Technique - A very effective experimental method involving nonequilibrium conditions was devised for laboratory studies of stripping. The experimental procedure consisted of charging the cooling tower basin with a known volume of waste water to be tested and then

circulating the liquid through the tower and observing the change of concentration with time. No feed was added to the tower after filling the basin and no blowdown was withdrawn. Operation in this manner was time-dependent and would not appear to embrace a simple mathematical description. It resulted, nevertheless, that a simple balance of the material entering and leaving the system would give an equation which would accurately and quickly determine the stripping constant $K$. From the ultimate BOD content that could be reached by prolonged treatment, the procedure gave directly the amount of volatile BOD in the original waste water. Analysis of the operation[2] showed that the BOD in the cooling tower as a function of time was

$$x_2 = x_1 \left[ 1 - \frac{aQt}{V_0} \right]^{\frac{K-a}{a}} \tag{11}$$

Equation (11) shows that as time progresses during the stripping operation, the concentration of methanol declines from its initial value of $x_0$. The quantity, $a$, in equation (11) was computed from the experimental data by:

$$a = \left[ V_0 - V_F \right] tQ \tag{12}$$

where $V_0$ and $V_F$ were the initial and final liquid volumes in the basin (i.e., at $t = o$ and $t = t$).

---

(2) The disappearance of BOD, $x$, could be expressed as a first order process according to the relation

$$\frac{d(Vx)}{dt} + KQx = 0$$

where $V$ was the liquid volume in the system at time, $t$, and $Q$ was the constant liquid recirculation rate. The rate of liquid disappearance could be expressed as

$$\frac{dV}{dt} = aQ$$

where $a$ was the constant water evaporation rate. Mathematical manipulation of these equations gave

$$\frac{dx}{x} = (a - K) \frac{Qdt}{V_0 - aQt},$$

which, when integrated, was Equation (11).

The important utility of Equation (11) was obtaining $K$ from the experimental data. Taking the logarithms of both sides of the equation yielded:

$$\log x = \log x_0 + \left(\frac{K - a}{a}\right) \log \left[1 - \frac{aQt}{V_0}\right] \qquad (13)$$

or

$$\log x = \log \left(\frac{x_0}{V_0}\right) + \left(\frac{K - a}{a}\right) \log \left[V_0 - aQt\right] \qquad (13a)$$

It can be seen from this equation that a log-log plot of $x$ versus $(1 - aQt/V_0)$ resulting in a straight line would have a slope of $\left(\frac{K - a}{a}\right)$ from which $K$ may be calculated.

The analysis of stripping thus far was developed for a single component. The result, nevertheless, was equally valid for multicomponent systems. The detailed treatment of the latter, more general case is presented in Appendix "G".

Investigation of the Methanol Stripping Constant: (Description of Experiments) - A comprehensive series of tests was conducted to determine the practical significance of the theoretical developments. Initially, attention was given specifically to methanol which represented the major volatile constituents in the waste stream systems, and experimental results were based on methanol concentrations instead of BOD. Thirty-one experiments were performed consisting of 26 experiments with Rome sixth effect condensate, two with Macon combined condensate, two with Macon decker filtrate, and one with a methanol-water mixture. The experiments were the non-steady state type usually lasting from 40 to 60 minutes with one exception lasting 228 minutes. The duration of the experiment was determined by the amount of initial charge of waste water. The air flow velocities were variable in the range of 200 to 600 feet per minute, and the liquid loading--that is the recirculation rate--ranged between 1.00 and 4.00 gallons per minute per square foot. A steam-heated heat exchanger maintained a liquid temperature of 125°F at the top of the tower, and this temperature was manually controllable within ±3°F. The top temperature was maintained constant for all runs. The basin temperature was determined by the process operating conditions. The temperature and humidity of the entering air were at the ambient conditions of the laboratory. The dry bulb temperature in all cases was close to 75°F, but the relative humidity was more widely variant between 50 and 90 per cent. Data from each experiment included initial charge volume, liquid flow rate, air flow rate, final charge volume, total elapsed time of the experiment, methanol concentration, and BOD concentration. Table 5 shows two typical sets of data from the batch stripping experiments, while complete data are given in Appendix "D".

## TABLE 5

## EXAMPLE DATA FROM NON-STEADY STATE STRIPPING EXPERIMENTS

Experiment 7-22
Methanol-Water

Experiment 7-23
Rome 6th Effect Condensate

Initial Volume = 12.0 liters

Initial Volume = 30.0 liters

Final Volume = 4.0 liters

Final Volume = 6.24 liters

Duration of Experiment = 52 mins

Duration of Experiment = 228 mins

Liquid-to-Gas Ratio
$(L/G) = 1.35 \dfrac{lbs/H_2O}{lbs\ dry\ air}$

Liquid-to-Gas Ratio
$(L/G) = 1.35 \dfrac{lbs\ H_2O}{lbs\ dry\ air}$

| Time (mins) | Methanol Concentration (mg/l) | Time (mins) | Methanol Concentration (mg/l) |
|---|---|---|---|
| 0 | 590 | 0 | 645 |
| 5 | 340 | 30 | 260 |
| 11 | 170 | 60 | 80 |
| 15 | 130 | 90 | 25 |
| 20 | 75 | 120 | 8 |
| 30 | 40 | 150 | 4 |
| 40 | 35 | | |

(Analysis of Data) - The experimental data were reduced to yield the variables in Equation (13), the quantities $(V_0 - aQt)$ and $x$ being of primary interest. A log-log plot of these two variables resulted in graphs as typically illustrated in Figure 8.

This plot shows several aspects of the nature of trace component removal by batch stripping. The first plot shows that with increasing time (i.e., as the system volume is reduced) the concentration of the volatile component decreases. Also, the functional relationship between these variables is logarithmic, demonstrated by the straight line correlation of data on log-log coordinates. Equation (13) predicts this type of behavior if the ratio $\left(\dfrac{K - a}{a}\right)$ is a constant.

All experiments were displayed on a log-log graph of the type shown in Figure 8, and the data produced a linear graph in all cases. The linear behavior was observed over three cycles of methanol concentration, and from this result it could be firmly concluded that $K$ ($K$ being the stripping constant based on methanol concentration measurements rather than BOD) was independent of methanol concentration. This

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10.0

System Volume $(V_0 - aQt)$

1.0

0.1

1.0    5.0   10.0                    100.0                  1000

Methanol Concentration,   mg/l

△   6th Effect Condensate; Initial Volume = 12 liters;
    pH 10.3
○   6th Effect Condensate; Initial Volume = 30 liters;
    pH 10.2
□   Synthetic waste composed of 10 mls methanol in
    12 liters of initial water volume; pH 9.9
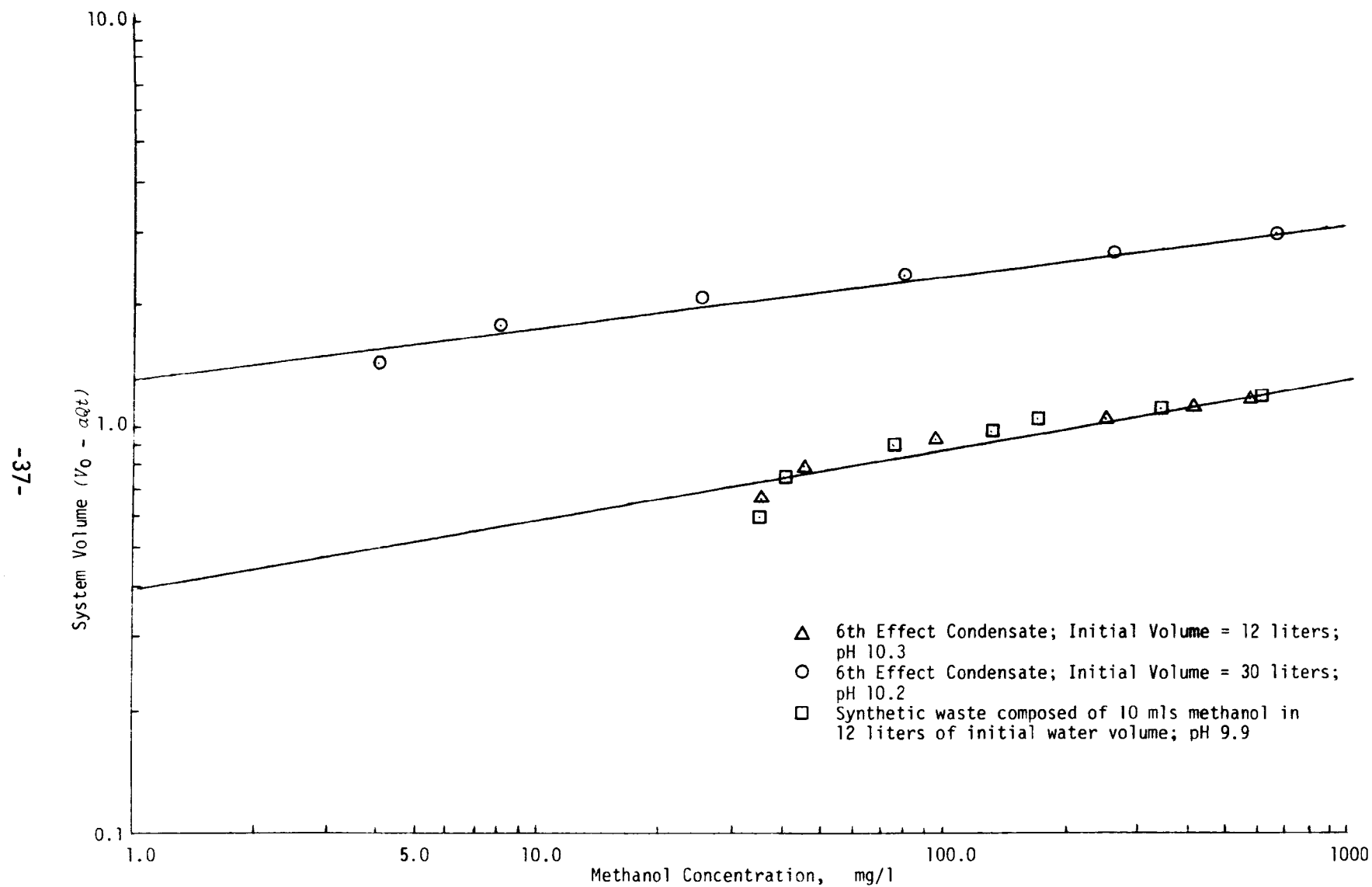
FIGURE 8:   STRIPPING EXPERIMENT - BASIN VOLUME VERSUS METHANOL CONCENTRATION

result did not mean that $K$ would not vary from day to day or would not vary with different waste waters. It did mean, however, that for a specified set of volatile components $K$ would be constant.

(Effects of $L/G$) - Since concentration did not affect methanol removal and since temperature was held constant, it was possible to concentrate on the effects of liquid and air flow rates on treatment. These two variables could be studied by operating the stripping experiments at various liquid-to-gas $(L/G)$ ratios, where $L$ was the liquid phase flow rate (waste water recirculation) in pounds per minute and $G$ was the gas phase flow rate (air) in pounds of dry air per minute.

For this analysis Equations (9) and (10) were used. As described in the theoretical development section, the constants $HTU_H$ and $HTU_M$ could be evaluated numerically with the aid of a computer. Several sets of experimental data from the laboratory cooling tower were analyzed in this manner. After those values were derived, they could be inserted in Equations (9) and (10), and the performance of the laboratory cooling tower could be evaluated for any other set of operating conditions. Figure 9 shows the theoretical line resulting from the numerical analyses of Equations (9) and (10). This theoretical evaluation was based on an assigned inlet wet and dry bulb air temperature which was on the average representative of the individual experiments. The individual experiments shown on the figure were calculated from Equation (10).

Figure 9 shows that the relationship between $K$ and $L/G$ was a nonlinear one. The result would be expected since the gas phase removed the volatile constituent and the use of less air, that is higher liquid-to-gas ratio, would produce less stripping. The scatter in the calculated data resulted from the uncontrollable variation of the wet bulb temperature of the entering air. Although the water temperature at the top of the tower was maintained at approximately 125°F, the bottom (basin) temperature fluctuated with changes in the inlet wet bulb temperature of the air. This affected the entire temperature profile in the tower and the volatibility of methanol which directly varied $K$. Despite the amount of scatter in the experimental data, it was obvious that low $L/G$ values (i.e., high air rates for a fixed liquid rate) resulted in more efficient treatment.

(Effect of Temperature) - Finally, a series of experiments were conducted to evaluate the effect of water temperature on the air stripping of methanol. Figure 10 summarizes the results and clearly demonstrates that increasing the water temperature in the tower increases treatment. This behavior was predictable by theory as denoted by the theoretical line, and was derived from the numerical manipulation of Equations (9) and (10). While the results of these experiments were for methanol only, any volatile material would be expected to behave similarly with some variations in the slope of the curve because of difference in vapor pressures.
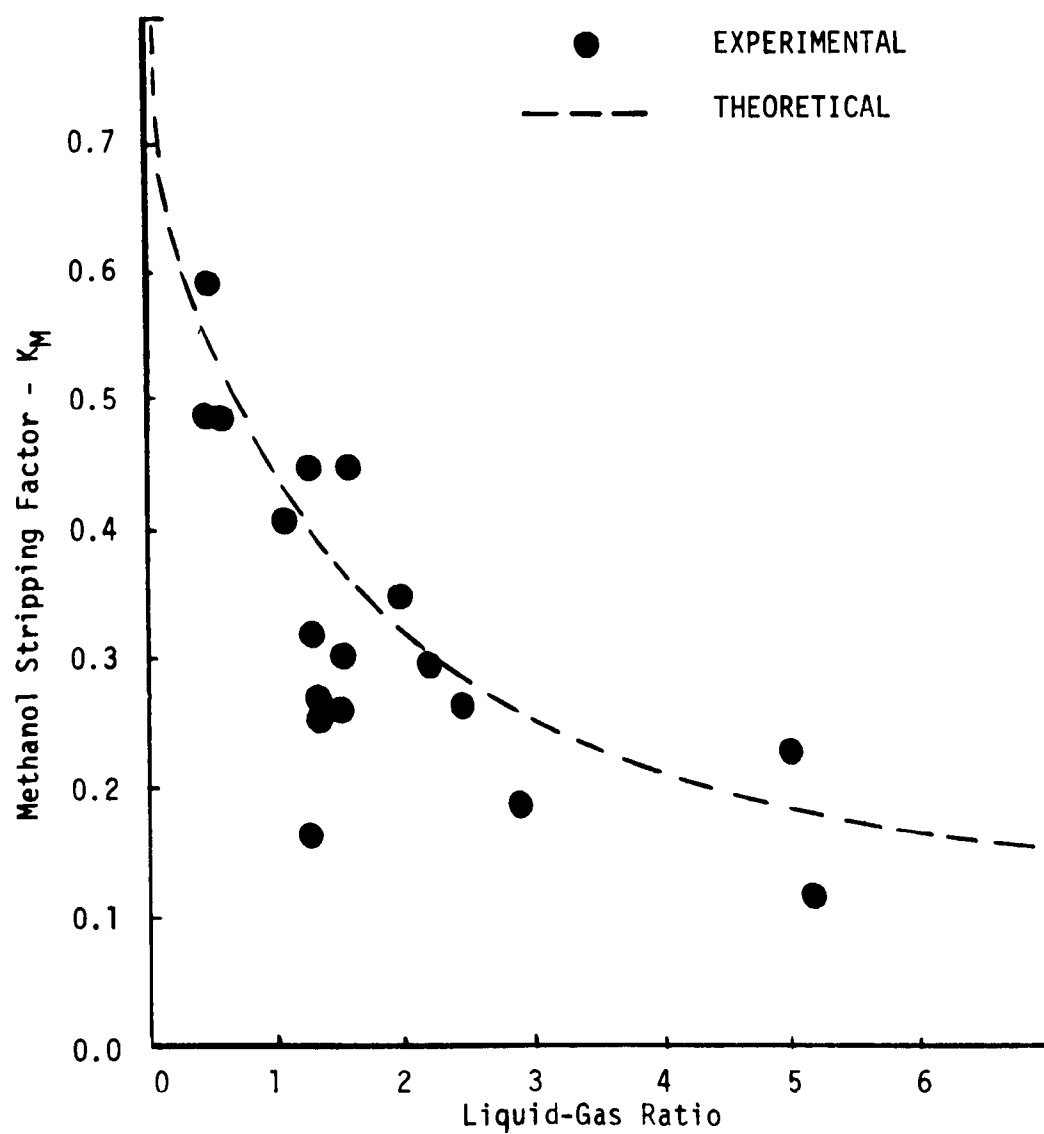
FIGURE 9:  EFFECT OF LIQUID/AIR RATIO ON STRIPPING
OF METHANOL IN A PILOT COOLING TOWER
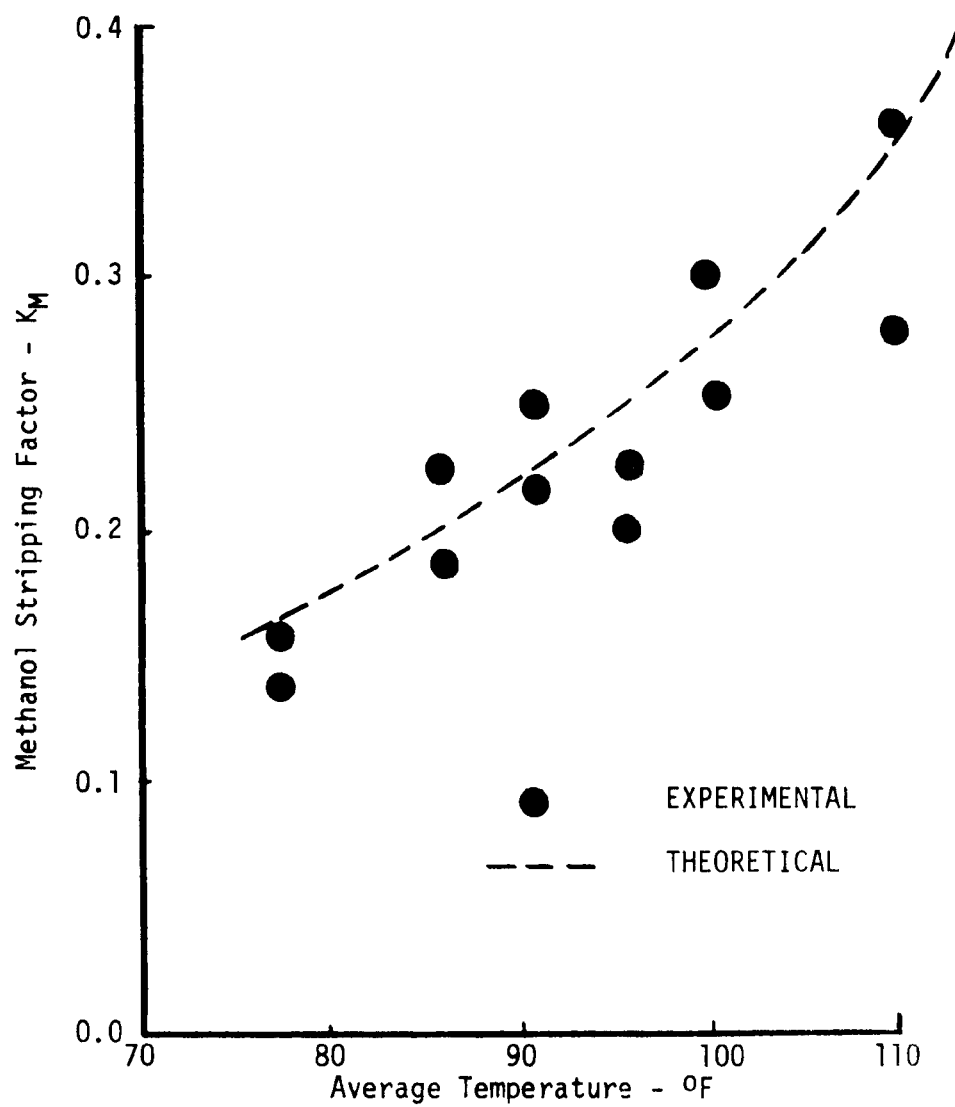
FIGURE 10:   EFFECT OF LIQUID TEMPERATURE ON STRIPPING
OF METHANOL IN A PILOT COOLING TOWER

Investigation of Overall BOD Stripping Constant - The foregoing strip-
ping studies, involving only methanol, yielded a very significant
insight into the operation and capabilities of cooling towers as
strippers of volatile components from the water phase. Paper mill waste
water, however, consisted of many constituents, both volatile and non-
volatile. It was necessary, therefore, to investigate the effects of
the remaining constituents on treatment by stripping. An experimental
program was carried out identical to the one performed on methanol ex-
cept that BOD of the waste water was obtained in addition to the meth-
anol concentration during a batch experiment.

Due to the fact that BOD was more difficult to determine as accurately
as the concentration of methanol and, at the same time knowing that both
volatile and nonvolatile constituents were contributing to the BOD
properties of the waste waters, it was necessary to employ a slightly
different treatment of the experimental data. Equation (13) was still
the basic guideline, but being based on the material balance of volatile
components, it could not be quantitatively applied in its existing form.
It could, however, be used to suggest ways of presenting and verifying
the results of the batch experiment involving BOD measurements. Instead
of employing concentration directly, the fraction of the original BOD
in the waste, ( 1 - R), was defined by:

$$(1 - R) = \frac{xV}{x_0 V_0} \tag{14}$$

where $x$ was BOD concentration and $x_0$ being the initial concentration

and    $V$ was the quantity of material remaining in the basin with $V_0$ being
       the initial liquid charge to the tower and basin.

This definition provided a  dimensionless indication of BOD treatment.

The maximum time for an experiment $(t_m)$ was limited by the initial quan-
tity of material charged to the system $(V_0)$, by the fraction of water
vaporized $(a)$, and by the liquid recirculation rate $(Q)$ and was computed
by

$$t_m = \frac{V_0}{Qa} \tag{15}$$

This maximum time provided a basis by which experimental results involv-
ing various operating conditions could be normalized if a dimensionless
time variable were defined as

$$\Theta = \frac{t}{t_m} \tag{16}$$

where $t$ was the time during the experiment and $t_m$ was the final or maximum time of the experiment.

A total of 14 batch experiments were performed on two samples of Rome sixth effect condensate. The results of these experiments are given in Figures 11 and 12. Both figures show that as $\Theta$ increases (i.e., time increases) the fraction of the original BOD remaining decreased rapidly at first and more slowly for longer $\Theta$. These results are particularly significant because they show the fraction of the original BOD that is not strippable, and this unstrippable BOD represents the nonvolatile components. The data show that 16 to 31 per cent of the original BOD of this waste water was not volatile in one case (Figure 11) and in the other case (Figure 12) the nonvolatile portion was 11 to 23 per cent of the initial BOD. If the data are plotted according to Equation (13), the resulting log-log plot is a straight line showing that $K$ is a straight line for the volatile BOD. Figure 13 presents such a plot for one set of data. The relationships between $K$ and volatile BOD are discussed in more detail in Appendix "G".

Although the experiments were performed with sixth effect condensate exclusively, the series of experiments with the batch stripping technique proved that this selected mill waste water contained a volatile BOD of 69 to 89 per cent of the total BOD, and this placed an upper limit on the degree of treatment that could be expected from air stripping of a waste water of this type.

Significance of Batch Stripping Experiments - The batch stripping type of experiment had the particular advantage of providing a very convenient and simple method of determining the amount of volatile BOD contained in the waste water being tested. The knowledge of the volatile BOD content indicates immediately the extent of treatment that can be attained by stripping. From $K$, it is possible to predict the actual treatment in a cooling tower. Since the thermal characteristics of most cooling towers have been completely determined, the volatilization rate, $a$, of water in the tower is known. Hence the equation

$$R = \frac{K \left(1 + \frac{B}{L}\right)}{K + \frac{B}{L}} \tag{5}$$

can be written in terms of relative volatility. Thus

$$R = \frac{\left(\frac{K}{a}\right)(a)\left(1 - \frac{B}{L}\right)}{\left(\frac{K}{a}\right) a + \frac{B}{L}} \tag{17}$$
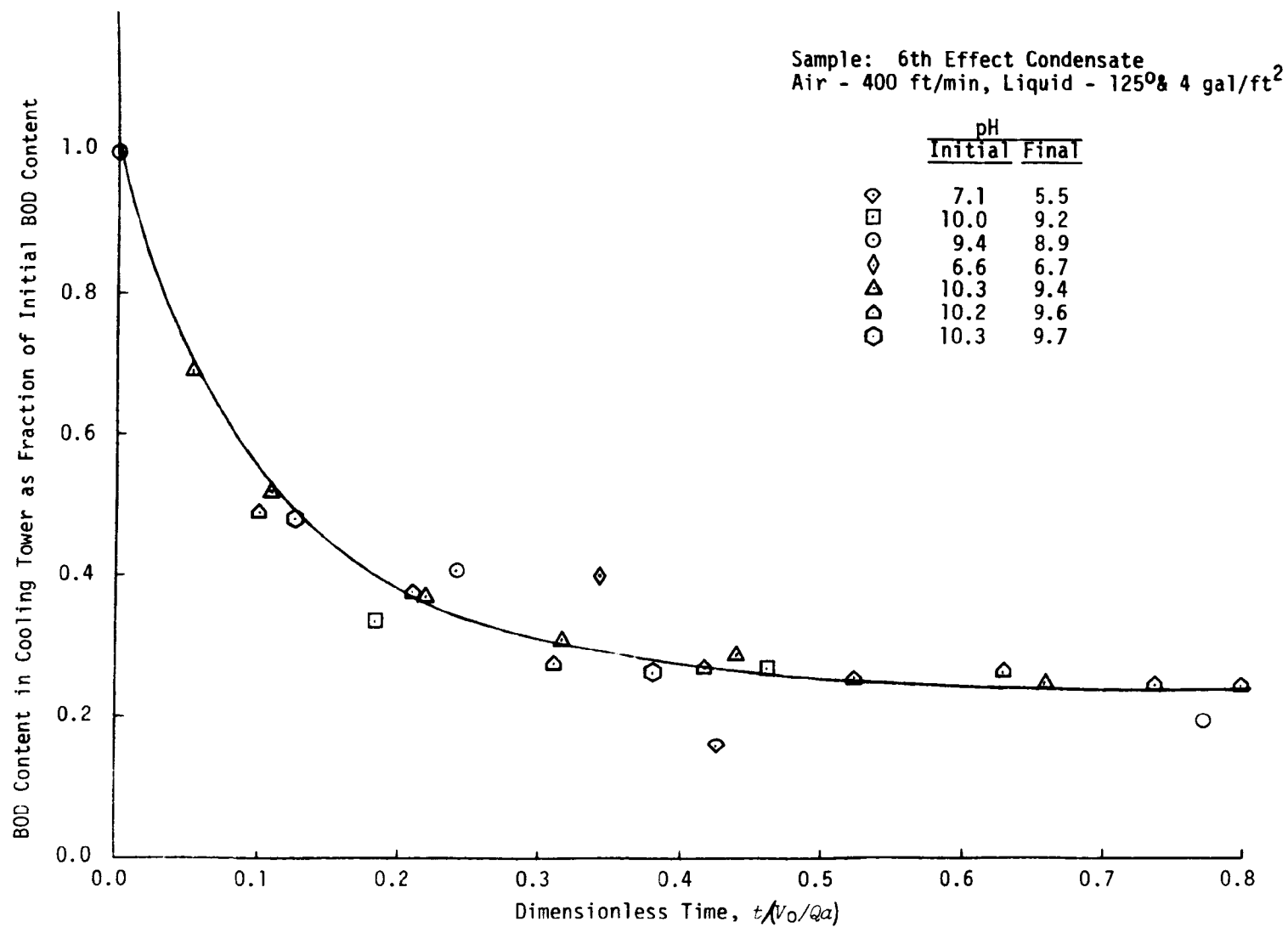
FIGURE 11: STRIPPING EXPERIMENT - FRACTION OF BOD REMAINING VERSUS DIMENSIONLESS TIME, ROME 6TH EFFECT, 7-15-68 SAMPLE
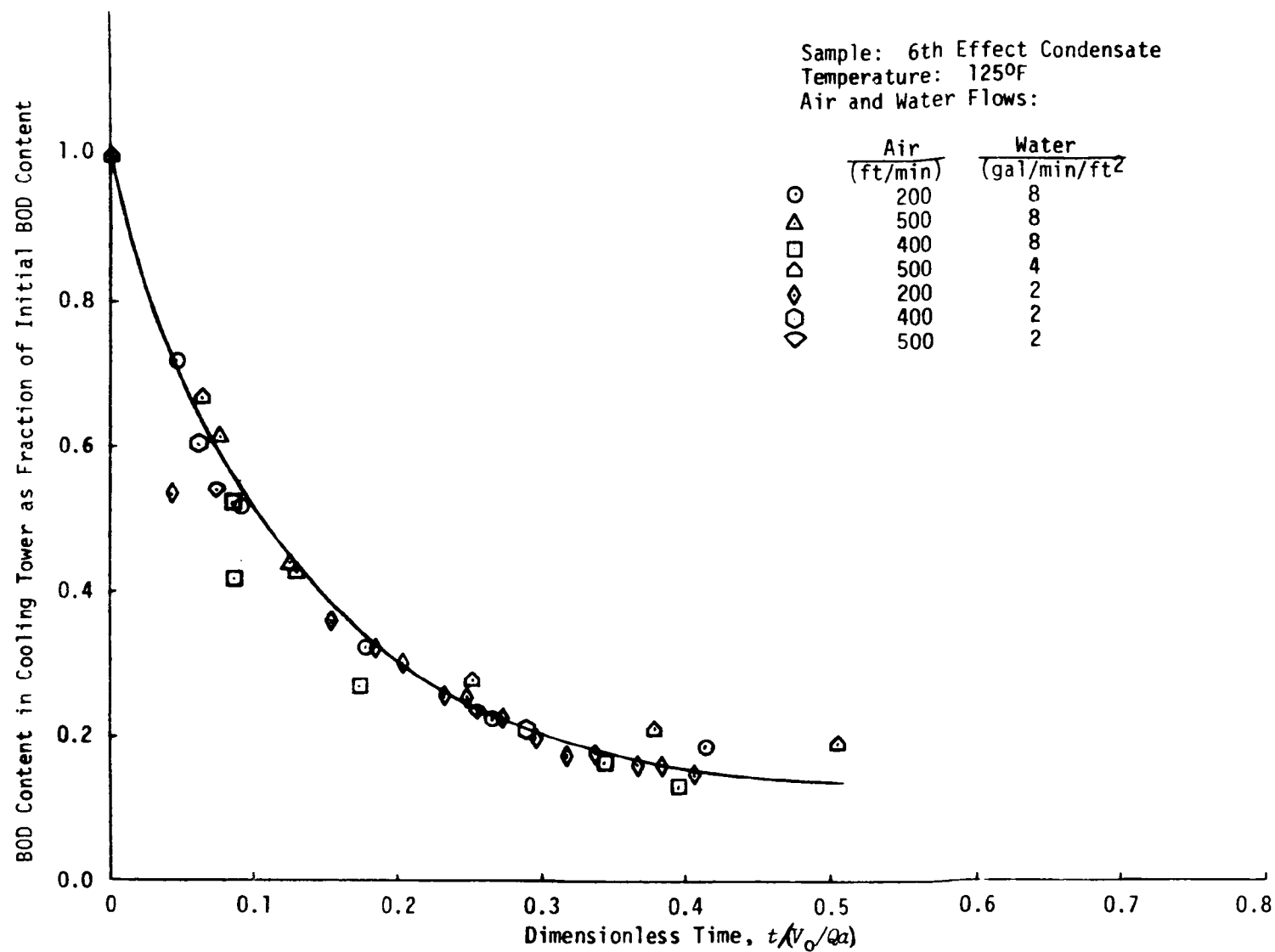
FIGURE 12: STRIPPING EXPERIMENT - FRACTION OF BOD REMAINING VERSUS DIMENSIONLESS TIME, ROME 6TH EFFECT AUGUST 1, 1968
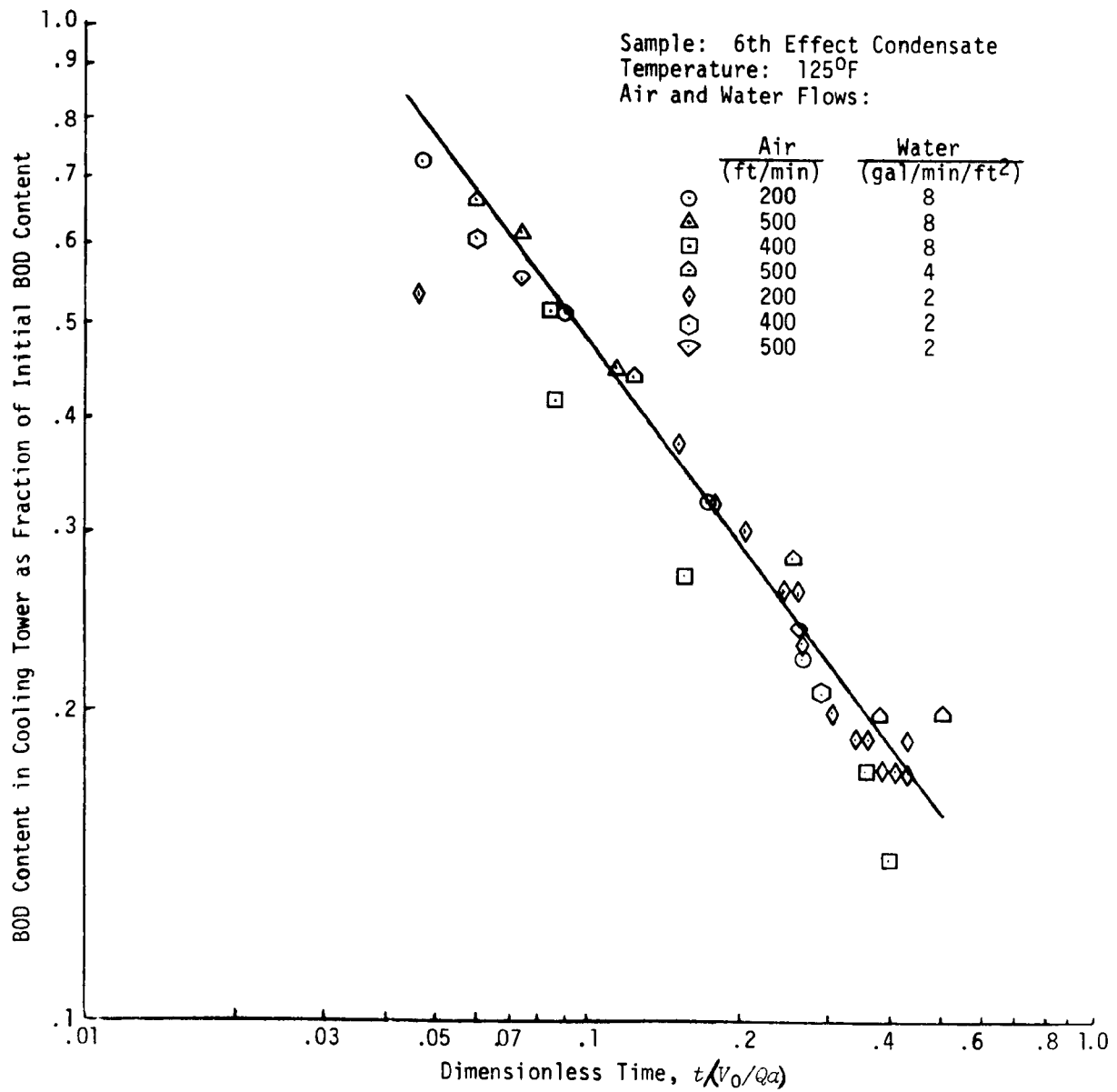
FIGURE 13: LOG-LOG RELATIONSHIP BETWEEN BOD CONTENT IN COOLING
TOWER AND THE DIMENSIONLESS TIME, $\frac{t}{V_0/Qa}$

where $(\frac{K}{a})$ is the volatility of the treatable materials relative to water. $^a$Hence for a waste water with $\frac{K}{a}$ known and a cooling tower for which $a$ is known, the amount of volatile materials that can be removed in the cooling tower can be calculated directly with Equation (17). The value of $(\frac{K}{a})$ can be determined experimentally in a simple laboratory experiment as outlined previously in Section VI. This experiment is also very important because the fraction of BOD that is volatile is evaluated and determines the limiting treatment that could be expected in the cooling tower.

SECTION VII

FULL-SCALE MILL STUDIES

## Design and Construction of Cooling Tower

After the cooling tower system had been studied and proven successful
in laboratory and pilot-scale facilities, a full-scale tower was de-
signed, constructed, and operated to demonstrate its application in
reducing oxygen-demanding wastes. The design of this tower was unique
since both cooling and waste water treatment had to be considered.
Practically all past experience in the design of cooling towers had
been concerned only with cooling and the water streams involved had
been clean relative to the water streams being processed in this study.

The tower had to meet basic cooling design requirements to provide cool-
ing water for use in barometric condensers if it was to serve its major
function in the water reuse system. The factors, however, to be con-
sidered in sizing and selecting the proper tower for a given cooling
service were thoroughly documented and their effects on tower design
were well established from past experience (13, 14, 15). The criteria
necessary to establish the cooling characteristics of the tower above
included the volume of water to be processed, the temperature of the
hot water input, the temperature of the treated water, and the wet bulb
temperature of the ambient air. In addition to these variables, the
only other quantity to be fixed was the volume of air to be used or,
as otherwise stated, the liquid-to-air ratio. The air volume require-
ment, however, was more a function of BOD treatment than cooling and
was subject to other considerations.

All exploratory studies demonstrated that air stripping was the princi-
pal treatment mechanism. It was demonstrated further that stripping was
highly dependent on the liquid-to-gas ratio and the temperature in the
tower. To achieve the best possible conditions for stripping, it would
be necessary to employ the minimum liquid-to-gas ratio and the maximum
tower temperature. Physical limitations of the tower structure and the
operating expense of moving large volumes of air made it necessary to
compromise treatment with cost. Such considerations revealed that a
liquid-to-air ratio as low as 1.2 could be used. Tower temperatures
were determined by the cooled water requirement of the barometric con-
densers where the treated water was being reused. Laboratory tests,
already discussed in the experimental studies, showed that the methanol
removal corresponded to essentially the same percentage reduction in
volatile BOD. Changes in the ambient wet bulb air temperature also af-
fected the average tower temperature. Fluctuations from these effects,
however, could be compensated for by using a continuously variable speed
fan. Based on cost considerations, however, only two-speed fans were
economically feasible. This arrangement was judged capable of compen-
sating for seasonal changes in wet bulb temperatures. In experiments

with the tower it was found that only one fan speed was necessary; the maximum fan speed was used in all quantitative tests. The low fan speed has been used effectively during low wet bulb periods.

One of the major problems anticipated with the cooling tower system was foaming, primarily due to plans to handle decker filtrate. Every effort was made to minimize the occurrence of foam, and a short laboratory study was conducted to evaluate both operational and design methods that could be used to control foaming. From an operational standpoint, the most critical variable was pH, and foaming tended to be greatest when the pH was near the neutral point and was considerably less under highly acid or basic conditions. See Appendix "E" for the details of this study. From a design point of view, the tower basin was arranged to keep the entire free liquid surface area under a rain of falling water at all times, and a hanging wall was designed so that water leaving the basin had to flow under and up into the pump sump area. This retained the surface foam in the tower basin where the falling waste water beat it down. Both crossflow and counterflow induced draft towers were considered for this application. Both types of towers were found satisfactory, but two modifications were thought to be necessary on the crossflow design. It was believed that, in the crossflow configuration, foam generation could occur in the open pan distribution system and in the open air plenum area. Suppliers were asked to submit bids on a modified crossflow design which would eliminate the exposed air-liquid interfaces at these points. The conventional counterflow tower, however, was finally chosen because of costs. As a final guard against foam, defoaming agents could be added to the tower basin; and later in operation small quantities were necessary.

The tower finally selected and installed was a counterflow design consisting of two identical cells of 36 x 36 feet and 31 feet high. Each cell was equipped with a 75 HP motor and a 16 foot stainless steel fan capable of delivering 550,000 CFM in a 14 foot high fan stack. The main structure consisted of treated redwood with corrugated fiberglass sheathing and ten rows of plastic fill material. Because of the corrosive nature of the waste water stream, stainless steel (in some cases coated iron was substituted) was specified for all metals which would be in contact with the liquid and air streams.

The unit was capable of providing cooled water at 90°F at the rate of 7000-8000 GPM from the tower basin to the barometric condensers on the last effects of two sets of six-effect evaporators operating on kraft mill black liquor. The heated water plus the condensed vapors (approximately 200 GPM) was pumped from the condenser hot wells to the cooling tower for cooling and reuse. Evaporation losses and the continuous blowdown of 700-1500 GPM was compensated for by adding combined condensate from the first five evaporator effects (760 GPM), discharge from the noncondensables and scrubber jets (580-640 GPM), decker filtrate (350-700 GPM), and river water (0-600) GPM to the hot wells. The volume

of water flowing to the cooling tower was expected to be in the range of 7500-9500 GPM with a temperature range of 120-135°F. The tower was designed to operate with ambient air condition having a wet bulb temperature up to 80°F. The Fluor Products Company of Santa Rosa, California, constructed the tower. The remainder of the tower system was constructed by Georgia Kraft Company personnel or was sublet. Photographs of the installation are shown in Figures 14 and 15.

The cooling tower-barometric condenser system has performed extremely well. This is an indication that the overall design of the system has been most satisfactory. Two items are worthy of note: (1) Due to the anticipated buildup of biological growth on the tower fill material, it is necessary that the fill be rigid or provided with supports. In this particular tower it has been necessary to modify the original support mechanism to assure the necessary rigidity. (2) The presence of very small quantities of oils and fatty materials in the water causes a reduction in cooling efficiency. This is discussed more fully in Section VII under the heading of Cooling Characteristics.

Generally the tower produces a more uniform and controllable supply of water for the barometric condensers than was available from the river via the mill power house.

## Collection of Experimental Data

The cooling tower evaporator system could operate in many modes with various waste streams in or out of the system as indicated schematically in Figure 16. The tower could be operated with sixth effect vapors with sufficient fresh water being added to balance evaporation. Sixth-effect vapors plus combined condensate plus fresh water could be used. Or other waste streams such as decker filtrate and turpentine decanter underflow might be included. An extensive series of demonstration studies of these modes were conducted from May 1969 through February 1970. The objectives of these studies were to determine:

1. The treatability of selected waste streams;

2. The effects of nutrients added to these streams and the ensuing biological action generated;

3. The effects of water inlet temperature;

4. The extent of atmospheric emissions;

5. The optimum operating conditions;

6. The operating and treatment stability during process upsets;

7. Economics.
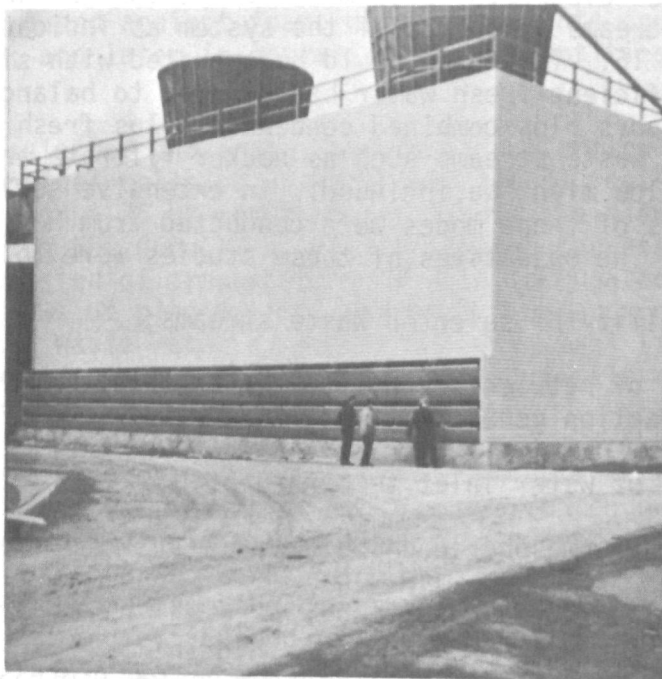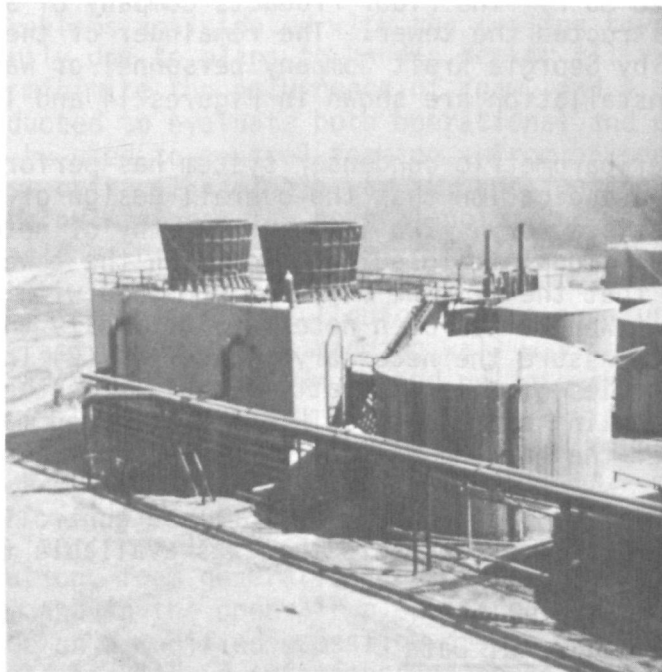
FIGURE 14: PHOTOGRAPHS OF COMPLETED FULL-SCALE INSTALLATION
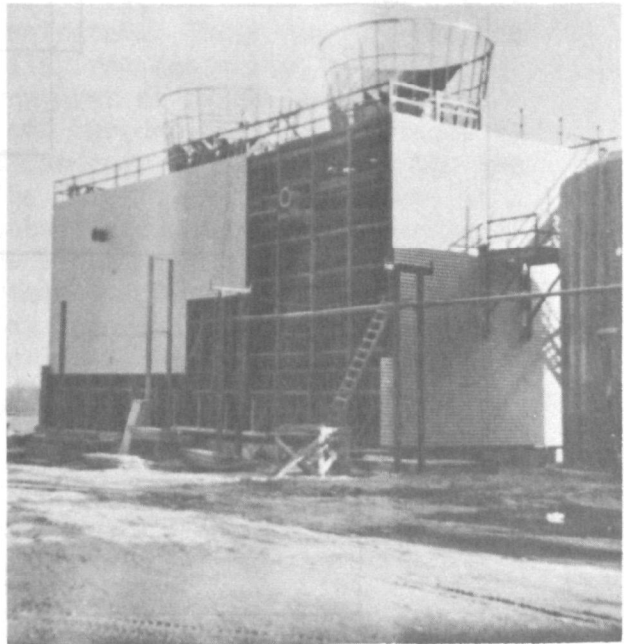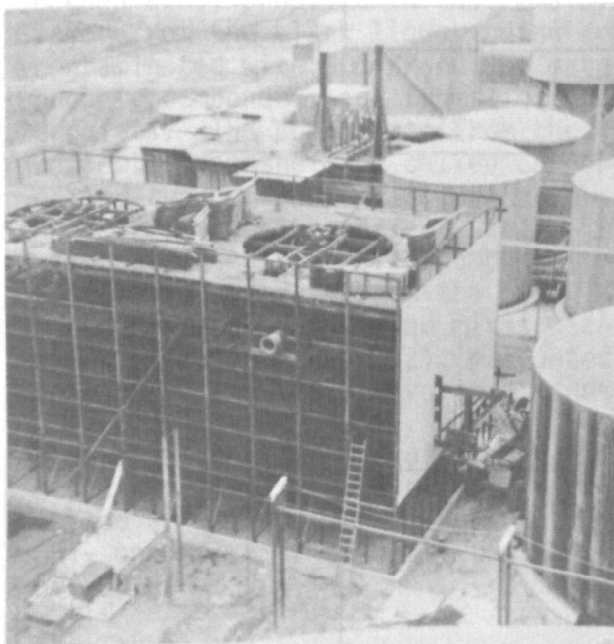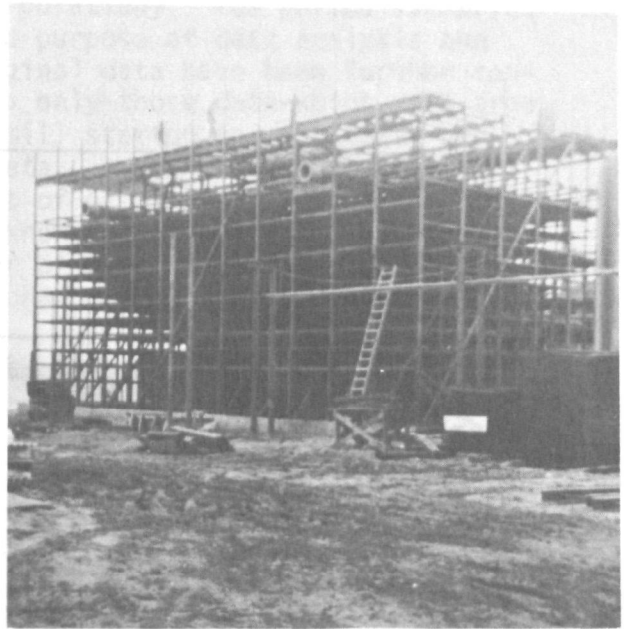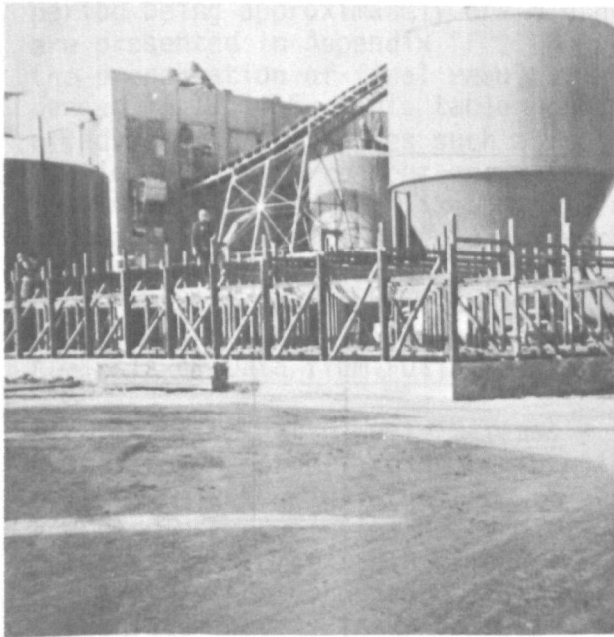
FIGURE 15: PHOTOGRAPHS OF FULL-SCALE INSTALLATION DURING CONSTRUCTION
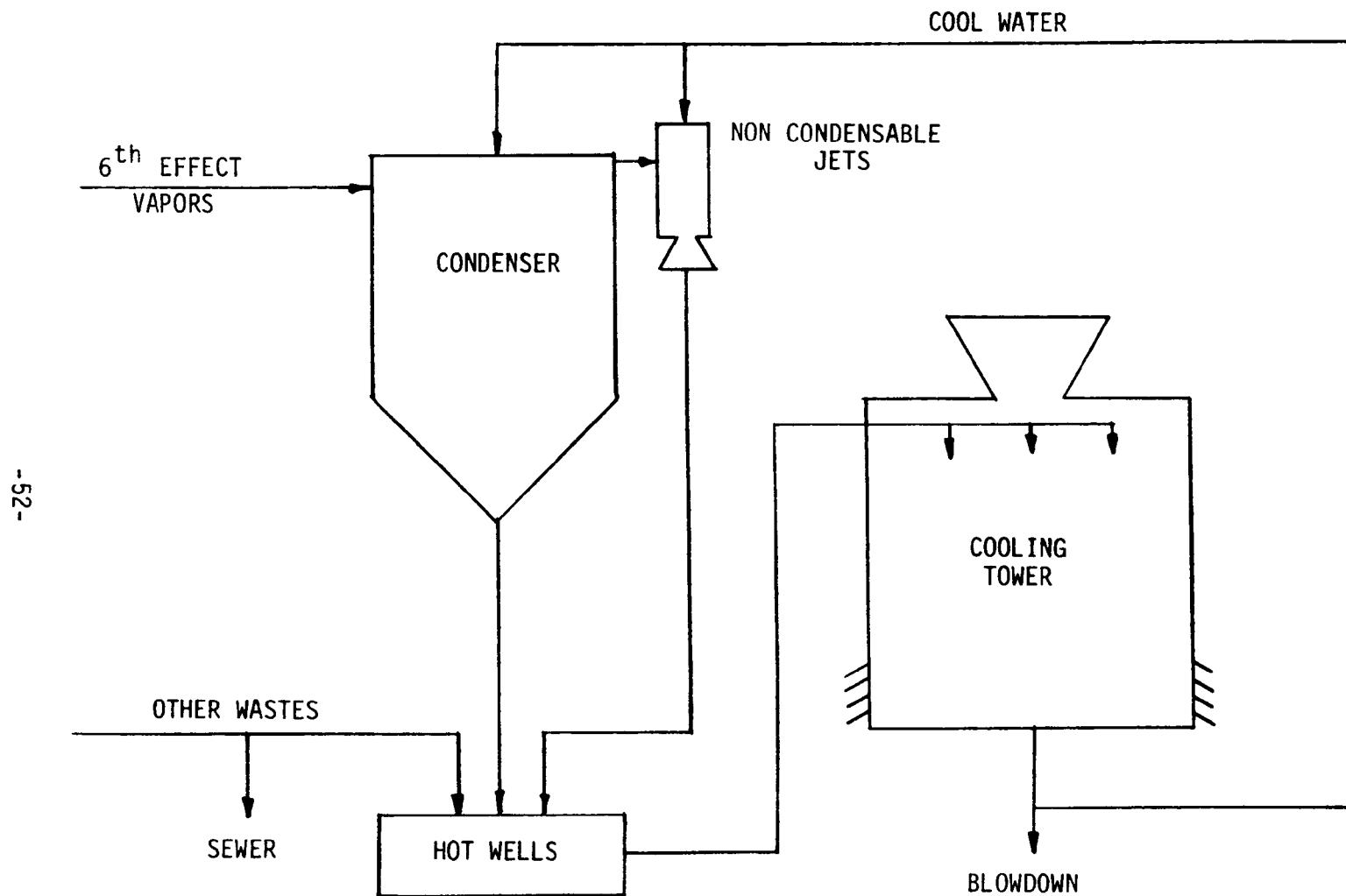
FIGURE 16: SCHEMATIC OF COOLING TOWER-EVAPORATOR CONDENSER SYSTEM

The data investigating the outlined items of interest were obtained on a daily basis and summarized and reported on a period basis (a period being approximately one month's duration). The period summaries are presented in Appendix "F". For the purpose of data analysis and the presentation of final results, original data have been further condensed in Table 6. This table contains only those data which were free of adverse circumstances such as pulp mill startup and shutdown, production upsets, erroneous analytical data, improper operation of the cooling tower, and the like. While not of great overall significance, the omission of data affected by such known adverse circumstances led to considerable variation in the number of days of acceptable, trouble-free operation on each separate study phase.

## Analysis of Data from Full-Scale Studies

Studies of Selected Waste Streams - In analyzing the experimental results it is appropriate to begin with a review of the properties of the streams selected for study and in particular the multi-effect evaporator condensate. In the Macon mill, as in most pulp mills, the evaporator systems are sextuple effect and produce three types of condensate. One type is the condensate from the first effect which is clean stream condensate that is returned to the process steam boiler. The other condensates, produced in the remaining effects, are from vapors evaporated from the black liquor being concentrated. These condensates are contaminated with BOD-producing materials from condensed, volatile, organic components and from liquid carry-over of black liquor spray droplets. The condensate from the second through the fifth effects is collected together and called combined condensate, and constitutes the second type of condensate produced. The third type of condensate is that from the sixth effect, which is considerably more contaminated with condensed, volatile components and liquid carry-over. This condensate is separate from the other condensates because it goes to the barometric condensers and mixes with the barometric condenser cooling water. Table 1 (page 12), presented earlier, describes the typical characteristics of the various condensates.

At the Macon mill, the differences in combined condensate and sixth effect condensate were clearly evident. The combined condensate contained up to 7,000 pounds of BOD per day, while the sixth effect, with only one-third to one-half the volume, contained up to 12,000 pounds of BOD per day.

The other streams studied were decker filtrate and turpentine decanter underflow. The decker filtrate, being the wash water from the final pulp washing operation, amounted to a relatively large volume compared to the other wastes and contained up to 16,000 pounds of BOD per day. Turpentine decanter underflow was a low volume flow stream containing up to 3000 pounds of BOD per day.

TABLE 6

SUMMARY OF COOLING TOWER DATA

| Phase | No. Days | Waste Streams to Tower | | | | | | | | Nutrients Added[3] | Total Flow to Tower | Blowdown Flow | Fresh BOD to Tower | Avg. BOD Removal | Tower Temp.[4] | BOD Removal | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 6th Effect Cond. | | Comb. Cond. | | Decker Filtrate | | Turpentine Decanter Underflow | | | | | | | | Avg. | Max. | Min. |
| | | Vol.[1] | BOD[2] | Vol. | BOD | Vol. | BOD | Vol. | BOD | | | | | | | | | |
| | | mgd | lbs/day | mgd | lbs/day | mgd | lbs/day | mgd | lbs/day | | mgd | mgd | lbs/day | lbs/day | °F | % | % | % |
| 1 | 5 | 0.29 | 5,188 | 0.46 | 2,743 | 0 | 0 | 0 | 0 | 0 | 9.28 | 0.42 | 7,931 | 6,289 | 97.2 | 79.3 | 83.7 | 70.7 |
| 2 | 7 | 0.29 | 9,065 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10.16 | 0.33 | 9,065 | 7,917 | 97.8 | 87.3 | 91.9 | 75.2 |
| 3 | 7 | 0.29 | 6,168 | 0.93 | 6,544 | 1.58 | 6,938 | 0 | 0 | 0 | 11.42 | 2.39 | 19,650 | 8,166 | 105.9 | 41.6 | 54.3 | 17.0 |
| 4 | 6 | 0.29 | 6,012 | 0.52 | 3,157 | 1.58 | 5,419 | 0 | 0 | 0 | 11.53 | 2.03 | 14,588 | 6,707 | 100.9 | 46.0 | 74.1 | 16.3 |
| 5 | 25 | 0.29 | 7,346 | 0 | 0 | 1.72 | 13,372 | 0 | 0 | 0 | 11.13 | 1.56 | 17,718 | 9,002 | 104.5 | 50.8 | 66.5 | 28.4 |
| 6 | 21 | 0.29 | 11,843 | 0 | 0 | 1.91 | 12,928 | 0 | 0 | 0 | 11.83 | 1.79 | 24,699 | 12,477 | 103.6 | 50.5 | 70.5 | 29.5 |
| 7 | 13 | 0.29 | 9,734 | 0 | 0 | 1.55 | 10,926 | 0 | 0 | Low | 10.91 | 1.49 | 20,660 | 10,728 | 103.6 | 51.9 | 68.2 | 34.2 |
| 8 | 8 | 0.29 | 6,511 | 0.98 | 5,847 | 1.47 | 11,729 | 0 | 0 | Low | 11.41 | 2.37 | 24,087 | 11,986 | 105.5 | 49.8 | 49.6 | 26.6 |
| 9 | 14 | 0.29 | 7,499 | 0 | 0 | 1.74 | 16,045 | 0 | 0 | High | 10.00 | 1.63 | 23,447 | 10,981 | 101.2 | 46.8 | 68.8 | 36.2 |
| 10 | 4 | 0.29 | 6,883 | 1.03 | 5,619 | 1.46 | 11,404 | 0 | 0 | High | 12.44 | 2.27 | 23,906 | 9,676 | 104.2 | 40.5 | 45.4 | 31.7 |
| 11 | 17 | 0.29 | 6,110 | 0 | 0 | 1.63 | 14,259 | 0 | 0 | 0 | 11.21 | 1.65 | 20,147 | 8,092 | 93.7 | 40.2 | 62.2 | 13.2 |
| 12 | 24 | 0.29 | 6,833 | 0 | 0 | 1.60 | 15,947 | 0 | 0 | 0 | 11.22 | 1.60 | 22,533 | 8,793 | 94.0 | 39.0 | 62.3 | 14.6 |
| 13 | 15 | 0.29 | 6,773 | 0 | 0 | 1.67 | 14,742 | 0.03 | 2,231 | 0 | 11.61 | 1.67 | 23,746 | 9,488 | 92.9 | 40.0 | 60.5 | 24.8 |

(1) Volume of 0.29 mgd was determined from a heat and materials balance around the 6th body on the two evaporator sets.
(2) Determined by difference from BOD balance around 6th effect condenser.
(3) Low - approximately 2.5 pounds of N and 0.5 pounds of P per 100 lbs of BOD; high - approximately 5.0 pounds of N and 1.0 pounds of P per 100 lbs of BOD.
(4) Average of daily temperature in tower feed and basin.

In the operation of the cooling tower the waste streams were added in varying quantities to the barometric condenser cooling water as makeup and treated to give considerable reduction in BOD load discharged in the total mill effluent and at the same time reduced the water demand for the barometric condensers. It should be noted, as shown in Figure 16 (page 52), that sixth effect condensate was a part of the barometric condenser water at all times and the waste streams which constituted makeup were the combined condensate, decker filtrate, and turpentine decanter underflow.

The data of Table 6 (page 54) served as the basic information for determining the effect of using different waste streams, adding nutrients and changing the cooling tower operating temperatures. Unfortunately, however, differences in blowdown rates prevented direct comparison of the data, and a series of theoretical assumptions and calculations had to be made to remove this effect.

The calculations began with period No. 2 when sixth effect condensate was the only waste stream being treated. By using Equation (5) on the data, the stripping constant for this period could be derived. Hence

$$K = \frac{P\left(\frac{B}{L}\right)}{\left(1 + \frac{B}{L}\right) - P} = \frac{(0.873)\left(\frac{0.33}{10.16}\right)}{\left(1 + \frac{0.33}{10.16}\right) - 0.873} = 0.177$$

This constant could then be used to evaluate the treatability of sixth effect condensate under other blowdown rates.

The blowdown rate in period No. 1 was 0.42 mgd, and the cooling tower recirculation rate was 9.28 mgd. Therefore, since the BOD in the sixth effect was distributed in these streams, the percentage of treatment was

$$R = \frac{(0.177)\left(1 + \frac{0.42}{9.28}\right)}{0.177 + \frac{0.42}{9.28}} = 0.833 \text{ or } 83.3\%$$

The BOD in the sixth effect feed to the tower was 5188 lbs/day, and 83.3 per cent of it was removed by stripping. Therefore, the BOD removal from the sixth effect feed stream was (5188 x 0.833) or 4322 pounds of BOD. The experimental data showed that 6289 pounds of BOD were removed per day; hence the BOD removal from the combined condensate was taken to be (6289 - 4322) or 1967 pounds of BOD per day. The removal efficiency for the combined condensate could then be calculated as

$$\frac{1967}{2743} \times 100 = 71.7\%$$

where 2743 pounds of BOD/day was the BOD feed to the tower in the combined condensate stream.

The calculation procedure used to apportion the BOD treatment between sixth effect condensate and combined condensate in period No. 1 was employed to apportion the treatment between sixth effect condensate and decker filtrate in periods Nos. 5, 6, 11, and 12. A weighted average stripping content for decker filtrate, $K_{DF}$, from these four periods of 0.058 was then used as the $K_{DF}$ in periods Nos. 3 and 4 to calculate a stripping constant for combined condensate. Therefore, an average stripping constant, $K$, was developed for all streams. The average constant for sixth effect, $K_{6th}$, was taken from period No. 2 and assumed to be the same for all periods at a value of 0.177. The average constant for combined condensate, $K_{CC}$, was obtained from a weighted average of periods Nos. 1, 3, and 4 and is 0.119. A direct comparison between periods Nos. 12 and 13 was used to develop the stripping constant, $K_{TU}$ for turpentine decanter underflow. This was felt to be valid because of the close similarity of periods Nos. 12 and 13. This gives a value of 0.115 for the stripping constant of the turpentine decanter underflow, $K_{DU}$.

After average stripping constants had been estimated for all streams, the percent removal for each waste stream was apportioned using the various $K$'s. These data are shown in Table 7 along with the actual and calculated BOD removal accomplished in the system. As shown by Table 7, the calculated BOD removal in pounds/day was obtained using the average $K$'s with each of the waste stream loadings and then adding the expected BOD removal from each stream together. This is compared with the total BOD removal observed. With the exception of periods Nos. 7-10, where nutrients were added, there is good agreement between the calculated and observed removals.

In calculating the results of Table 7, it was necessary to neglect the effect of temperature. This, however, was not believed serious over the temperature range of 93°F to 106°F. According to data on the laboratory cooling tower (Figure 10), the effect of temperature in estimating the stripping constants for sixth effect condensate and combined condensate could produce at the most a 10 to 20 per cent error.

While the data of Table 7 are estimates, it is believed that the approximate range of treatabilities of the streams tested could be assigned. It appears that with a liquid recirculation rate of about 10 mgd and a blowdown rate of about 1.5 to 2.0 mgd, the efficiency of treatment was between 55 and 65 per cent for sixth effect condensate, 45 and 55 per cent for combined condensate and turpentine decanter underflow, and 25 and 35 per cent for decker filtrate.

## TABLE 7

## STRIPPING CONSTANTS AND REMOVAL EFFICIENCIES FOR FULL-SCALE TOWER

| Period | $B/C$ | $K_{6th}$ | $K_{CC}$ | $K_{DF}$ | $P_{6th}$ | $P_{CC}$ | $P_{DF}$ | Lbs/Day Actual | Lbs/Day[6] Calculated | Difference Lbs/Day | % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0452 | .177 | .099 | -- | 83.3 | 71.7 | -- | 6,289 | 6,398 | - 109 | - 1.7 |
| 2 | .0325 | .177 | -- | -- | 87.3 | -- | -- | 7,917 | 7,917 | 0 | 0 |
| 3 | .2090 | .177 | .123 | .058[1] | 55.4 | 44.7 | 26.3 | 8,166 | 8,108 | + 58 | + 0.1 |
| 4 | .1760 | .177 | .131 | .058[1] | 59.0 | 50.1 | 29.1 | 6,707 | 6,146 | + 561 | + 9.1 |
| 5 | .1401 | .177 | -- | .056 | 63.6 | -- | 32.4 | 9,002 | 9,138 | - 136 | - 1.5 |
| 6 | .1513 | .177 | -- | .080 | 62.0[2] | -- | 39.7 | 12,477 | 11,467 | +1010 | + 8.8 |
| 7 | .1365 | .212 | -- | .065 | 69.1[2] | -- | 36.6 | 10,728 | 9,943 | + 785 | + 7.9 |
| 8 | .2080 | .209 | .406 | .065[4] | 60.5[2] | 79.9 | 32.6 | 11,986 | 9,265 | +2721 | +29.4 |
| 9 | .1630 | .251 | -- | .072 | 70.5[3] | -- | 35.5 | 10,981 | 9,430 | +1551 | +16.4 |
| 10 | .1824 | .248 | .032 | .072[5] | 68.2[3] | 17.9 | 33.5 | 9,676 | 9,880 | - 204 | - 2.1 |
| 11 | .1470 | .177 | -- | .052 | 62.7 | -- | 29.9 | 8,092 | 8,451 | - 359 | - 4.2 |
| 12 | .1420 | .177 | -- | .046 | 63.4 | -- | 28.0 | 8,793 | 9,610 | - 817 | - 8.5 |
| 13 | .1440 | .177 | -- | .058[1] | 63.1 | -- | 32.8 | 9,488 | 10,242 | - 754 | - 7.4 |

(1) This $K_{DF}$ is the average of the $K_{DF}$ values calculated for periods Nos. 5, 6, 11 and 12.  $K$ values are calculated by use of Equation (5).
(2) Assumed 5 per cent increase due to nutrient addition.
(3) Assumed 10 per cent increase due to nutrient addition.
(4) Assumed same $K_{DF}$ as period 7.
(5) Assumed same $K_{DF}$ as period 9.
(6) Calculated removal assumes $K_{6th}$ = 0.177, $K_{CC}$ = 0.119, $K_{DF}$ = 0.058 and $K_{DU}$ = 0.115.

Effects of Nutrients - By comparing periods Nos. 6, 7, and 9 (Table 6, page 54), the effects of adding nutrients in the tower feed on treatment of sixth effect condensate and decker filtrate can be determined. Likewise, a comparison of periods Nos. 3, 8, and 10 should show the effects of nutrients on a combination of three waste streams. In periods Nos. 3 and 6, no supplemental nutrients were added, whereas in periods Nos. 7 and 8 approximately 2.5 pounds of nitrogen and 0.5 pounds of phosphorus were added per 100 pounds of BOD, and in periods Nos. 9 and 10 this amount was doubled. Using Equation (5) and the average stripping constants previously discussed for sixth effect, combined condensate, and decker filtrate, the comparison in Table 8 can be developed.

## TABLE 8

### EFFECTS OF NUTRIENTS ON BOD REMOVAL

| Period | Nutrient Level | Expected % BOD Removal Without Nutrients* | Actual % BOD Removal | Difference |
|--------|----------------|-------------------------------------------|----------------------|------------|
| 6th Effect Condensate plus Decker Filtrate | | | | |
| 6 | 0 | 46.3 | 50.5 | 4.2 |
| 7 | Low | 48.0 | 51.9 | 3.9 |
| 9 | High | 40.0 | 46.8 | 6.8 |
| 6th Effect Condensate plus Combined Condensate plus Decker Filtrate | | | | |
| 3 | 0 | 41.3 | 51.6 | 0.3 |
| 8 | Low | 38.5 | 49.8 | 11.3 |
| 10 | High | 41.3 | 40.5 | -0.8 |

---

*Based on individual treatment efficiencies for sixth effect, combined condensate, and decker filtrate when $K_{6th}$ = 0.177, $K_{CC}$ = 0.119, and $K_{DF}$ = 0.058.

The results for all combinations of sixth effect condensate, combined condensate, and decker filtrate are rather inconsistent but do indicate a general trend toward minor improvement in treatment efficiency as found in the laboratory experiments when nutrients were added.

Bio-assays (see Appendix "H") conducted during these periods showed that the total number of viable organisms per ml present with no nutrient additions was approximately $1.8 \times 10^5$. With 2.5 pounds of

nitrogen and 0.5 pounds of phosphorus per 100 pounds of BOD, the organism count went up to approximately $1.6 \times 10^7$. When this nutrient additional level was doubled, the viable organism count exceeded $10^9$ per ml. This increase in biological activity tends to support that nutrient addition does improve the overall biological conditions in the tower.

It should be noted that during the entire experimental period, considerable amounts of slime were present in the tower, and even at the zero nutrient level some biological treatment must occur.

Cooling Characteristics - In the design of the tower it was not anticipated that the contaminants in the waste waters circulating through the tower would significantly affect evaporation and cooling. Based on the standard criteria for evaluating cooling tower performance (16), however, it has been determined that the tower is operating at about 80 per cent of the cooling efficiency that would be expected using uncontaminated water. It has been found that small amounts of oils and fatty materials build up in the water, and these are believed to be responsible for the failure of the tower to yield the expected cooling performance. Thus it is recommended that cooling towers to be used on pulp mill wastes be designed with an additional 20 per cent allowance for decreased evaporation rates due to contaminants in the water.

Treatment of Blowdown - Because of the concentrating effect of the cooling tower on the various waste streams, there was some question as to the amenability of the tower blowdown to treatment in subsequent waste treatment facilities. The laboratory scale bio-oxidation unit, as described in Section V, was used to simulate treatment of the blowdown in an aerated lagoon with five-day retention. The results of these studies showed an average BOD removal efficiency of 86.4 per cent. Therefore, it is evident that the character of the blowdown would not adversely affect conventional biological waste treatment facilities.

Atmospheric Emissions - Table 1 (page 12) indicates that the waste streams being treated in the tower contain concentrations of organic sulfur compounds responsible for odor problems associated with the kraft pulping process. Because of the concern for all potential environmental pollution problems, several studies of the emissions from the tower were made. A summary of the data on gaseous sulfur emissions is included in Table 9. As expected, these studies show emissions of several organic and inorganic sulfur compounds in low concentrations. No noticeable odor problems associated with the cooling tower have been reported, and it is believed that with the dilution and dispersion of the stack gases, no significant odor problem would be experienced.

Table 9 shows that the noncondensable jets from the barometric condensers and the turpentine decanter underflow are the most significant contributors to the sulfur emissions. If further control of sulfur emissions were desirable, it would be possible to reduce them to the

level shown in the bottom line in Table 9. The noncondensables could be removed and burned rather than discharged to the hot well. It should also be possible to prestrip the turpentine underflow to remove the highly volatile organic sulfur components prior to its introduction into the tower.

## TABLE 9

### AVERAGE GASEOUS EMISSIONS FROM COOLING TOWER (PPM)

| Waste Streams Treated | Sulfur Dioxide | Hydrogen Sulfide | Methyl Mercaptan | Dimethyl Sulfide | Dimethyl Disulfide |
|---|---|---|---|---|---|
| 6th effect condensate, decker filtrate, turpentine decanter underflow, noncondensable jet stream | .047 | 1.4 | 2.3 | 1.5 | 2.1 |
| 6th effect condensate, decker filtrate, noncondensable jet stream | .138 | 1.3 | 1.7 | 0.5 | 0.8 |
| 6th effect condensate, decker filtrate | .106 | 0.4 | 0.0 | 0.3 | 1.8 |

Advantages of the Cooling Tower System - The BOD removed by the cooling tower during the experimental period amounts to about 25-30 per cent of the entire organic pollution load discharged from the mill. Thus it is estimated that the aeration requirements in a subsequent treatment facility for this mill can be reduced by this amount.

After taking into account the reduction in power required for pumping cooling water from the river to the mill, the net power required to operate the cooling tower is about 135 HP. At the Macon mill 8-10 mgd less river water is required, resulting in an estimated 265 HP reduction in pumping power. The BOD reduction efficiency of the cooling tower, then, can be estimated at about 70-75 lbs BOD/HP/day. This compares very favorably with the reductions in conventional aerated lagoons which under optimum conditions can be expected to remove only about 50 lbs BOD/HP/day.

Another advantage which may or may not apply to other mills is that a more constant supply of cooling water is attributable to the system, and this has resulted in more stable evaporator operation. The evaporation of waste water in the tower reduces the hydraulic load on subsequent treatment facilities by a small amount in addition to the more significant BOD reduction.

The operation of the system has been quite reliable and relatively trouble-free. While some foaming has occurred in the tower basin on occasion, this has been easily controlled by addition of defoamers. The maintenance and defoamer cost of the system are probably less than for equivalent treatment in an aerated lagoon system.

Economics - The initial cost of installing the cooling tower system was $239,000. A breakdown of the cost by major items is as follows:

| | | |
|---|---|---|
| 1. | Cooling Tower | $ 66,000 |
| 2. | Basin | 11,000 |
| 3. | Pumps | 13,000 |
| 4. | Piping and Valves | 34,500 |
| 5. | Electrical | 36,000 |
| 6. | Instrumentation | 15,000 |
| 7. | Miscellaneous | 4,000 |
| 8. | Labor | 36,000 |
| | Construction Total | $215,500 |
| | Engineering and Supervision | 23,500 |
| | Total | $239,000 |

The estimated cost to install surface condensers for the Mead Division mill is $229,000.

Due to the reuse of cooled water in the noncondensable jets and evaporation and carry-over losses from the tower, the volume of mill effluent is reduced by about one million gallons over what could be achieved by surface condensers. As indicated earlier, this cooling tower accomplishes about a 10,000 lb/day reduction in total mill effluent BOD. The reduction in BOD is not normally achieved where surface condensers are used. There would be several ways to calculate the value of the reduction in volume and BOD, but at the Macon mill, where treatment in a combined system is planned, the cost savings is in the neighborhood of $250,000 in construction costs alone. The savings in annual operating cost for these volume and BOD reductions is expected to be about $20,000. This exceeds the $13,500 per year required for the net 135 HP necessary for the cooling tower plus approximately $5,000/year defoamer cost.

In addition to the very favorable cost factors, the simpler operation of a direct contact condenser offers operating advantages over the surface condenser where the inherent resistance to heat transfer of the tube walls and fouling of the tubes must be considered.

It is anticipated that this installation will continue to provide test data and remain available as a continuing demonstration project for all mills of the industry interested in making a similar installation.

# SECTION VIII

## ACKNOWLEDGEMENTS

We wish to acknowledge the Research and Development Committee, its chairman, Mr. E. V. McSwiney, and the Mead Division staff and manager, Mr. W. E. Davey, of Georgia Kraft Company for their support and encouragement in this project.

All of the project activities were coordinated and administered by Dr. R. B. Estridge, Director of Research and Development, Georgia Kraft Company.

The design, construction, and operation of the laboratory and pilot units were performed by a team from Georgia Kraft Company's Research and Development Center consisting of Dr. Estridge and Messrs. B. G. Turner, James T. Van Horn, Rodney Jones, and Michael Wise.

The design, construction, and operation of the full-scale unit at Georgia Kraft Company's Mead Division mill were performed by a team from the Research and Development Center and Mead Division Engineering and Technical Departments consisting of Dr. Estridge and Messrs. Turner, Robert L. Smathers, Pat McHugh, E. L. Wilson, Ray Johnson, and Sam Rose.

The assistance of Dr. L. J. Thibodeaux of the University of Arkansas in the pilot studies and theoretical analysis is gratefully acknowledged.

This report was prepared by Dr. J. Andrew McAlister and Mr. Turner with assistance from Mr. Jones and Mrs. Sue Williams.

The aid provided by Mr. William J. Lacy, Mr. George R. Webster, Mr. Ralph Scott (Project Officer), and Mr. Edmond P. Lomasney of the Office of Research and Monitoring, Environmental Protection Agency, was greatly appreciated.

This project was partially funded by the Environmental Protection Agency, Office of Research and Monitoring, under a Section 6(b) Research and Development Grant by the Industrial Pollution Control Branch of the Division of Applied Science and Technology, Office of Research and Monitoring, Washington, D. C.

# SECTION IX

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# SECTION X

## PUBLICATIONS AND PATENTS

Three publications have been written as a result of this study.

1. Turner, B. G. and Van Horn, James T., "Identification of Volatile Components in Kraft Mill Evaporator Condensates". Presented and declared winner of 1969 Southeastern TAPPI and 1970 National TAPPI Paper Awards Contests. To be submitted for publication in the journal of TAPPI.

2. Estridge, R. B., Turner, B. G., Smathers, R. L., and Thibodeaux, L. J., "Treatment of Selected Kraft Mill Wastes in a Cooling Tower". TAPPI 54, No. 1 (January 1971).

3. Thibodeaux, L. J., Estridge, R. B., and Turner, B. G., "Measurement of Relative Volatilization Rates of the Water-Miscible Fractions in an Aqueous Effluent." Presented at National AIChE Meeting in Cincinnati, Ohio, May 16-19, 1971.

No patents have been produced or applied for under this project.

# SECTION XI

## GLOSSARY

### Frequently Used Abbreviations:

BOD = Biological Oxygen Demand (5-day, 20°C); volatile BOD is the
total amount of BOD which can be removed by extended stripping.

cc/min = Cubic centimeters per minute.

COD = Chemical Oxygen Demand.

ft/min = Feet per minute.

gpm = Gallons per minute.

lbs/day = Pounds per day.

mls = Milliliters.

mg/l = Milligrams per liter.

mgd = million gallons per day.

ppm = Parts per million.

### Symbols:

#### Roman

$a$ = Evaporation rate, expressed as fraction of a unit of liquid
which is evaporated as it passes from top to bottom of tower.

$B$ = Blowdown flow rate from tower basin.

$d$ = Differential Operator.

$G$ = Gas (or air) flow rate.

$HTU$ = Height transfer unit.

$h$ = Enthalpy of moist air; h* indicates enthalpy of saturated air.

$K$ = Stripping constant, expressed as fraction of volatile material
removed from a unit of liquid as it passes from top to bottom of
tower.

$k$ = Proportionality constants in Equations (2) and (3).

$L$ = Liquid flow rate through tower.

$Q$ = Flow rate of water recirculating to tower.

$R$ = Removal of BOD as fraction or as percent of BOD in feed liquid.

$T$ = Pounds of water vapor evaporated per hour from water in tower.

$t$ = Temperature in degrees Fahrenheit; down time in minutes.

$V$ = Volume of liquid added to cooling tower in batch experiments.

$x$ = Liquid phase concentration.

$y$ = Vapor phase concentration.

$z$ = Column packing height.


## Greek Symbols

$\Theta$ = Dimensionless time unit definition Equation (16).


## Subscripts:

CC = Combined condensate.

DF = Decker filtrate.

F = Feed liquid.

H = Heat transfer.

h = Henry's Law.

L = Liquid.

M = Methanol, also mass transfer.

m = Maximum.

Tu = Turpentine.

T = Water evaporated into exhaust air stream from tower.

wb = Wet Bulb.

Z = Position (height) in tower.

o = Initial conditions in batch experiments.

1 = Condition at top of tower.

2 = Condition at bottom of tower.

6th = Sixth effect condensate.

## Superscripts:

\* = Equilibrium.

SECTION XII

APPENDICES

## TABLE 1

### ANALYSIS OF SIXTH EFFECT CONDENSATE
### USED IN SPARGING EXPERIMENTS

| Measurement | Analytical Results for Experiment | | | | | |
|---|---|---|---|---|---|---|
| | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 | No. 6 |
| BOD, mg/l | 1600 | 1380 | 1400 | 1366 | 810 | 843 |
| COD, mg/l | 5080 | 5222 | 4019 | 3704 | 3039 | 1830 |
| Conductivity, umhos | 2300 | 2600 | 1800 | 1500 | 930 | 500 |
| pH | 10.7 | 10.2 | 10.1 | 9.6 | 9.0 | 8.7 |
| Phenolphthalein Alkalinity, mg/l | 378 | 222 | 148 | -- | -- | -- |
| Total Alkalinity, mg/l | 788 | 862 | 502 | -- | -- | 114 |
| Total Solids, mg/l | 3500 | 4036 | 2756 | 2448 | 1492 | 720 |
| Dissolved Solids, mg/l | 3500 | 3986 | 2696 | 2394 | 1492 | 636 |
| Suspended Solids, mg/l | 0 | 50 | 60 | 54 | 0 | 84 |
| Total Volatile Solids, mg/l | 1348 | 1254 | 924 | 990 | 736 | 368 |
| Dissolved Volatile Solids, mg/l | 1348 | 1254 | 924 | 990 | 736 | 276 |
| Suspended Volatile Solids, mg/l | 0 | 0 | 0 | 0 | 0 | 92 |

## TABLE 2
### BOD AND COD DATA FOR SIXTH EFFECT CONDENSATE SPARGING EXPERIMENTS

| Experiment | Elapsed Time (mins) | BOD Results | | COD Results | |
|---|---|---|---|---|---|
| | | For N$_2$ Sparging (mg/l) | For Air Sparging (mg/l) | For N$_2$ Sparging (mg/l) | For Air Sparging (mg/l) |
| No. 1 | 0 | 1600 | 1600 | 5080 | 5080 |
| | 1 | -- | 1320 | 4920 | 4920 |
| | 1.5 | -- | 1200 | -- | -- |
| | 2 | -- | -- | 4680 | 4680 |
| | 3 | -- | -- | 4800 | 4440 |
| | 4 | -- | 1200 | 4720 | 4840 |
| | 22 | -- | -- | 4610 | 4243 |
| | 25.5 | -- | -- | 4732 | 4406 |
| | 27 | 1022 | 948 | -- | -- |
| | 28.5 | -- | -- | 4120 | 3835 |
| | 47.5 | 1460 | 1210 | -- | -- |
| | 48 | -- | -- | 4039 | 3794 |
| No. 2 | 0 | 1380 | 1380 | 5222 | 5222 |
| | 2 | 1330 | 1380 | 5386 | 5059 |
| | 4 | -- | 1360 | 5098 | 5137 |
| | 22 | -- | -- | 4863 | 4902 |
| | 24.5 | -- | -- | -- | -- |
| | 26 | -- | -- | 4923 | 4846 |
| | 46.5 | -- | -- | 4885 | 4692 |
| | 51 | -- | -- | 4769 | 4731 |
| No. 3 | 0 | 1400 | 1400 | 4019 | 4019 |
| | 1.5 | 1380 | 1300 | 3862 | 3862 |
| | 3 | 1280 | 1250 | 3901 | 3901 |
| | 5 | 1185 | 1080 | 3861 | 3861 |
| | 22 | 1166 | 966 | 3541 | 3618 |
| | 27 | -- | -- | 3846 | 3580 |
| | 47 | -- | -- | 3618 | 3541 |
| | 52 | -- | -- | 3732 | 3503 |
| No. 4 | 0 | 1366 | 1366 | 3704 | 3704 |
| | 2 | 1200 | 1100 | 3658 | 3519 |
| | 4.5 | 933 | 933 | 3565 | 3426 |
| | 22.0 | 1133 | 1150 | -- | -- |
| | 26.5 | 833 | 1050 | 3440 | 3283 |
| | 47.0 | -- | -- | 3332 | 3284 |
| | 51.5 | -- | -- | 3185 | 3038 |
| | 71.5 | 1033 | 900 | 3136 | 2744 |
| No. 5 | 0 | 810 | 810 | 3039 | 3039 |
| | 5.0 | 703 | 766 | 2692 | 3028 |
| | 23.5 | 1066 | 666 | 2500 | 2308 |
| | 29 | 770 | 600 | 2115 | 2404 |
| | 47.5 | 940 | 986 | 2211 | 2115 |
| | 53.0 | 950 | 840 | 2381 | 2000 |
| | 71.0 | 920 | 810 | 1905 | 1809 |
| No. 6 | 0 | 843 | 843 | 1830 | 1830 |
| | 19 | 810 | 759 | 1658 | 1516 |
| | 46 | 722 | 775 | 1675 | 1675 |
| | 62.5 | 850 | 800 | 1675 | 1618 |

# APPENDIX B
## DESCRIPTION OF LABORATORY COOLING TOWERS

### A. Purpose of Laboratory Cooling Towers

Basic laboratory experiments had shown that air stripping was the
major factor in the reduction of BOD in combined condensate and
decker filtrate, and that biological action and chemical oxidation
were only minor mechanisms. It was desirable that these mechanisms
be investigated in a cooling tower large enough to retain the
principal features of a typical industrial installation, yet small
enough to allow the processing of the air and liquid streams with
conventional laboratory devices. A laboratory tower design was
developed which had features similar to the Macon pilot plant and
to the proposed demonstration tower. Besides simulation, the
design provided for visual inspection of the air-liquid contacting
process, and it had the necessary physical arrangements and
auxiliary equipment to allow complete quantitative measurements of
widely varying operating conditions. So that the BOD removal
mechanisms could be separated and still be studied under identical
conditions, it became necessary to build two identical laboratory
towers.

### B. Design, Construction, and Operation of Laboratory Cooling Towers

The laboratory cooling towers were counter-current flow, columnar
gas-liquid contactors of 0.25 square foot cross-sectional area
(6 inches by 6 inches) and Plexiglass construction. Overall height
was approximately 12 feet, 10 of which were packed with Poly-Grid
media stacked vertically on 1-1/8 inch centers. The sections of
packing were cut with random grid positions so that when stacked
in the tower the grid network would not form vertical channels
through the network structure. The Poly-Grid was a plastic
material of high void packing consisting of sections 1-1/4 inch
high with a grid mesh of 2 inches by 2 inches. At three equally
spaced levels along the height of the towers, liquid deflectors
were glued to the corners to force the falling liquid to distribute
itself over the tower cross-section; otherwise, much of the liquid
would run down the corners of the tower. Air for cooling was drawn
through the tower (induced draft) by two turbine type fans (Staplex
high-volume air samplers) located atop the column. A squeeze-
action, positive displacement, Randolph pump (The Randolph Company,
Houston, Texas) provided liquid flow. Auxiliary equipment included
a heat exchanger to reheat the cooled liquid plus rotameters,
thermometers, pressure devices, rheostats, and sample parts. A
schematic diagram describes the apparatus in Figure B-1.

Preliminary simulation runs were performed with the flow of liquid routed as shown in Figure B-1. Fresh waste water was fed through a rotameter combined with recycle waste water from the lower basin, heated and then introduced into the tower above the packing. A flow distribution plate spread the water flow evenly over the tower cross-section. When the liquid trickled and splashed downward as it descended the tower, it was contacted by a stream of air moving upward. The process of water cooling (predominant tower process) took place as water molecules left the liquid phase and attempted to saturate the air. This interphase transport of water molecules and their accompanying latent heat of vaporization resulted in the cooling of the remaining liquid water. The cooled water was collected in the basin, at which point part was recycled and part was removed as blowdown to maintain steady state operation.

Air flow through the tower was controlled by variable power transformers connected in the power supply to the Staplex air samplers, and the amount of air flow was determined from pressure drop measurements on gas riser tubes which passed through the water flow distribution plate. There were nine tubes, 1 inch in diameter and 6 inches long. A 2-inch inclined water manometer measured the pressure drop across the tubes. The pressure drop was correlated with the air flow through the tubes, and a pressure-drop/air-flow calibration curve was prepared for routine operation. For calibration purposes, the air flow through the tubes was determined from impact pressures which, in turn, were carefully measured with a small pitot tube positioned at the discharge end of the gas riser tubes. The application of conventional fluid flow laws and the assumption of smooth tube walls afforded a calculation of gas flows in the calibration measurements.

Cooling was not of primary concern; it was considered only as it was involved in the BOD treatment process. Waste water treatment parameters were monitored primarily while cooling parameters were recorded only as support information. A list of the variables monitored and the analyses performed while the units were in continuous operation included:

1. Feed rate
2. Recycle rate
3. Blowdown rate
4. Air rate
5. Liquid inlet temperature
6. Basin temperature
7. Air inlet and outlet wet bulb and dry bulb temperatures
8. BOD, COD, pH, conductivity, sulfide content, and total solids content of feed and blowdown.
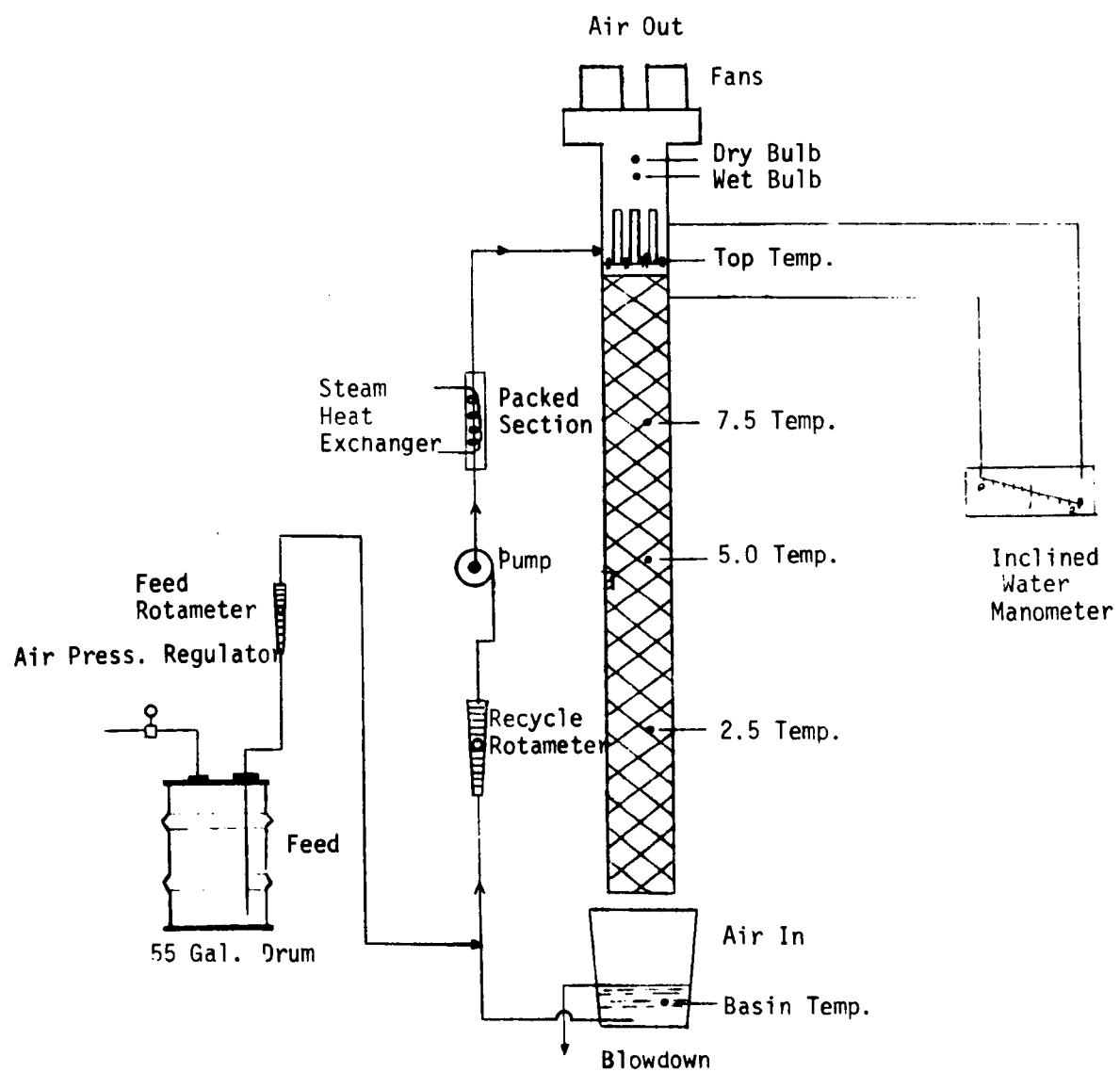
FIGURE B-1:  SCHEMATIC DIAGRAM OF LABORATORY COOLING TOWER

Notes were made of the foaming conditions within the towers and the basins, and temperatures in some experiments were recorded at intermediate points within the tower.

# APPENDIX C
## EXPERIMENTAL DATA INVESTIGATING TREATMENT MECHANISMS IN LABORATORY COOLING TOWERS

### TABLE 1

### EXPERIMENTAL DATA FOR BATCH EXPERIMENTS COMPARING AIR STRIPPING WITH CHEMICAL OXIDATION

| Experiment | Elapsed Time (mins) | Stripping with Nitrogen | | | | | Stripping with Air | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | Inlet Temp. (°C) | Basin Temp. (°C) | Liq. Volume in Basin (l) | BOD (ppm) | Methanol (ppm) | Inlet Temp. (°C) | Basin Temp. (°C) | Liq. Volume in Basin (l) | BOD (ppm) | Methanol (ppm) |
| No. 1* | 0 | 50 | 20.0 | 24.0 | 807 | 310 | 40 | 15.0 | 24.0 | 873 | 400 |
| | 5 | 50 | 19.5 | 23.4 | 747 | 290 | 40 | 15.0 | 23.5 | 710 | 310 |
| | 10 | 52 | 18.0 | 22.9 | 655 | 240 | 57 | 16.0 | 23.0 | 675 | 280 |
| | 15 | 45 | 18.0 | 22.3 | 605 | 225 | 50 | 16.0 | 22.5 | 677 | 240 |
| | 30 | 53 | 14.5 | 20.6 | 540 | 160 | 55 | 19.0 | 20.9 | 595 | 160 |
| | 40 | 52 | 16.0 | 19.5 | 485 | 110 | 50 | 19.0 | 19.8 | 570 | 140 |
| No. 2* | 0 | 52 | 32.0 | 8.0 | 684 | 290 | 52 | 34.0 | 8.0 | 684 | 290 |
| | 5 | 45 | 30.0 | 7.5 | 522 | 174 | 45 | 28.0 | 7.5 | 490 | 165 |
| | 10 | 55 | 20.0 | 7.0 | 487 | 149 | 53 | 26.0 | 7.0 | 454 | 130 |
| | 15 | 54 | 18.0 | 6.5 | 449 | 94 | 55 | 22.0 | 6.5 | 416 | 100 |
| | 30 | 52 | 17.0 | 5.0 | 391 | 40 | 52 | 22.0 | 5.0 | 359 | 48 |
| | 55 | -- | -- | -- | -- | -- | 55 | 22.0 | 2.6 | 325 | T |
| | 58 | 55 | 17.0 | 1.8 | 530 | 0 | -- | -- | -- | -- | -- |

* Experiment conditions: gas flow, 50 CFM; liquid recirculation rate, 0.5 GPM.
T = Trace

APPENDIX C
(Continued)

TABLE 2

EXPERIMENTAL DATA FOR CONTINUOUS FLOW EXPERIMENTS COMPARING AIR STRIPPING WITH BIOLOGICAL TREATMENT
FULL NUTRIENT LOADING - FEED RATE, 220 CC/MIN; RECIRCULATION RATE, .5 GPM

| Exp. No. | Tower | Air Speed ft/min | Temp Inlet °C | Temp Basin °C | pH Init. | pH Final | Cond. Init. umhos | Cond. Final umhos | Solids Init. ppm | Solids Final ppm | Methanol Init. mg/l | Methanol Final mg/l | NH₃ as N Init. mg/l | NH₃ as N Final mg/l | Total PO₄ Init. mg/l | Total PO₄ Final mg/l | Blow-down Rate cc/min | COD Init. mg/l | COD Final mg/l | BOD Init. mg/l | BOD Final mg/l | % BOD Removal | % Removal of Volatile BOD | % BOD Removal as MeOH | Volatile BOD % | MeOH % Removal |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Strip | 200 | 50.0 | 26.0 | 9.25 | 8.8 | 1200 | 1400 | 1672 | 2180 | 250 | 60 | ----- | No Data | ---- | ---- | 176.0 | 2465 | 2435 | 962 | 721 | 40.5 | 65.8 | 20.4 | 61.4 | 80.8 |
|  | Bio | 200 | 48.0 | 25.0 | 9.25 | 8.2 | 1200 | 1260 | 1672 | 1964 | 250 | 60 | ----- | No Data | ---- | ---- | 172.0 | 2465 | 2500 | 962 | 667 | 46.2 | 75.2 | 20.5 | 61.4 | 81.2 |
| 2 | Strip | 200 | 51.5 | 25.0 | 8.95 | 8.65 | 980 | 1040 | 1444 | 1664 | 250 | 63 | ----- | No Data | ---- | ---- | 156 | 2180 | 1880 | 1048 | 685 | 53.5 | 76.9 | 19.0 | 69.5 | 82.1 |
|  | Bio | 200 | 53.0 | 25.0 | 8.95 | 7.80 | 980 | 1200 | 1444 | 1848 | 250 | 60 | ----- | No Data | ---- | ---- | 156 | 2180 | 1940 | 1048 | 645 | 56.2 | 80.8 | 19.2 | 69.5 | 83.0 |
| 3 | Strip | 200 | 51.0 | 25.0 | 9.45 | 9.2 | 1260 | 1370 | 2016 | 2420 | 220 | 60 | 6.0 | .4 | 3.1 | 9.9 | 176.0 | 2320 | 2100 | 1020 | 638 | 50.0 | 81.4 | 16.4 | 61.4 | 78.2 |
|  | Bio | 200 | 51.5 | 26.0 | 9.45 | 8.2 | 1260 | 1650 | 2016 | 2516 | 220 | 63 | 6.0 | .27 | 3.1 | 6.2 | 180.0 | 2320 | 2245 | 1020 | 465 | 62.5 | 101.8 | 16.0 | 61.4 | 76.6 |
| 4 | Strip | 400 | 52.1 | 22.0 | 9.34 | 9.2 | 930 | 1040 | 1228 | 1620 | 210 | No Data | 40 | 3.8 | 16.0 | 16.0 | 148 | 2080 | 1855 | 1033 | 633 | 58.2 | 83.74 | -- | 69.5 | No Data |
|  | Bio | 400 | 52.0 | 19.5 | 9.34 | 8.06 | 930 | 1340 | 1228 | 1928 | 210 | 50 | 40 | 14.4 | 16.0 | 22.5 | 156 | 2080 | 2020 | 1033 | 376 | 74.5 | 107.1 | 16.4 | 69.5 | 83.1 |
| 5 | Strip | 400 | 51.5 | 21.0 | 9.3 | 9.1 | 960 | 1000 | 1208 | 1532 | 250 | No Data | ----- | No Data | ---- | ---- | 165 | 1910 | 1620 | 1135 | 500 | 66.6 | 95.8 | -- | 69.5 | No Data |
|  | Bio | 400 | 51.5 | 20.0 | 9.3 | 8.2 | 960 | 1320 | 1208 | 1920 | 250 | No Data | ----- | No Data | ---- | ---- | 156 | 1910 | 1800 | 1135 | 300 | 81.0 | 116.7 | -- | 69.5 | No Data |
| 6 | Strip | 400 | 51.9 | 21.0 | 8.5 | 7.5 | 740 | 900 | 1088 | 1544 | 235 | * | 84.0 | 13.8 | 27.3 | 36.3 | 125.0 | 1848 | 1473 | 738 | 466 | 64.2 | 83.5 | 30.2* | 76.8 | 98.8 |
|  | Bio | 400 | 52.0 | 18.2 | 8.5 | 7.2 | 740 | 1120 | 1088 | 1536 | 235 | * | 84.0 | 16.3 | 27.3 | 41.0 | 141.0 | 1848 | 1408 | 738 | 279 | 75.8 | 98.75 | 30.1* | 76.8 | 98.6 |
| 7 | Strip | 560 | 50.1 | 19.0 | 9.4 | 8.8 | 770 | 790 | 1076 | 1512 | 250 | 50 | 56.0 | 5.4 | 16.0 | 20.0 | 140 | 2035 | 1630 | 950 | 446 | 65.0 | 84.6 | 22.3 | 76.8 | 87.3 |
|  | Bio | 560 | 51.5 | 18.0 | 9.4 | 8.04 | 770 | 1040 | 1076 | 1404 | 250 | 0 | 56.0 | 20.2 | 16.0 | 27.5 | 141 | 2035 | 1665 | 950 | 343 | 76.9 | 100.1 | 25.6 | 76.8 | 100.0 |
| 8 | Strip | 560 | 51.4 | 21.5 | 9.3 | 8.3 | 820 | 860 | 1068 | 1684 | 230 | 30 | ----- | No Data | ---- | ---- | 141 | 1895 | 1605 | 1165 | 513 | 71.6 | 93.2 | 17.6 | 76.8 | 91.7 |
|  | Bio | 560 | 52.0 | 20.0 | 9.3 | 8.1 | 820 | 1140 | 1068 | 1688 | 230 | 10 | ----- | No Data | ---- | ---- | 146 | 1895 | 1660 | 1165 | 347 | 80.0 | 104.0 | 18.6 | 76.8 | 97.1 |
| 9 | Strip | 560 | 51.4 | 20.0 | 9.3 | 8.6 | 760 | 780 | 960 | 1156 | 210 | 50 | 54.0 | 17.7 | 17.5 | 25.0 | 148 | 1740 | 1420 | 1050 | 596 | 61.8 | 80.5 | 16.3 | 76.8 | 84.0 |
|  | Bio | 560 | 52.0 | 19.0 | 9.3 | 8.1 | 760 | 900 | 960 | 1188 | 210 | 0 | 54.0 | 7.5 | 17.5 | 22.5 | 154 | 1740 | 2280 | 1050 | 416 | 72.3 | 94.0 | 19.4 | 76.8 | 100.0 |

(*)  Less than 10 mg/l.

(**)  $\dfrac{\text{% BOD Removal}}{\text{% Volatile BOD}}$ = % Removal of Volatile BOD.

## TABLE 3

### EXPERIMENTAL DATA FOR CONTINUOUS FLOW EXPERIMENTS COMPARING AIR STRIPPING WITH BIOLOGICAL TREATMENT
#### FULL NUTRIENT LOADING - FEED RATE, 118 CC/MIN; RECIRCULATION RATE, .25 GPM

| Exp. No. | Tower | Air Speed ft/min | Temperature Inlet °C | Temperature Basin °C | pH Init. | pH Final | Cond. Init. umhos | Cond. Final umhos | Solids Init. ppm | Solids Final ppm | Methanol Content Init. mg/l | Methanol Content Final mg/l | Total NH₃ as N Init. mg/l | Total NH₃ as N Final mg/l | Total PO₄ Init. mg/l | Total PO₄ Final mg/l | Blow-down Rate cc/min | COD Init. mg/l | COD Final mg/l | BOD Init. mg/l | BOD Final mg/l | % BOD Removal | % Removal of Volatile BOD ** | % BOD Removal as MeOH | Volatile BOD % | MeOH % Removal |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Strip | 200 | 51.5 | 24.0 | 9.5 | 9.15 | 660 | 670 | 840 | 1072 | 210 | 50 | 33.0 | 2.9 | 13.0 | 17.5 | 90 | 1600 | 1210 | 700 | 410 | 55.3 | 67.6 | 23.9 | 81.8 | 81.9 |
|   | Bio | 200 | 52.0 | 24.0 | 9.5 | 7.9 | 660 | 900 | 840 | 1260 | 210 | 0 | 33.0 | 17.7 | 13.0 | 22.5 | 100 | 1600 | 1262 | 700 | 322 | 61.0 | 74.6 | 29.2 | 81.8 | 100.0 |
| 2 | Strip | 200 | 51.4 | 26.0 | 9.5 | 9.05 | 650 | 670 | 800 | 1040 | 210 | 50 | ----- No Data ----- | | | | 88 | 1750 | 1356 | 805 | 430 | 60.2 | 73.6 | 20.8 | 81.8 | 82.3 |
|   | Bio | 200 | 49.0 | 24.0 | 9.5 | 7.75 | 650 | 880 | 800 | 1196 | 210 | 0 | ----- No Data ----- | | | | 96 | 1750 | 1253 | 805 | 214 | 70.5 | 86.3 | 25.4 | 81.8 | 100.0 |
| 3 | Strip | 200 | 51.6 | 19.7 | 9.5 | 8.9 | 563 | 570 | 736 | 928 | 260 | 30 | 46.0 | 1.7 | 17.5 | 17.5 | 73 | 1690 | 1375 | 935 | 560 | 62.9 | 75.0 | 25.1 | 84.0 | 92.9 |
|   | Bio | 200 | 52.0 | 18.0 | 9.5 | 8.0 | 563 | 880 | 736 | 1088 | 260 | 10 | 46.0 | 25.6 | 17.5 | 27.5 | 82 | 1690 | 1375 | 935 | 410 | 70.4 | 83.8 | 26.3 | 84.0 | 97.3 |
| 4 | Strip | 400 | 50.9 | 19.7 | 9.4 | 8.5 | 810 | 900 | 1160 | 1520 | 260 | 0 | 93.0 | 9.3 | 29.5 | 25.0 | 85.5 | 1750 | 1325 | 661 | 384 | 58.0 | 69.8 | 38.2 | 83.2 | 100.0 |
|   | Bio | 400 | 50.0 | 18.7 | 9.4 | 7.89 | 810 | 1140 | 1160 | 1588 | 260 | * | 93.0 | 15.6 | 29.5 | 45.0 | 73.5 | 1750 | 1716 | 661 | 166 | 84.4 | 101.0 | 37.3* | 83.2 | 98.8 |
| 5 | Strip | 400 | 51.2 | 20.0 | 9.3 | 8.3 | 780 | 840 | 1204 | 1440 | 260 | * | ----- No Data ----- | | | | 75.0 | 1600 | 1335 | 678 | 373 | 65.0 | 77.2 | 36.4* | 83.2 | 98.8 |
|   | Bio | 400 | 51.0 | 19.5 | 9.3 | 7.9 | 780 | 1260 | 1204 | 1672 | 260 | * | ----- No Data ----- | | | | 73.3 | 1600 | 1325 | 678 | 160 | 85.4 | 102.6 | 36.4* | 83.2 | 98.8 |
| 6 | Strip | 400 | 51.3 | 20.0 | 9.0 | 8.1 | 870 | 1140 | 1396 | 1884 | 340 | * | 36.0 | 5.0 | 29.5 | 27.5 | 71.5 | No Data | No Data | 714 | 433 | 63.2 | 80.8 | 45.5* | 78.2 | 99.1 |
|   | Bio | 400 | 50.0 | 19.0 | 9.0 | 7.7 | 870 | 1430 | 1396 | 1968 | 340 | * | 36.0 | 12.8 | 29.5 | 42.5 | 68.0 | No Data | No Data | 714 | 214 | 82.7 | 105.8 | 45.5* | 78.2 | 99.2 |
| 7 | Strip | 560 | 50.2 | 17.0 | 9.2 | 7.6 | 910 | 1060 | 1200 | 1604 | 250 | * | 30.0 | 5.7 | 17.5 | 32.5 | 71.5 | 1820 | 1635 | 730 | 427 | 64.5 | 82.5 | 32.5* | 78.2 | 98.8 |
|   | Bio | 560 | 51.5 | 17.9 | 9.2 | 7.4 | 910 | 1160 | 1200 | 1736 | 250 | 0 | 30.0 | 12.1 | 17.5 | 42.5 | 78.4 | 1820 | 1472 | 730 | 192 | 82.5 | 105.5 | 33.3 | 78.2 | 100.0 |
| 8 | Strip | 560 | 50.5 | 19.8 | 9.2 | 7.7 | 800 | 970 | 1144 | 1400 | 340 | 80 | ----- No Data ----- | | | | 68.5 | 1938 | 1530 | 730 | 343 | 72.7 | 93.2 | 39.1 | 78.2 | 86.4 |
|   | Bio | 560 | 50.0 | 19.0 | 9.2 | 7.32 | 800 | 1450 | 1144 | 1784 | 340 | 10 | ----- No Data ----- | | | | 77.0 | 1938 | 1746 | 730 | 169 | 84.8 | 108.6 | 44.4 | 78.2 | 98.1 |
| 9 | Strip | 560 | 49.5 | 17.0 | 8.6 | 7.5 | 850 | 1165 | 996 | 1720 | 120 | * | 84.0 | 7.4 | 25.2 | 39.5 | 56.0 | 1820 | 1750 | 706 | 497 | 66.7 | 86.75 | 15.9* | 76.8 | 98.0 |
|   | Bio | 560 | 47.0 | 15.0 | 8.6 | 7.1 | 850 | 1650 | 996 | 2068 | 120 | * | 84.0 | 13.1 | 25.2 | 52.6 | 45.0 | 1820 | 1810 | 706 | 293 | 84.2 | 109.4 | 16.0* | 76.8 | 98.4 |

(*) Less than 10 mg/l.

(**) $\dfrac{\text{% BOD Removal}}{\text{% Volatile BOD}}$ = % Removal of Volatile BOD.

APPENDIX C
(Continued)

## TABLE 4

### EXPERIMENTAL DATA FOR CONTINUOUS FLOW EXPERIMENTS COMPARING AIR STRIPPING WITH BIOLOGICAL TREATMENT
### FULL NUTRIENT LOADING - FEED RATE, 470 CC/MIN; RECIRCULATION RATE, 1.0 GPM

| Exp. No. | Tower | Air Speed ft/min | Temperature Inlet °C | Temperature Basin °C | pH Init. | pH Final | Cond. Init. umhos | Cond. Final umhos | Solids Init. ppm | Solids Final ppm | Methanol Content Init. mg/l | Methanol Content Final mg/l | NH3 as N Init. mg/l | NH3 as N Final mg/l | Total PO4 Init. mg/l | Total PO4 Final mg/l | Blowdown Rate cc/min | COD Init. mg/l | COD Final mg/l | BOD Init. mg/l | BOD Final mg/l | % BOD Removal | % Removal of Volatile BOD | % BOD Removal as MeOH | Volatile BOD % | MeOH % Removal |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Strip | 200 | 52.5 | 34.0 | 8.94 | 8.8 | 1200 | 1480 | 1728 | 2232 | 320 | 80 | --- No Data --- | | --- No Data --- | | 405 | 2350 | 2420 | 985 | 614 | 46.5 | 75.75 | 24.8 | 61.4 | 78.5 |
| | Bio | 200 | 50.3 | 30.0 | 8.94 | 8.1 | 1200 | 1340 | 1728 | 2072 | 320 | 100 | --- No Data --- | | --- No Data --- | | 395 | 2350 | 2035 | 985 | 439 | 61.6 | 100.4 | 23.3 | 61.4 | 73.7 |
| 2 | Strip | 200 | 52.8 | 33.5 | 9.9 | 9.7 | 2660 | 2550 | 4250 | 4140 | 320 | 100 | --- No Data --- | | --- No Data --- | | 370 | 5140 | 4360 | 1545 | 1040 | 47.0 | 76.6 | 15.2 | 61.4 | 75.4 |
| | Bio | 200 | 51.0 | 28.0 | 9.9 | 9.3 | 2660 | 2460 | 4260 | 4068 | 320 | 100 | --- No Data --- | | --- No Data --- | | 340 | 5140 | 4200 | 1545 | 950 | 55.6 | 90.7 | 15.6 | 61.4 | 77.4 |
| 3 | Strip | 200 | 53.6 | 33.0 | 10.35 | 10.09 | 3450 | 4450 | 6084 | 7476 | 360 | 110 | --- No Data --- | | --- No Data --- | | 370 | 6950 | 7640 | 1440 | 1433 | 21.8 | 35.5 | 18.4 | 61.4 | 76.0 |
| | Bio | 200 | 52.5 | 28.5 | 10.35 | 9.99 | 3450 | 4550 | 6084 | 7040 | 360 | 110 | --- No Data --- | | --- No Data --- | | 420 | 6950 | 7400 | 1440 | 1340 | 16.95 | 27.6 | 17.7 | 61.4 | 72.7 |
| 4 | Strip | 400 | 51.1 | 28.0 | 9.0 | 8.8 | 1120 | 1370 | 1760 | 2320 | 280 | 80 | 19.0 | 1.4 | 25.3 | 34.8 | 376 | 2500 | 2540 | 1000 | 592 | 47.7 | 77.6 | 21.0 | 61.4 | 77.2 |
| | Bio | 400 | 63.0 | 26.0 | 9.0 | 8.7 | 1120 | 1440 | 1760 | 2232 | 280 | 100 | 19.0 | .6 | 25.3 | 35.2 | 400 | 2500 | 2610 | 1000 | 662 | 43.7 | 71.2 | 18.9 | 61.4 | 69.6 |
| 5 | Strip | 400 | 52.4 | 30.9 | 9.0 | 8.7 | 1130 | 1320 | 1772 | 2200 | 130 | 80 | --- No Data --- | | --- No Data --- | | 363 | 2610 | 2370 | 1091 | 635 | 55.1 | 89.7 | 6.1 | 61.4 | 52.5 |
| | Bio | 400 | 54.0 | 27.9 | 9.0 | 8.4 | 1130 | 1400 | 1772 | 2252 | 130 | 80 | --- No Data --- | | --- No Data --- | | 416 | 2610 | 2640 | 1091 | 628 | 49.0 | 79.8 | 5.3 | 61.4 | 45.5 |
| 6 | Strip | 400 | 52.4 | 31.0 | 8.78 | 7.95 | 690 | 895 | 888 | 1124 | 230 | 60 | 154.0 | 10.4 | 25.2 | 28.7 | 313 | 1558 | 1248 | 1008 | 567 | 62.6 | 74.6 | 18.3 | 84.0 | 82.6 |
| | Bio | 400 | 54.0 | 26.0 | 8.78 | 7.90 | 690 | 840 | 888 | 1072 | 230 | * | 154.0 | 9.9 | 25.2 | 27.5 | 384 | 1558 | 1119 | 1008 | 531 | 57.1 | 68.0 | 21.4* | 84.0 | 98.2 |
| 7 | Strip | 560 | 56.1 | 28.0 | 8.6 | 8.0 | 800 | 930 | 1344 | 1668 | 280 | * | 53.0 | 30.6 | 21.0 | 27.7 | 313 | 1552 | 1314 | 673 | 390 | 61.4 | 73.9 | 39.5* | 83.2 | 98.8 |
| | Bio | 560 | 53.5 | 24.0 | 8.6 | 7.8 | 800 | 980 | 1344 | 1572 | 280 | * | 53.0 | 8.9 | 21.0 | 25.0 | 360 | 1552 | 1260 | 673 | 329 | 62.5 | 75.2 | 39.3* | 83.2 | 98.6 |
| 8 | Strip | 560 | 54.5 | 28.0 | 8.6 | 8.0 | 775 | 920 | 1052 | 1520 | * | * | --- No Data --- | | --- No Data --- | | 328 | 1527 | 1269 | 792 | 452 | 60.25 | 79.6 | 33.5 | 76.8 | 30.2* |
| | Bio | 560 | 52.0 | 25.0 | 8.6 | 7.7 | 775 | 950 | 1052 | 1368 | * | * | --- No Data --- | | --- No Data --- | | 320 | 1527 | 1180 | 792 | 318 | 72.5 | 94.3 | 33.5 | 76.8 | 31.9* |
| 9 | Strip | 560 | 51.0 | 22.0 | 8.8 | 8.0 | 750 | 990 | 1172 | 1448 | * | * | 25.0 | 9.7 | 23.2 | 30.3 | 317 | 1487 | 1562 | 697 | 441 | 57.3 | 74.6 | 38.1 | 76.8 | 32.6* |
| | Bio | 560 | 52.0 | 20.0 | 8.8 | 7.5 | 750 | 1050 | 1172 | 1564 | * | * | 25.0 | 14.6 | 23.2 | 30.5 | 327 | 1487 | 1199 | 697 | 264 | 73.5 | 95.6 | 38.1 | 76.8 | 30.4* |

(*) Less than 10 mg/l.

(**) $\dfrac{\% \text{ BOD Removal}}{\% \text{ Volatile BOD}}$ = % Removal of Volatile BOD.

TABLE 5

EXPERIMENTAL DATA FOR CONTINUOUS FLOW EXPERIMENTS COMPARING AIR STRIPPING WITH BIOLOGICAL TREATMENT
ONE-HALF NUTRIENT LOADING

| Exp. No. | Tower | Air Speed ft/min | Feed Rate cc/min | Recir. Rate GPM | Temperature Inlet °C | Temperature Basin °C | Ambient Temp. Wet Bulb °F | Ambient Temp. Dry Bulb °F | pH Init. | pH Final | Cond. Init. umhos | Cond. Final umhos | Solids Init. ppm | Solids Final ppm | Methanol Content Init. mg/l | Methanol Content Final mg/l | NH₃ as N Init. mg/l | NH₃ as N Final mg/l | Total PO₄ Init. mg/l | Total PO₄ Final mg/l | Blow-down Rate cc/min | COD Init. mg/l | COD Final mg/l | BOD Init. mg/l | BOD Final mg/l | % BOD Removal | % Removal of Volatile BOD | % BOD Removal as MeOH | Volatile BOD % | MeOH % Removal |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Strip | 200 | 118 | .25 | 52.0 | 15.0 | 55.0 | 68.0 | 8.65 | 8.0 | 780 | 1000 | 1208 | 1536 | 320 | 95 | 19.0 | 3.4 | 14.7 | 17.2 | 58.0 | 2105 | 1800 | 925 | 608 | 67.6 | 89.0 | 28.7 | 75 | 85.4 |
|  | Bio | 200 | 118 | .25 | 48.0 | 14.5 | 55.0 | 68.0 | 8.65 | 7.2 | 780 | 1470 | 1208 | 2180 | 320 | * | 19.0 | 5.3 | 14.7 | 19.7 | 70.0 | 2105 | 2120 | 925 | 364 | 76.6 | 100.8 | 33.0* | 75 | 99.1 |
| 2 | Strip | 400 | 118 | .25 | 50.5 | 16.0 | 54 | 67 | 9.05 | 8.35 | 600 | 750 | 784 | 980 | 331 | 61 | 24.0 | 3.5 | 11.5 | 13.7 | 52.2 | 1450 | 1135 | 782 | 426 | 75.9 | 90.4 | 37.8 | 83 | 91.9 |
|  | Bio | 400 | 118 | .25 | 47.0 | 12.0 | 54 | 67 | 9.05 | 8.2 | 600 | 1380 | 784 | 2044 | 331 | * | 24.0 | 3.7 | 11.5 | 26.7 | 41.0 | 1450 | 1929 | 782 | 468 | 79.2 | 94.3 | 40.7* | 83 | 99.5 |
| 3 | Strip | 560 | 118 | .25 | 49.4 | 19.0 |  |  | 9.0 | 9.0 | 1280 | 1500 | 2268 | 2884 | 250 | 28 | 18.0 | .4 | 7.0 | 9.8 | 61.3 | -- | -- | 862 | 711 | 57.0 | 92.8 | 26.6 | 61 | 94.2 |
|  | Bio | 560 | 118 | .25 | 47.0 | 17.0 |  |  | 9.0 | 8.55 | 1280 | 2000 | 2268 | 3572 | 250 | 25 | 18.0 | .6 | 7.0 | 7.0 | 63.4 | -- | -- | 862 | 673 | 58.0 | 94.5 | 26.7 | 61 | 94.6 |
| 4 | Strip | 200 | 220 | .50 | 53.5 | 29.0 | 59.0 | 70.0 | 8.6 | 8.5 | 880 | 1210 | 1384 | 1884 | 320 | 95 | 9.0 | 3.4 | 12.5 | 16.7 | 126 | 2300 | 2010 | 997 | 632 | 63.7 | 81.6 | 25.9 | 77 | 83.0 |
|  | Bio | 200 | 220 | .50 | 52.5 | 23.5 | 59.0 | 70.0 | 8.6 | 7.25 | 880 | 1480 | 1384 | 1996 | 320 | * | 9.0 | 2.7 | 12.5 | 12.2 | 120 | 2300 | 1940 | 997 | 353 | 80.6 | 103.2 | 30.7* | 77 | 99.2 |
| 5 | Strip | 400 | 220 | .50 | 50.8 | 23.0 |  |  | 8.3 | 7.7 | 520 | 625 | 712 | 900 | 348 | 69 | 26.0 | 3.2 | 11.5 | 12.5 | 135 | -- | -- | 933 | 495 | 67.44 | 74.6 | 31.8 | 85 | 87.8 |
|  | Bio | 400 | 220 | .50 | 50.0 | 19.0 |  |  | 8.3 | 7.7 | 520 | 765 | 712 | 1164 | 348 | 28 | 26.0 | 3.0 | 11.5 | 15.0 | 118 | -- | -- | 933 | 493 | 71.65 | 79.2 | 34.7 | 85 | 95.7 |
| 6 | Strip | 560 | 220 | .50 | 50.5 | 18.5 |  |  | 8.9 | 7.7 | 520 | 675 | 752 | 1140 | 342 | 58 | 16.0 | 5.2 | 9.7 | 12.7 | 110 | 1388 | 997 | 893 | 438 | 75.47 | 83.4 | 34.1 | 89 | 91.5 |
|  | Bio | 560 | 220 | .50 | 50.8 | 15.0 |  |  | 8.9 | 7.6 | 520 | 830 | 752 | 1240 | 342 | * | 16.0 | 2.8 | 9.7 | 13.1 | 102 | 1388 | 1260 | 893 | 419 | 78.24 | 86.6 | 36.7* | 89 | 99.3 |
| 7 | Strip | 200 | 470 | 1.0 | 54.5 | 34.0 |  |  | 9.25 | 8.7 | 690 | 730 | 1216 | 1300 | 350 | 125 | 24.0 | 5.8 | 13.2 | 14.2 | 385 | 2238 | 1885 | 946 | 689 | 40.33 | 53.4 | 25.4 | 69 | 70.8 |
|  | Bio | 200 | 470 | 1.0 | 51.5 | 34.0 |  |  | 9.25 | 8.1 | 690 | 810 | 1216 | 1468 | 350 | 110 | 24.0 | 3.5 | 13.2 | 13.4 | 360 | 2238 | 1829 | 946 | 580 | 53.03 | 70.2 | 27.3 | 69 | 75.9 |
| 8 | Strip | 400 | 470 | 1.0 | 53.8 | 27.5 | 60.5 | 70.0 | 8.6 | 7.5 | 520 | 650 | 648 | 1016 | 332 | 56 | 19.0 | 5.7 | 13.0 | 17.1 | 280 | 1490 | 1158 | 637 | 286 | 73.8 | 89.3 | 45.6 | 83 | 90.0 |
|  | Bio | 400 | 470 | 1.0 | 53.5 | 23.0 | 60.5 | 70.0 | 8.6 | 7.5 | 520 | 740 | 648 | 932 | 332 | 15 | 19.0 | 4.4 | 13.0 | 16.7 | 283 | 1490 | 1153 | 637 | 222 | 79.4 | 95.9 | 49.3 | 83 | 97.3 |
| 9 | Strip | 560 | 470 | 1.0 | 51.3 | 22.0 | 57.0 | 70.0 | 9.0 | 8.7 | 895 | 1070 | 1280 | 1740 | 315 | * | 26.0 | 3.5 | 14.2 | 19.2 | 285 | 2170 | 2020 | 942 | 596 | 61.7 | 81.2 | 31.9* | 75 | 99.0 |
|  | Bio | 560 | 470 | 1.0 | 54.0 | 19.0 | 57.0 | 70.0 | 9.0 | 8.3 | 895 | 1290 | 1280 | 1904 | 315 | * | 26.0 | 2.4 | 14.2 | 19.5 | 273 | 2170 | 2025 | 942 | 507 | 68.8 | 90.6 | 31.9* | 75 | 99.1 |

(*) Less than 10 mg/l.

(**) $\dfrac{\% \text{ BOD Removal}}{\% \text{ Volatile BOD}}$ = % Removal of Volatile BOD.

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## TABLE 6

### EXPERIMENTAL DATA FOR CONTINUOUS FLOW EXPERIMENTS COMPARING AIR STRIPPING WITH BIOLOGICAL TREATMENT
#### NO NUTRIENTS

| Exp. No. | Tower | Air Speed ft/min | Feed Rate cc/min | Recir. Rate GPM | Temp Inlet °C | Temp Basin °C | Ambient Wet Bulb °F | Ambient Dry Bulb °F | pH Init. | pH Final | Cond. Init. umhos | Cond. Final umhos | Solids Init. ppm | Solids Final ppm | Methanol Init. mg/l | Methanol Final mg/l | NH3 as N Init. mg/l | NH3 as N Final mg/l | Total PO4 Init. mg/l | Total PO4 Final mg/l | Blow-down Rate cc/min | COD Init. mg/l | COD Final mg/l | BOD Init. mg/l | BOD Final mg/l | % BOD Removal | % Removal of Volatile BOD* | % BOD Removal as MeOH | Volatile BOD % | MeOH Removal |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Strip | 200 | 118 | .25 | 51.0 | 17.0 | 52.0 | 65.0 | 8.6 | 8.8 | 750 | 910 | 1168 | 1400 | 215 | 155 | 5.9 | 1.2 | 0.80 | 1.0 | 62.0 | 1850 | 1640 | 970 | 663 | 64.0 | 83.3 | 13.4 | 75 | 62.1 |
|  | Bio | 200 | 118 | .25 | 50.0 | 9.0 | 52.0 | 65.0 | 8.6 | 7.8 | 750 | 1140 | 1168 | 1640 | 215 | 82 | 5.9 | 2.4 | 0.80 | .50 | 60.0 | 1850 | 1750 | 970 | 526 | 72.4 | 94.1 | 17.4 | 75 | 80.6 |
| 2 | Strip | 400 | 118 | .25 | 48.0 | 15.0 | 55.5 | 68.0 | 8.8 | 8.95 | 770 | 980 | 1204 | 1564 | 215 | 74 | 7.7 | 1.7 | * | * | 58.6 | 1960 | 1740 | 1200 | 847 | 64.9 | 84.5 | 14.4 | 76 | 82.9 |
|  | Bio | 400 | 118 | .25 | 51.0 | 11.0 | 55.5 | 68.0 | 8.8 | 7.90 | 770 | 1410 | 1204 | 2236 | 215 | 55 | 7.7 | 2.7 | * | * | 47.0 | 1960 | 2220 | 1200 | 862 | 71.4 | 92.3 | 15.6 | 76 | 89.8 |
| 3 | Strip | 560 | 118 | .25 | 48.0 | 15.0 | 59.0 | 71.0 | 8.9 | 8.9 | 800 | 1030 | 1228 | 1620 | 195 | 28 | 7.7 | 0.1 | 1.05 | 1.10 | 55 | 1665 | 1794 | 1326 | 898 | 68.5 | 89.3 | 13.3 | 76 | 93.3 |
|  | Bio | 560 | 118 | .25 | 49.5 | 12.0 | 59.0 | 71.0 | 8.9 | 8.0 | 800 | 1600 | 1228 | 2404 | 195 | 50 | 7.7 | 1.2 | 1.05 | 0.5 | 55 | 1665 | 2415 | 1326 | 945 | 66.8 | 87.2 | 12.6 | 76 | 88.1 |
| 4 | Strip | 200 | 220 | .50 | 54.0 | 28.0 | 57.0 | 66.5 | 8.5 | 8.6 | 795 | 1070 | 1312 | 1676 | 315 | 65 | 8.9 | 0.90 | * | * | 120.0 | 1940 | 1940 | 1112 | 796 | 61.0 | 73.4 | 24.4 | 77 | 88.8 |
|  | Bio | 200 | 220 | .50 | 53.0 | 26.0 | 57.0 | 66.5 | 8.5 | 8.3 | 795 | 1140 | 1312 | 1764 | 315 | 75 | 8.9 | 1.7 | * | * | 127.5 | 1940 | 1890 | 1112 | 780 | 59.4 | 71.4 | 23.7 | 77 | 86.2 |
| 5 | Strip | 400 | 220 | .50 | 53.0 | 20.0 | 59.0 | 65.0 | 8.38 | 8.55 | 810 | 1120 | 1128 | 1720 | 285 | 60 | 9.9 | .3 | * | * | 122.8 | 2100 | 2140 | 1147 | 762 | 62.9 | 75.6 | 21.3 | 70 | 88.2 |
|  | Bio | 400 | 220 | .50 | 49.0 | 17.0 | 59.0 | 65.0 | 8.38 | 8.2 | 810 | 1240 | 1128 | 1868 | 285 | 60 | 9.9 | 1.2 | * | * | 114.2 | 2100 | 2200 | 1147 | 797 | 64.0 | 77.0 | 21.5 | 70 | 89.1 |
| 6 | Strip | 560 | 220 | .50 | 52.0 | 19.0 | 59.0 | 72.0 | 8.4 | 8.25 | 620 | 800 | 1016 | 1272 | 285 | 68 | 7.9 | 0.3 | * | * | 117 | 1620 | 1360 | 999 | 621 | 67.0 | 82.0 | 24.2 | 78 | 87.3 |
|  | Bio | 560 | 220 | .50 | 52.0 | 14.0 | 59.0 | 72.0 | 8.4 | 8.0 | 620 | 1150 | 1016 | 1868 | 285 | 62 | 7.9 | 0.6 | * | * | 110 | 1620 | 1988 | 999 | 738 | 63.1 | 77.2 | 24.7 | 78 | 89.1 |
| 7 | Strip | 200 | 470 | 1.0 | 54.2 | 36.0 | 55.0 | 69.0 | 8.9 | 8.85 | 980 | 1230 | 1504 | 1916 | 291 | 120 | 1.7 | 2.1 | 0.75 | 0.75 | 360 | 2420 | 2235 | 1149 | 851 | 43.4 | 62.5 | 16.8 | 58 | 68.4 |
|  | Bio | 200 | 470 | 1.0 | 54.0 | 34.0 | 55.0 | 69.0 | 8.9 | 8.85 | 980 | 1280 | 1504 | 1932 | 291 | 50 | 1.7 | 1.2 | 0.75 | 0.75 | 375 | 2420 | 2285 | 1149 | 862 | 40.2 | 57.9 | 21.2 | 58 | 86.3 |
| 8 | Strip | 400 | 470 | 1.0 | 50.5 | 27.5 | 62.0 | 71.0 | 9.0 | 9.2 | 1500 | 2000 | 2452 | 3052 | 235 | 120 | 10.0 | 0.6 | 0.60 | 1.0 | 320 | 3100 | 3150 | 1596 | 1490 | 36.4 | 64.8 | 9.3 | 50 | 65.2 |
|  | Bio | 400 | 470 | 1.0 | 50.5 | 24.0 | 62.0 | 71.0 | 9.0 | 9.2 | 1500 | 2125 | 2452 | 3316 | 235 | 80 | 10.0 | 0.6 | 0.60 | 1.0 | 312 | 3100 | 3300 | 1596 | 1516 | 36.8 | 65.5 | 11.1 | 50 | 77.4 |
| 9 | Strip | 560 | 470 | 1.0 | 52.5 | 24.0 | 58.0 | 67.0 | 8.8 | 8.8 | 880 | 1080 | 1268 | 1652 | 245 | 75 | 9.1 | .3 | 0.50 | 0.5 | 325 | 1930 | 1830 | 1066 | 755 | 51.2 | 64.8 | 17.6 | 69 | 78.8 |
|  | Bio | 560 | 470 | 1.0 | 52.0 | 21.0 | 58.0 | 67.0 | 8.8 | 8.75 | 880 | 1170 | 1268 | 1800 | 245 | 75 | 9.1 | .6 | 0.50 | 0.8 | 305 | 1930 | 2060 | 1066 | 796 | 51.8 | 65.6 | 17.9 | 69 | 80.1 |

(*) Less than 0.5 mg/l

(**) $\dfrac{\% \text{ BOD Removal}}{\% \text{ Volatile BOD}}$ = Removal of Volatile BOD.

# EXPERIMENTAL INVESTIGATIONS OF AIR STRIPPING

## TABLE 1
### EXPERIMENTAL CONDITIONS FOR BATCH STUDIES OF AIR STRIPPING

| Exp. No. | Type of Waste Water | Volumes Init. (l) | Volumes Final (l) | Inlet Water Temperature (°F) | Air Rate (ft³/min) | Recycle Rate (gal/min) | Total Time (min) |
|---|---|---|---|---|---|---|---|
| 1 | 6th Effect Condensate | 8.0 | 4.20 | 125 | 100 | 1.00 | 38 |
| 2 | 6th Ef. | 8.1 | 4.50 | 125 | 100 | 1.00 | 28 |
| 3 | 6th Ef. | 10.0 | 2.08 | 125 | -- | -- | 48 |
| 4 | 6th Ef. | 12.0 | 4.18 | 125 | -- | .50 | 59 |
| 5 | 650 mg/l MeOH in $H_2O$ | 12.0 | 4.66 | 125 | -- | .50 | 52 |
| 6 | 6th Ef. | 30.0 | 6.14 | 125 | -- | .50 | 228 |
| 7 | 6th Ef. | 12.0 | 7.45 | 125 | -- | .50 | 30 |
| 8 | 6th Ef. | 12.0 | 7.05 | 125 | 50 | 1.00 | 47 |
| 9 | 6th Ef. | 12.0 | 7.30 | 125 | 100 | 1.00 | 23 |
| 10 | 6th Ef. | 12.0 | 6.07 | 125 | 125 | .50 | 39 |
| 11 | 6th Ef. | 16.0 | 9.45 | 125 | 50 | .50 | 90 |
| 12 | 6th Ef. | 12.0 | 8.55 | 125 | 100 | .25 | 49 |
| 13 | 6th Ef. | 12.0 | 8.95 | 125 | 125 | .25 | 35 |
| 14 | 6th Ef. | 8.0 | 3.42 | 128 | 50 | .25 | 90 |
| 15 | 6th Ef. | 8.0 | 2.88 | 125 | 140 | .50 | 60 |
| 16 | 6th Ef. | 8.0 | 1.80 | 130 | 140 | .50 | 60 |
| 17 | 6th Ef. | 8.0 | 2.56 | 130 | 100 | 1.00 | 36 |
| 18 | 6th Ef. | 8.0 | 3.64 | 130 | 100 | 1.00 | 30 |
| 19 | 6th Ef. | 8.0 | 3.42 | 130 | 140 | 1.00 | 30 |
| 20 | 6th Ef. | 8.0 | 3.64 | 130 | 100 | 1.00 | 30 |
| 21 | 6th Ef. | 8.0 | 2.82 | 124 | 100 | .25 | 90 |
| 22 | 6th Ef. | 8.0 | 4.94 | 130 | 50 | 1.00 | 24 |
| 23 | 6th Ef. | 8.0 | 3.80 | 128 | 100 | 1.00 | 30 |
| 24 | 6th Ef. | 8.0 | 2.30 | 128 | 140 | 1.00 | 28 |
| 25 | 6th Ef. | 8.0 | 2.25 | 130 | 100 | .50 | 52 |
| 26 | 6th Ef. | 8.0 | 1.94 | 130 | 140 | .50 | 52 |
| 27 | 6th Ef. | 8.0 | 2.98 | 135 | 155 | 1.00 | 23 |
| 28 | Macon Combined Cond. | 3.34 | 1.90 | 125 | 164 | 1.00 | 10 |
| 29 | Macon Decker Filtrate | 3.27 | 2.33 | 125 | 164 | 1.00 | 10 |
| 30 | Macon Combined Cond. | 12.0 | 3.2 | 125 | 50 | .50 | 75 |
| 31 | Macon Decker Filtrate | 8.0 | 2.4 | 125 | 50 | .50 | 60 |

## TABLE 2

### BOD5 AND METHANOL DETERMINATIONS FOR BATCH STRIPPING EXPERIMENTS

| Exp. No. | Time mins | BOD5 ppm | Methanol ppm |
|---|---|---|---|
| 1 | 0 | 1183 | 580 |
| | 5 | -- | 290 |
| | 10 | -- | 160 |
| | 15 | 482 | 85 |
| | 38 | 527 | -- |
| 2 | 0 | 1325 | 580 |
| | 5 | -- | 285 |
| | 10 | -- | 140 |
| | 15 | -- | 57 |
| | 28 | 373 | -- |
| 3 | 0 | 1124 | 600 |
| | 5 | -- | 250 |
| | 10 | -- | 100 |
| | 15 | 594 | 60 |
| | 30 | -- | 35 |
| | 48 | 922 | <35 |
| 4 | 0 | 1080 | 560 |
| | 5 | 835 | 410 |
| | 10 | 665 | 250 |
| | 15 | -- | -- |
| | 30 | 525 | 45 |
| | 59 | 824 | <45 |
| 5 | 0 | -- | 590 |
| | 5 | -- | 340 |
| | 10 | -- | 170 |
| | 15 | -- | 130 |
| | 30 | -- | 40 |
| | 42 | -- | <35 |
| 6 | 0 | 990 | 645 |
| | 30 | 548 | 260 |
| | 228 | 1222 | < 4 |
| 7 | 0 | 1431 | 690 |
| | 5 | -- | 360 |
| | 10 | 790 | 200 |
| | 15 | -- | 190 |
| | 30 | 606 | 40 |
| 8 | 0 | 1067 | 730 |
| | 5 | 798 | 560 |
| | 10 | 604 | 390 |
| | 30 | 323 | 50 |
| | 47 | 341 | 10 |

| Exp. No. | Time mins | BOD5 ppm | Methanol ppm |
|---|---|---|---|
| 9 | 0 | 1165 | 470 |
| | 5 | 529 | 390 |
| | 10 | 375 | 150 |
| | 23 | 247 | <10 |
| 10 | 0 | 1223 | 780 |
| | 5 | 870 | 430 |
| | 10 | 605 | 180 |
| | 30 | 433 | 10 |
| | 39 | 470 | 0 |
| 11 | 0 | 1422 | 440 |
| | 10 | 798 | 285 |
| | 30 | -- | 280 |
| | 45 | 548 | 220 |
| | 65 | -- | 90 |
| | 90 | 370 | -- |
| 12 | 0 | 1098 | 820 |
| | 5 | -- | 600 |
| | 10 | 700 | 440 |
| | 30 | -- | 80 |
| | 49 | 323 | 30 |
| 13 | 0 | 1098 | 890 |
| | 5 | -- | 565 |
| | 10 | 640 | 420 |
| | 30 | -- | 50 |
| | 35 | 343 | 30 |
| 14 | 0 | 1245 | -- |
| | 5 | 958 | -- |
| | 15 | 925 | -- |
| | 23 | 1030 | -- |
| 15 | 0 | 862 | 250 |
| | 5 | 834 | 120 |
| | 15 | 756 | 51 |
| | 30 | 687 | 27 |
| | 60 | 925 | <10 |
| 16 | 0 | 933 | 348 |
| | 5 | 638 | 128 |
| | 15 | 437 | 74 |
| | 30 | 350 | <10 |
| | 60 | 398 | <10 |

| Exp. No. | Time mins | BOD5 ppm | Methanol ppm |
|---|---|---|---|
| 17 | 0 | 782 | 331 |
| | 5 | 520 | 100 |
| | 15 | 445 | <10 |
| | 30 | 359 | <10 |
| | 36 | 386 | <10 |
| 18 | 0 | 648 | 332 |
| | 5 | 365 | 166 |
| | 15 | 156 | <10 |
| | 30 | 244 | <10 |
| 19 | 0 | 942 | 315 |
| | 5 | 784 | 207 |
| | 15 | 569 | <10 |
| | 30 | 529 | <10 |
| 20 | 0 | 997 | 320 |
| | 5 | 877 | 150 |
| | 15 | 579 | 45 |
| | 30 | 479 | <10 |
| 21 | 0 | 970 | 215 |
| | 5 | 745 | 155 |
| | 15 | 765 | 110 |
| | 30 | 588 | 25 |
| | 45 | 596 | 35 |
| | 90 | 637 | 10 |
| 22 | 0 | 1149 | 291 |
| | 5 | 876 | 170 |
| | 15 | 600 | 70 |
| | 24 | 566 | 35 |
| 23 | 0 | 1596 | 235 |
| | 5 | 1550 | 140 |
| | 15 | 1274 | 85 |
| | 30 | 1470 | 25 |
| 24 | 0 | 1066 | 245 |
| | 5 | 845 | 70 |
| | 15 | 670 | 35 |
| | 28 | 783 | <10 |
| 25 | 0 | 1147 | 285 |
| | 5 | 931 | 130 |
| | 15 | 670 | 120 |
| | 30 | 646 | 65 |
| | 52 | 686 | 25 |

| Exp. No. | Time mins | BOD5 ppm | Methanol ppm |
|---|---|---|---|
| 26 | 0 | 999 | 285 |
| | 5 | 916 | 105 |
| | 15 | 638 | 45 |
| | 30 | 627 | 25 |
| | 52 | 753 | <10 |
| 27 | 0 | 1245 | -- |
| | 5 | 958 | -- |
| | 15 | 925 | -- |
| | 23 | 1030 | -- |
| 28 | 0 | 998 | 440 |
| | 5 | 365 | 120 |
| | 10 | 234 | 70 |
| 29 | 0 | 612 | 140 |
| | 5 | 378 | 50 |
| | 10 | 405 | 35 |
| 30 | 0 | 1167 | 320 |
| | 5 | 956 | 250 |
| | 10 | 944 | 205 |
| | 15 | 773 | 165 |
| | 30 | 595 | 70 |
| | 75 | 513 | 0 |
| 31 | 0 | 863 | 120 |
| | 5 | 747 | 75 |
| | 10 | 741 | 50 |
| | 15 | 743 | 40 |
| | 30 | 450 | 0 |
| | 60 | 545 | 0 |

TABLE 3

EXPERIMENTAL DATA FOR CONTINUOUS FLOW EXPERIMENTS* INVESTIGATING EFFECTS OF
WATER TEMPERATURE ON AIR STRIPPING

| Exp. No. | Water Temperature Inlet °F | Water Temperature Basin °F | Air Flow cfm | Feed Rate cc/min | Blowdown Rate cc/min | Air Temperature Dry Bulb °F | Air Temperature Wet Bulb °F | Wastewater pH Feed | Wastewater pH Blowdown | BOD Fresh Feed mg/l | BOD Blowdown mg/l | COD Fresh Feed mg/l | COD Blowdown mg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 53 | 25 | 125 | 470 | 307 | 67.5 | 65.5 | 9.9 | 8.9 | 1410 | 763 | 2993 | 2400 |
| 2 | 40 | 26 | 125 | 470 | 400 | 67.5 | 65.5 | 9.9 | 8.1 | 1410 | 750 | 2993 | 2324 |
| 3 | 42 | 28 | 75 | 470 | 393 | 67.5 | 65.5 | 9.0 | 8.5 | 1343 | 835 | 2908 | 2429 |
| 4 | 53 | 31 | 75 | 470 | 327 | 67.5 | 65.5 | 9.8 | 8.3 | 1305 | 850 | 2993 | 2372 |
| 5 | 42 | 35 | 50 | 470 | 413 | 79.5 | 73.0 | 9.3 | 9.2 | 950 | 430 | 2167 | 1701 |
| 6 | 52 | 40 | 50 | 470 | 369 | 80.5 | 73.0 | 9.3 | 9.2 | 1010 | 415 | 2276 | 1636 |
| 7 | 52 | 30 | 100 | 470 | 316 | 84.5 | 74.0 | 9.4 | 9.2 | 890 | 280 | 2276 | 1517 |
| 8 | 40 | 30 | 100 | 470 | 377 | 85.5 | 75.0 | 9.4 | 9.2 | 890 | 300 | 2276 | 1517 |

*Liquid Recirculation Rate = 1.0 GPM.

## APPENDIX E

### INVESTIGATION OF FOAMING IN LABORATORY COOLING TOWER

Foaming was observed to occur at various times during the operation of the Rome laboratory tower. This foaming occurred mainly in the packed section of the tower and occasionally in the basin. Since a full-scale tower would process large quantities of liquid and would use considerable amounts of air, an intolerable nuisance condition would likely result. A recent report(*) concerning the use of cooling towers in black liquor evaporation and the foaming problems encountered prompted a study of foaming. The report stated that foaming could be controlled by maintaining a continuous blowdown and thereby controlling the solids concentration at 250 ppm. Further information contained in the report revealed that before the tower was installed the pH of the water was approximately 6.0 with solids concentration averaging 50 ppm; and after installation of the tower the pH of the recycled liquid increased to approximately 7.5.

Preliminary studies were undertaken to attempt to correlate solids concentration and pH with foaming. A quantitative measure was devised for the foaming in the packed section. Visual observation of the action of liquid and air in the tower made direct assessment of the foam level possible. Foaming originated at packing support points within the tower and could conveniently be measured by counting the number of packing grid heights (one grid height = 1.25 inches) above the support locations upon which foaming was taking place.

An experiment with the laboratory cooling tower was performed whereby the solids concentration was allowed to increase from 314 to 1570 ppm. Although the solids content increased five fold, no foaming increase was noted. Many experiments of shorter duration, where the concentration doubled, showed the same negative effect on increased foaming.

The most important variable related to foaming tendency in the tower was pH. Data collected on 84 observations of foam height under varied experimental conditions were fairly well correlated with liquid pH. Figure E-1 shows the foaming tendency measured as foam height versus wastewater pH. This figure shows that the nearer the pH is to a neutral value, the more likely a foaming condition is to occur. The normal pH of the condensate feed was 9.5 and was typically reduced to 9.0 upon recirculation.

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(*)  Cohn, R.G. and Tonn, E.T., "Use of a Cooling Tower in Black Liquor Evaporation", *TAPPI 47*, No. 3, pp 163A-165A (1965).
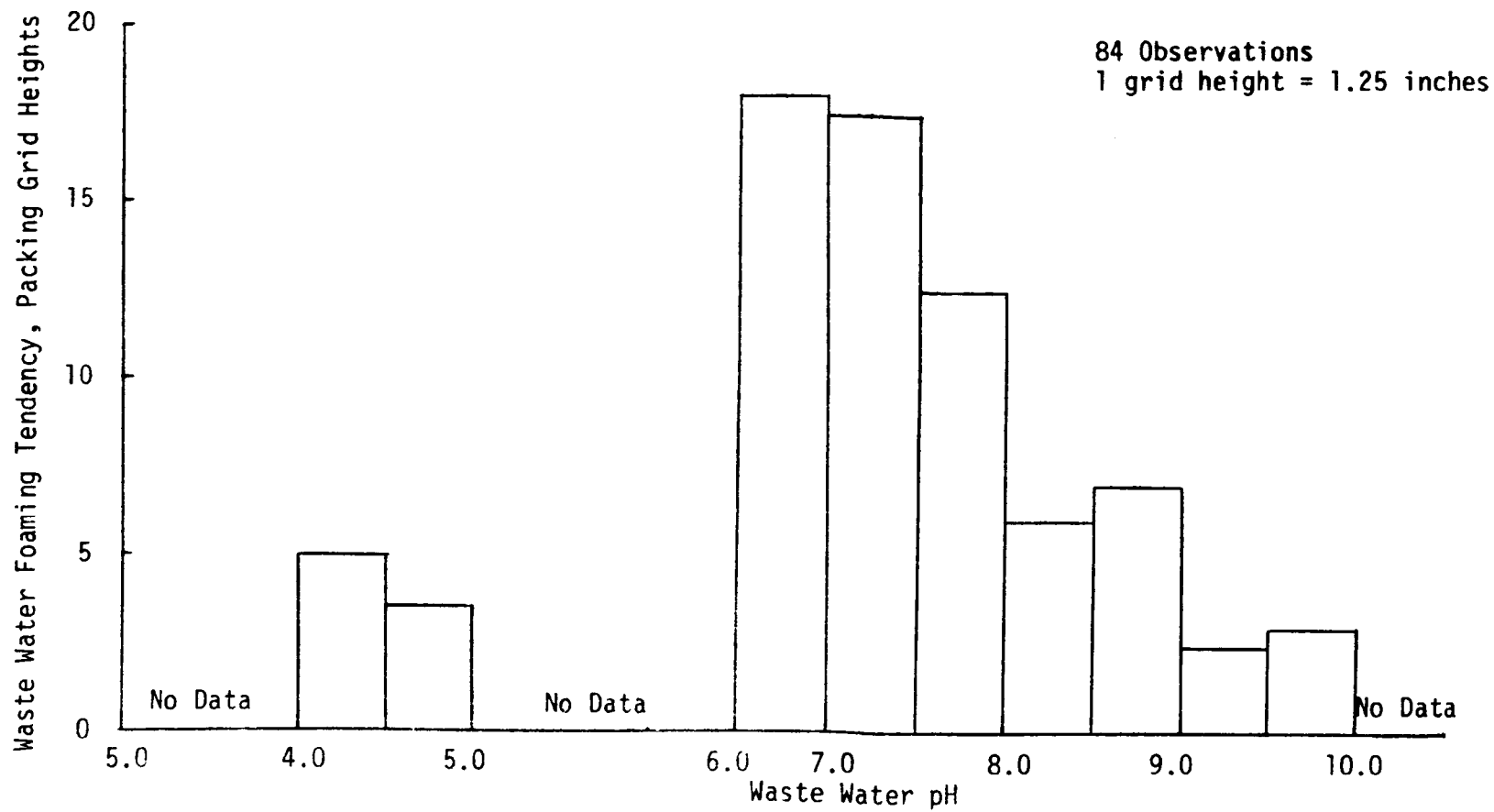
FIGURE E-1: FOAMING TENDENCY AS A FUNCTION OF WASTE WATER pH

Other experimental observations noted that increasing air flows and decreasing temperature tended to promote foaming. Decker filtrate produced considerably more foam than the condensate streams, although the foaming tendency of the latter stream varied considerably among samples.

## TABLE 1

### BOD DATA FOR FULL-SCALE COOLING TOWER OPERATION

| Period | Date | BOD (mg/l) | | | | | |
|--------|------|---------|---------|-----------------|--------------------|--------------|----------------------|
| | | To Tower | From Tower | Decker Filtrate | Combined Condensate | 6th* Effect | Turpentine Underflow |
| 1 | May 14, 1969 | 357 | 310 | -- | 665 | 970 | |
| | 15 | 490 | 410 | -- | 618 | 2563 | |
| | 16 | 540 | 467 | -- | 445 | 2477 | |
| | 17 | 605 | 568 | -- | 730 | 1649 | |
| | 18 | 672 | 583 | -- | 853 | 3066 | |
| 2 | May 19, 1969 | 598 | 507 | -- | -- | 3567 | |
| | 20 | 445 | 368 | -- | -- | 3149 | |
| | 21 | 478 | 368 | -- | -- | 4312 | |
| | 22 | 413 | 297 | -- | -- | 4474 | |
| | 23 | 450 | 368 | -- | -- | 3286 | |
| | 24 | 470 | 345 | -- | -- | 4794 | |
| | 25 | 463 | 395 | -- | -- | 2652 | |
| 3 | May 26, 1969 | 648 | 648 | 585 | 866 | 321 | |
| | 27 | 577 | 571 | 475 | 782 | 683 | |
| | 28 | 622 | 510 | 495 | 729 | 4387 | |
| | 29 | 685 | 593 | 553 | 794 | 3881 | |
| | 30 | 785 | 658 | 647 | 843 | 5905 | |
| | 31 | 657 | 598 | 565 | 994 | 1799 | |
| | June 1 | 513 | 480 | 397 | 905 | 876 | |
| 4 | June 2, 1969 | 342 | 287 | 212 | 638 | 2294 | |
| | 3 | 573 | 557 | 585 | 776 | 594 | |
| | 4 | 623 | 565 | 440 | 812 | 3312 | |
| | 5 | 510 | 440 | 383 | 725 | 2246 | |
| | 6 | 602 | 440 | 365 | 625 | 6299 | |
| | 7 | 458 | 458 | 462 | 797 | 168 | |
| 5 | June 9, 1969 | 533 | 435 | 450 | -- | 4176 | |
| | 11 | 695 | 595 | 525 | -- | 5386 | |
| | 12 | 808 | 735 | 700 | -- | 4353 | |
| | 14 | 655 | 593 | 583 | -- | 2916 | |
| | 15 | 607 | 482 | 478 | | 5720 | |
| | 16 | 806 | 690 | 826 | -- | 4132 | |
| | 17 | 950 | 805 | 910 | -- | 5574 | |
| | 18 | 775 | 687 | 890 | -- | 2671 | |
| | 19 | 822 | 770 | 862 | -- | 2080 | |
| | 22 | 688 | 612 | 595 | -- | 3678 | |

(*) BOD (mg/l) for 6th effect calculated from #BOD and flow in mgd.

TABLE 1
(Continued)

| Period | Date | BOD (mg/l) | | | | | |
|--------|------|---------|----------|---------|-----------|--------|------------|
| | | To Tower | From Tower | Decker Filtrate | Combined Condensate | 6th Effect | Turpentine Underflow |
| 5 (Cont.) | July 4, 1969 | 790 | 770 | 807 | -- | 1276 | |
| | 5 | 675 | 634 | 690 | -- | 1852 | |
| | 6 | 552 | 547 | 572 | -- | 1061 | |
| | 7 | 620 | 590 | 743 | -- | 803 | |
| | 8 | 527 | 438 | 418 | -- | 4069 | |
| | 9 | 465 | 390 | 445 | -- | 2961 | |
| | 10 | 610 | 582 | 625 | -- | 1289 | |
| | 11 | 667 | 643 | 625 | -- | 2169 | |
| | 12 | 672 | 622 | 685 | -- | 2749 | |
| | 15 | 1095 | 1075 | 1107 | -- | 728 | |
| | 16 | 1252 | 1252 | 1270 | -- | 1139 | |
| | 17 | 1103 | 1067 | 1128 | -- | 2189 | |
| | 18 | 922 | 842 | 875 | -- | 3914 | |
| 6 | July 19, 1969 | 962 | 947 | 888 | -- | 1894 | |
| | 20 | 713 | 658 | 638 | -- | 2797 | |
| | 21 | 777 | 680 | 675 | -- | 4313 | |
| | 25 | 593 | 515 | 533 | -- | 3629 | |
| | 28 | 745 | 735 | 670 | -- | 1572 | |
| | 29 | 1020 | 987 | 1012 | -- | 2100 | |
| | 30 | 1207 | 1008 | 1012 | -- | 9143 | |
| | 31 | 1128 | 1042 | 1012 | -- | 4688 | |
| | Aug. 2, 1969 | 1017 | 890 | 1140 | -- | 5525 | |
| | 3 | 970 | 873 | 1018 | -- | 5131 | |
| | 5 | 712 | 623 | 665 | -- | 3961 | |
| | 6 | 793 | 702 | 1048 | -- | 3935 | |
| | 8 | 1355 | 1301 | 1283 | -- | 3784 | |
| | 11 | 728 | 678 | 758 | -- | 2247 | |
| | 12 | 750 | 728 | 738 | -- | 1548 | |
| | 13 | 1042 | 832 | 958 | -- | 8257 | |
| | 14 | 1045 | 873 | 910 | -- | 7535 | |
| | 15 | 953 | 777 | 933 | -- | 7615 | |
| | 16 | 970 | 953 | 1018 | -- | 1522 | |
| | 17 | 823 | 805 | 860 | -- | 1999 | |
| 7 | Aug. 22, 1969 | 818 | 750 | 825 | -- | 2625 | |
| | 23 | 815 | 783 | 753 | -- | 2041 | |
| | 24 | 863 | 750 | 728 | -- | 4897 | |
| | 25 | 780 | 617 | 613 | -- | 6622 | |
| | 26 | 721 | 626 | 669 | -- | 4089 | |
| | 27 | 697 | 613 | 632 | -- | 3709 | |

## TABLE 1
### (Continued)

| Period | Date | BOD (mg/1) To Tower | From Tower | Decker Filtrate | Combined Condensate | 6th Effect | Turpentine Underflow |
|---|---|---|---|---|---|---|---|
| 7 | Aug. 28, 1969 | 998 | 865 | 1010 | -- | 4761 | |
| (Cont.) | 29 | 1110 | 1052 | 1113 | -- | 2847 | |
| | 30 | 1041 | 942 | 1028 | -- | 4192 | |
| | Sept. 3 | 682 | 618 | 745 | -- | 2654 | |
| | 6 | 977 | 870 | 965 | -- | 4401 | |
| | 7 | 985 | 868 | 945 | -- | 4854 | |
| | | | | | | | |
| 8 | Sept. 9, 1969 | 740 | 666 | 845 | 626 | 2855 | |
| | 10 | 820 | 693 | 887 | 672 | 4518 | |
| | 11 | 738 | 653 | 892 | 672 | 2663 | |
| | 12 | 932 | 848 | 1223 | 712 | 2554 | |
| | 13 | 935 | 815 | 1067 | 806 | 4204 | |
| | 14 | 795 | 745 | 962 | 790 | 1383 | |
| | 15 | 745 | 715 | 797 | 732 | 1443 | |
| | 16 | 755 | 702 | 1070 | 630 | 1335 | |
| | | | | | | | |
| 9 | Sept. 18, 1969 | 981 | 927 | 1125 | -- | 1948 | |
| | 19 | 802 | 627 | 727 | -- | 5044 | |
| | 20 | 620 | 582 | 772 | -- | 280 | |
| | 21 | 823 | 718 | 837 | -- | 3337 | |
| | 22 | 790 | 750 | 825 | -- | 1679 | |
| | 23 | 981 | 898 | 1066 | -- | 3094 | |
| | 24 | 1043 | 857 | 1155 | -- | 6313 | |
| | 25 | 1315 | 1260 | 1288 | -- | 3064 | |
| | 26 | 1377 | 1295 | 1347 | -- | 3917 | |
| | 27 | 990 | 907 | 972 | -- | 3440 | |
| | 28 | 803 | 730 | 740 | -- | 3216 | |
| | 29 | 882 | 810 | 908 | -- | 2604 | |
| | Oct. 1, 1969 | 1047 | 927 | 1318 | -- | 1638 | |
| | 2 | 1215 | 1208 | 1317 | -- | 804 | |
| | | | | | | | |
| 10 | Oct. 5, 1969 | 673 | 627 | 797 | 650 | 1603 | |
| | 6 | 767 | 687 | 928 | 650 | 2939 | |
| | 7 | 800 | 765 | 1120 | 620 | 1133 | |
| | 8 | 1017 | 923 | 1392 | 699 | 3432 | |
| | | | | | | | |
| 11 | Oct. 10 | 1030 | 982 | 1072 | -- | 2413 | |
| | 11 | 832 | 800 | 915 | -- | 1432 | |
| | 12 | 863 | 797 | 857 | -- | 3134 | |
| | 15 | 820 | 809 | 613 | -- | 2079 | |
| | 16 | 1177 | 1103 | 1082 | -- | 3659 | |

TABLE 1
(Continued)

| Period | Date | BOD (mg/1) | | | | | |
|---|---|---|---|---|---|---|---|
| | | To Tower | From Tower | Decker Filtrate | Combined Condensate | 6th Effect | Turpentine Underflow |
| 11 (Cont.) | Oct. 17, 1969 | 1230 | 1083 | 1053 | -- | 6293 | |
| | 18 | 1042 | 1002 | 935 | -- | 2986 | |
| | 20 | 912 | 870 | 1010 | -- | 2899 | |
| | 21 | 952 | 840 | 1120 | -- | 4854 | |
| | 26 | 1462 | 1395 | 1383 | -- | 4168 | |
| | 27 | 1237 | 1173 | 1195 | -- | 3586 | |
| | 28 | 903 | 832 | 833 | -- | 3534 | |
| | Nov. 1 | 1417 | 1405 | 1492 | -- | 1946 | |
| | 2 | 1465 | 1403 | 1463 | -- | 3295 | |
| | 3 | 985 | 918 | 1282 | -- | 1128 | |
| | 5 | 882 | 695 | 922 | -- | 6152 | |
| 12 | Nov. 6 | 718 | 687 | 837 | -- | 524 | |
| | 7 | 822 | 718 | 723 | -- | 602 | |
| | 8 | 848 | 768 | 938 | -- | 2821 | |
| | 9 | 987 | 838 | 1005 | -- | 5657 | |
| | 10 | 1043 | 955 | 992 | -- | 3947 | |
| | 11 | 987 | 863 | 887 | -- | 5695 | |
| | 12 | 1032 | 955 | 1022 | -- | 4004 | |
| | 13 | 978 | 935 | 1108 | -- | 1877 | |
| | 18 | 1335 | 1265 | 1673 | -- | 4099 | |
| | 24 | 920 | 917 | 862 | -- | 1508 | |
| | 25 | 1042 | 1037 | 1035 | -- | 1233 | |
| | 26 | 818 | 773 | 937 | -- | 1651 | |
| | 29 | 753 | 728 | 772 | -- | 1469 | |
| | 30 | 980 | 930 | 935 | -- | 2801 | |
| | Dec. 10 | 1137 | 1127 | 1265 | -- | 755 | |
| | 12 | 1040 | 1023 | 978 | -- | 1946 | |
| | 14 | 828 | 813 | 795 | -- | 1466 | |
| | 15 | 1147 | 1125 | 1078 | -- | 2282 | |
| | 16 | 1257 | 1250 | 1267 | -- | -- | |
| | 28 | 673 | 625 | 770 | -- | 2544 | |
| | 29 | 703 | 607 | 713 | -- | 3728 | |
| | 30 | 558 | 448 | 595 | -- | 3627 | |
| 13 | Feb. 9, 1970 | 1155 | 1093 | -- | -- | -- | -- |
| | 13 | 1167 | 1067 | -- | -- | -- | -- |
| | 17 | 987 | 923 | -- | -- | -- | 6467 |
| | 18 | 1072 | 965 | 937 | -- | -- | 7733 |
| | 19 | 1315 | 1285 | 1190 | -- | -- | -- |
| | 21 | -- | -- | -- | -- | -- | 7700 |
| | 22 | -- | -- | -- | -- | -- | 9130 |
| | 23 | 1157 | 1120 | 993 | -- | -- | 8650 |
| | 24 | 1165 | 1108 | 1140 | -- | -- | 7430 |
| | 25 | 1150 | 1102 | 1018 | -- | -- | 8666 |

## TABLE 2

### METHANOL DATA FOR FULL-SCALE COOLING TOWER OPERATION

| Period | Date | Methanol (mg/1) | | | | | | |
|--------|------|-------|-------|--------|-------|--------|-----------|------|
| | | To Tower | From Tower | Decker Filtrate | Comb. Cond. | 6th Effect | Turpentine Underflow | Non-Cond. |
| 1 | May 17, 1969 | 150 | 80 | -- | 230 | | | |
| | 18 | 150 | 125 | -- | 270 | | | |
| 2 | May 19, 1969 | 110 | 80 | -- | -- | | | |
| | 20 | 100 | 85 | -- | -- | | | |
| | 21 | 100 | 80 | -- | -- | | | |
| | 22 | 120 | 60 | -- | -- | | | |
| | 23 | 100 | 60 | -- | -- | | | |
| | 24 | 120 | 60 | -- | -- | | | |
| | 25 | 140 | 60 | -- | -- | | | |
| 3 | May 26, 1969 | 120 | 65 | 70 | 220 | | | |
| | 27 | 130 | 90 | 80 | 260 | | | |
| 4 | June 3, 1969 | 175 | 125 | 70 | 350 | | | |
| | 4 | 180 | 100 | 100 | 340 | | | |
| | 5 | 180 | 140 | 100 | 345 | | | |
| 5 | June 9, 1969 | 53 | 89 | 50 | -- | | | |
| | 10 | 100 | 80 | 70 | -- | | | |
| | 11 | 100 | 68 | 44 | -- | | | |
| | 12 | 75 | 55 | 55 | -- | | | |
| | 14 | 94 | 70 | 48 | -- | | | |
| | 15 | 95 | 42 | 42 | -- | | | |
| | 16 | 86 | 56 | 90 | -- | | | |
| | 17 | 110 | 90 | 120 | -- | | | |
| | 18 | 122 | 78 | 94 | -- | | | |
| | 19 | 73 | 47 | 90 | -- | | | |
| | 22 | 88 | 57 | 74 | -- | | | |
| | July 4 | 160 | 85 | 110 | -- | | | |
| | 5 | 120 | 80 | 90 | -- | | | |
| | 6 | 105 | 75 | 85 | -- | | | |
| | 7 | 90 | 70 | 80 | -- | | | |
| | 8 | 105 | 85 | 85 | -- | | | |
| | 10 | 120 | 85 | 100 | -- | | | |
| | 11 | 105 | 80 | 95 | -- | | | |
| | 12 | 105 | 70 | 110 | -- | | | |
| | 15 | 170 | 105 | 90 | -- | | | |
| | 16 | 60 | 60 | 20 | -- | | | |
| | 17 | 125 | 100 | 140 | -- | | | |
| | 18 | 140 | 90 | 70 | -- | | | |

TABLE 2
(Continued)

| Period | Date | Methanol (mg/l) To Tower | From Tower | Decker Filtrate | Comb. Cond. | 6th Effect | Turpentine Underflow | Non-Cond. |
|---|---|---|---|---|---|---|---|---|
| 6 | July 21, 1969 | 140 | 80 | 100 | -- | | | |
| | 25 | 100 | 85 | 110 | -- | | | |
| | 29 | 120 | 85 | 110 | -- | | | |
| | 30 | 130 | 110 | 120 | -- | | | |
| | 31 | 130 | 90 | 80 | -- | | | |
| | Aug. 2 | 100 | 85 | 100 | -- | | | |
| | 3 | 100 | 70 | 110 | -- | | | |
| | 6 | 105 | 67 | 170 | -- | | | |
| | 7 | 150 | 92 | 175 | -- | | | |
| | 8 | 138 | 98 | 130 | -- | | | |
| | 11 | 115 | 96 | 115 | -- | | | |
| | 12 | 135 | 97 | 160 | -- | | | |
| | 13 | 142 | 105 | 122 | -- | | | |
| | 14 | 163 | 115 | 136 | -- | | | |
| | 15 | 118 | 86 | 130 | -- | | | |
| | 16 | 96 | 88 | 125 | -- | | | |
| | 17 | 122 | 95 | 130 | -- | | | |
| 7 | Aug. 22, 1969 | 195 | 129 | 90 | -- | | | |
| | 23 | 195 | 155 | 155 | -- | | | |
| | 29 | 130 | 82 | 75 | -- | | | |
| | 30 | 108 | 86 | 138 | -- | | | |
| | Sept. 3 | 105 | 62 | 90 | -- | | | |
| 8 | Sept. 10, 1969 | 75 | 34 | 59 | 140 | | | |
| | 11 | 110 | 84 | 76 | 230 | | | |
| | 12 | 84 | 80 | 110 | 220 | | | |
| | 13 | 130 | 84 | 78 | 210 | | | |
| | 14 | 100 | 85 | 80 | 220 | | | |
| | 15 | 100 | 39 | 90 | 190 | | | |
| | 16 | 115 | 74 | 91 | 210 | | | |
| 9 | Sept. 22, 1969 | 110 | 110 | 150 | 270 | 2185 | | |
| | 23 | 140 | 105 | 100 | 430 | 2037 | | |
| | 25 | 130 | -- | 160 | -- | | | |
| | Oct. 2, 1969 | 120 | 80 | 155 | -- | | | |
| 13 | Feb. 10, 1970 | 315 | 190 | 190 | 275 | -- | 3250 | 180 |
| | 10 | 310 | 140 | 215 | 335 | -- | 6000 | 160 |
| | 10 | 320 | 200 | 205 | 320 | -- | 4250 | 240 |
| | 11 | 190 | 47 | 175 | 500 | -- | 6500 | 270 |
| | 11 | 44 | 40 | 195 | 365 | -- | 4500 | 215 |
| | 11 | 94 | 34 | 39 | 78 | -- | 2575 | 92 |
| | 12 | 210 | 195 | 225 | 415 | -- | 3625 | 155 |
| | 12 | 140 | 125 | 170 | -- | -- | -- | 165 |
| | 12 | 240 | 225 | -- | -- | -- | -- | -- |

## TABLE 3

### FLOW RATES FOR FULL-SCALE COOLING TOWER OPERATION

| Period | Date | To Tower | From Tower | Sewer | Decker Filtrate | Comb. Cond. | 6th Effect | Turpentine Underflow |
|--------|------|----------|------------|-------|-----------------|-------------|------------|----------------------|
| 1 | May 14, 1969 | 6.84 | 6.37 | .44 | -- | .28 | .29 | |
| | 15 | 9.36 | 8.65 | .41 | -- | .48 | .29 | |
| | 16 | 10.05 | 9.29 | .41 | -- | .50 | .29 | |
| | 17 | 10.51 | 9.72 | .41 | -- | .50 | .29 | |
| | 18 | 9.68 | 8.89 | .44 | -- | .51 | .29 | |
| 2 | May 19, 1969 | 9.64 | 9.37 | .30 | -- | -- | .29 | |
| | 20 | 10.33 | 10.01 | .33 | -- | -- | .29 | |
| | 21 | 10.34 | 10.02 | .31 | -- | -- | .29 | |
| | 22 | 10.40 | 10.09 | .36 | -- | -- | .29 | |
| | 23 | 10.29 | 9.99 | .35 | -- | -- | .29 | |
| | 24 | 10.33 | 10.05 | .33 | -- | -- | .29 | |
| | 25 | 9.76 | 9.49 | .31 | -- | -- | .29 | |
| 3 | May 26, 1969 | 9.99 | 7.96 | 1.68 | 1.02 | .72 | .29 | |
| | 27 | 11.80 | 8.87 | 2.52 | 1.62 | .99 | .29 | |
| | 28 | 11.66 | 8.69 | 2.55 | 1.68 | .98 | .29 | |
| | 29 | 11.81 | 8.87 | 2.54 | 1.68 | .98 | .29 | |
| | 30 | 11.78 | 8.54 | 2.52 | 1.68 | .98 | .29 | |
| | 31 | 11.61 | 8.73 | 2.48 | 1.68 | .95 | .29 | |
| | June 1 | 11.39 | 8.54 | 2.43 | 1.68 | .91 | .29 | |
| 4 | June 2, 1969 | 11.79 | 9.31 | 2.10 | 1.68 | .53 | .29 | |
| | 3 | 11.00 | 8.48 | 2.12 | 1.68 | .56 | .29 | |
| | 4 | 11.58 | 8.96 | 2.18 | 1.68 | .56 | .29 | |
| | 5 | 11.85 | 9.23 | 2.13 | 1.68 | .54 | .29 | |
| | 6 | 10.47 | 8.62 | 1.48 | 1.11 | .44 | .29 | |
| | 7 | 12.48 | 9.83 | 2.19 | 1.68 | .52 | .29 | |
| 5 | June 9, 1969 | 11.12 | 9.09 | 1.79 | 1.68 | -- | .29 | |
| | 10 | 11.18 | 9.03 | 1.78 | 1.68 | -- | .29 | |
| | 11 | 12.24 | 10.19 | 1.66 | 1.68 | -- | .29 | |
| | 12 | 12.50 | 10.43 | 1.65 | 1.68 | -- | .29 | |
| | 14 | 10.63 | 8.79 | 1.77 | 1.68 | -- | .29 | |
| | 15 | 12.10 | 9.85 | 1.81 | 1.96 | -- | .29 | |
| | 16 | 10.67 | 8.63 | 1.60 | 1.75 | -- | .29 | |
| | 17 | 10.83 | 8.77 | 1.59 | 1.77 | -- | .29 | |
| | 18 | 9.94 | 8.18 | 1.36 | 1.47 | -- | .29 | |
| | 19 | 10.44 | 8.40 | 1.59 | 1.76 | -- | .29 | |
| | 22 | 11.21 | 9.02 | 1.69 | 1.89 | -- | .29 | |

TABLE 3
(Continued)

| Period | Date | | To Tower | From Tower | Sewer | Decker Filtrate | Comb. Cond. | 6th Effect | Turpentine Underflow |
|--------|------|--------|----------|------------|-------|-----------------|-------------|------------|----------------------|
| 5 | July 3, 1969 | | 9.38 | 7.57 | 1.69 | 1.68 | -- | .29 | |
| | 4 | | 10.33 | 8.47 | 1.26 | 1.58 | -- | .29 | |
| | 5 | | 10.90 | 8.97 | 1.29 | 1.64 | -- | .29 | |
| | 6 | | 11.19 | 9.27 | 1.29 | 1.63 | -- | .29 | |
| | 7 | | 11.48 | 9.35 | 1.57 | 1.84 | -- | .29 | |
| | 8 | | 11.44 | 9.36 | 1.56 | 1.79 | -- | .29 | |
| | 9 | | 11.27 | 9.18 | 1.59 | 1.80 | -- | .29 | |
| | 10 | | 10.00 | 8.00 | 1.54 | 1.71 | -- | .29 | |
| | 11 | | 10.89 | 8.80 | 1.56 | 1.79 | -- | .29 | |
| | 12 | | 10.67 | 8.33 | 1.84 | 1.74 | -- | .29 | |
| | 15 | | 12.86 | 10.69 | 1.50 | 1.87 | -- | .29 | |
| | 16 | | 12.26 | 10.29 | 1.33 | 1.68 | -- | .29 | |
| | 17 | | 11.95 | 9.98 | 1.39 | 1.69 | -- | .29 | |
| | 18 | | 11.86 | 9.88 | 1.34 | 1.65 | -- | .29 | |
| 6 | July 19, 1969 | | 11.74 | 9.75 | 1.34 | 1.70 | -- | .29 | |
| | 20 | | 10.67 | 8.64 | 1.42 | 1.74 | -- | .29 | |
| | 21 | | 10.79 | 8.75 | 1.41 | 1.75 | -- | .29 | |
| | 25 | | 12.19 | 9.28 | 2.23 | 2.61 | -- | .29 | |
| | 28 | | 14.44 | 9.16 | 1.47 | 2.00 | -- | .29 | |
| | 29 | | 11.23 | 9.11 | 1.76 | 1.83 | -- | .29 | |
| | 30 | | 11.90 | 9.72 | 1.34 | 1.90 | -- | .29 | |
| | 31 | | 11.70 | 9.64 | 1.34 | 1.77 | -- | .29 | |
| | Aug. | 2 | 12.11 | 9.37 | 2.08 | 1.50 | -- | .29 | |
| | | 3 | 12.55 | 8.90 | 2.97 | 1.76 | -- | .29 | |
| | | 5 | 12.46 | 8.84 | 2.96 | 3.33 | -- | .29 | |
| | | 6 | 11.95 | 8.79 | 2.52 | .69 | -- | .29 | |
| | | 7 | 11.65 | 9.32 | 1.96 | 1.66 | -- | .29 | |
| | | 8 | 12.87 | 11.03 | 1.47 | 1.55 | -- | .29 | |
| | | 11 | 11.73 | 9.85 | 1.55 | 1.63 | -- | .29 | |
| | | 12 | 11.59 | 9.71 | 1.51 | 1.59 | -- | .29 | |
| | | 13 | 11.18 | 9.36 | 1.45 | 1.53 | -- | .29 | |
| | | 14 | 11.59 | 9.78 | 1.45 | 1.53 | -- | .29 | |
| | | 15 | 12.46 | 10.21 | 1.88 | 1.61 | -- | .29 | |
| | | 16 | 12.03 | 9.99 | 1.67 | 1.55 | -- | .29 | |
| | | 17 | 12.52 | 9.99 | 1.88 | 1.96 | -- | .29 | |
| 7 | Aug. 22, 1969 | | 10.58 | 8.85 | 1.44 | 1.52 | -- | .29 | |
| | 23 | | 9.98 | 8.12 | 1.49 | 1.57 | -- | .29 | |
| | 24 | | 10.35 | 8.46 | 1.52 | 1.61 | -- | .29 | |
| | 25 | | 10.65 | 8.80 | 1.49 | 1.57 | -- | .29 | |
| | 26 | | 11.30 | 9.43 | 1.51 | 1.58 | -- | .29 | |
| | 27 | | 11.03 | 9.30 | 1.36 | 1.44 | -- | .29 | |

TABLE 3
(Continued)

| Period | | Date | | To Tower | From Tower | Sewer | Decker Filtrate | Comb. Cond. | 6th Effect | Turpentine Underflow |
|--------|---|------|---|----------|------------|-------|-----------------|-------------|------------|----------------------|
| 7 | Aug. | 28, | 1969 | 10.23 | 8.36 | 1.50 | 1.58 | -- | .29 | |
| (Cont.) | | 29 | | 10.89 | 8.82 | 1.70 | 1.78 | -- | .29 | |
| | | 30 | | 10.81 | 9.06 | 1.38 | 1.46 | -- | .29 | |
| | Sept. | 3 | | 12.78 | 10.70 | 1.71 | 1.78 | -- | .29 | |
| | | 6 | | 10.87 | 9.14 | 1.37 | 1.45 | -- | .29 | |
| | | 7 | | 11.15 | 9.37 | 1.41 | 1.49 | -- | .29 | |
| 8 | Sept. | 9, | 1969 | 11.61 | 8.86 | 2.31 | 1.46 | 1.01 | .29 | |
| | | 10 | | 10.75 | 8.01 | 2.38 | 1.43 | 1.03 | .29 | |
| | | 11 | | 11.17 | 8.41 | 2.40 | 1.45 | 1.03 | .29 | |
| | | 12 | | 11.59 | 8.79 | 2.43 | 1.47 | 1.03 | .29 | |
| | | 13 | | 11.09 | 8.37 | 2.35 | 1.41 | 1.02 | .29 | |
| | | 14 | | 10.94 | 8.18 | 2.39 | 1.45 | 1.02 | .29 | |
| | | 15 | | 11.58 | 8.86 | 2.36 | 1.45 | .98 | .29 | |
| | | 16 | | 12.57 | 9.81 | 2.39 | 1.50 | .97 | .29 | |
| 9 | Sept. | 18, | 1969 | 11.35 | 9.47 | 1.37 | 1.59 | -- | .29 | |
| | | 19 | | 8.13 | 6.49 | 1.22 | 1.29 | -- | .29 | |
| | | 20 | | 10.45 | 6.58 | 3.42 | 1.85 | -- | .29 | |
| | | 21 | | 9.93 | 7.40 | 2.05 | 1.82 | -- | .29 | |
| | | 22 | | 9.74 | 7.47 | 1.78 | 1.74 | -- | .29 | |
| | | 23 | | 10.62 | 8.33 | 1.79 | 1.75 | -- | .29 | |
| | | 24 | | 10.91 | 8.49 | 2.06 | 1.71 | -- | .29 | |
| | | 25 | | 10.45 | 8.41 | 1.50 | 1.75 | -- | .29 | |
| | | 26 | | 10.41 | 8.38 | 1.50 | 1.75 | -- | .29 | |
| | | 27 | | 10.16 | 8.23 | 1.54 | 1.64 | -- | .29 | |
| | | 28 | | 10.14 | 8.09 | 1.51 | 1.76 | -- | .29 | |
| | | 29 | | 9.63 | 7.59 | 1.49 | 1.75 | -- | .29 | |
| | Oct. | 1 | | 9.01 | 6.49 | 2.03 | 2.23 | -- | .29 | |
| | | 2 | | 10.47 | 8.46 | 1.50 | 1.72 | -- | .29 | |
| 10 | Oct. | 5, | 1969 | 11.94 | 9.22 | 2.24 | 1.42 | 1.01 | .29 | |
| | | 6 | | 11.94 | 9.22 | 2.25 | 1.41 | 1.03 | .29 | |
| | | 7 | | 12.95 | 10.23 | 2.26 | 1.40 | 1.04 | .29 | |
| | | 8 | | 12.91 | 10.06 | 2.32 | 1.53 | 1.53 | .29 | |
| 11 | Oct. | 10, | 1969 | 11.72 | 9.81 | 1.39 | 1.62 | -- | .29 | |
| | | 11 | | 11.91 | 9.65 | 1.75 | 1.71 | -- | .29 | |
| | | 12 | | 11.82 | 9.85 | 1.45 | 1.68 | -- | .29 | |
| | | 15 | | 9.40 | 7.75 | 1.21 | 1.36 | -- | .29 | |
| | | 16 | | 9.26 | 7.89 | .94 | 1.08 | -- | .29 | |
| | | 17 | | 8.11 | 7.17 | .56 | .85 | -- | .29 | |
| | | 18 | | 8.51 | 7.49 | .65 | .82 | -- | .29 | |

TABLE 3
(Continued)

| Period | Date | Flow (mgd) | | | | | | |
| | | To Tower | From Tower | Sewer | Decker Filtrate | Comb. Cond. | 6th Effect | Turpentine Underflow |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 11 (Cont.) | Oct. 20, 1969 | 9.82 | 8.48 | .96 | .90 | -- | .29 | |
| | 21 | 10.38 | 8.71 | 1.23 | .84 | -- | .29 | |
| | 26 | 11.73 | 9.72 | 1.54 | 1.72 | -- | .29 | |
| | 27 | 11.56 | 9.51 | 1.51 | 1.70 | -- | .29 | |
| | 28 | 11.09 | 9.09 | 1.54 | 1.71 | -- | .29 | |
| | Nov. 1 | 11.81 | 9.44 | 1.88 | 1.80 | -- | .29 | |
| | 2 | 10.63 | 8.55 | 1.58 | 1.79 | -- | .29 | |
| | 3 | 10.76 | 7.58 | 2.70 | 2.02 | -- | .29 | |
| | 5 | 11.38 | 7.96 | 2.85 | 1.86 | -- | .29 | |
| 12 | Nov. 6, 1969 | 11.59 | 8.29 | 3.02 | 1.92 | -- | .29 | |
| | 7 | 11.76 | 8.64 | 2.52 | 1.98 | -- | .29 | |
| | 8 | 11.73 | 8.62 | 2.60 | 1.82 | -- | .29 | |
| | 9 | 11.39 | 9.32 | 1.55 | 1.79 | -- | .29 | |
| | 10 | 10.61 | 8.59 | 1.53 | 1.73 | -- | .29 | |
| | 11 | 11.02 | 8.23 | 2.34 | 1.39 | -- | .29 | |
| | 12 | 11.29 | 8.56 | 2.16 | 1.63 | -- | .29 | |
| | 13 | 10.31 | 7.75 | 2.05 | 1.54 | -- | .29 | |
| | 18 | 11.79 | 10.04 | 1.07 | 1.11 | -- | .29 | |
| | 24 | 12.40 | 9.64 | 1.56 | 2.45 | -- | .29 | |
| | 25 | 11.21 | 9.51 | 1.52 | 1.41 | -- | .29 | |
| | 26 | 10.51 | 8.90 | 1.60 | 1.32 | -- | .29 | |
| | 29 | 10.52 | 9.10 | 1.52 | 1.13 | -- | .29 | |
| | 30 | 11.06 | 9.12 | 1.43 | 1.65 | -- | .29 | |
| | Dec. 10 | 11.41 | 9.53 | 1.64 | 1.59 | -- | .29 | |
| | 12 | 10.82 | 8.63 | 1.63 | 1.91 | -- | .29 | |
| | 14 | 10.49 | 8.33 | 1.55 | 1.87 | -- | .29 | |
| | 15 | 11.32 | 9.15 | 1.57 | 1.89 | -- | .29 | |
| | 16 | 11.62 | 9.42 | 1.61 | 1.92 | -- | .29 | |
| | 28 | 11.24 | 8.99 | 1.93 | 1.96 | -- | .29 | |
| | 29 | 11.53 | 9.35 | 1.87 | 1.89 | -- | .29 | |
| | 30 | 10.88 | 8.73 | 1.86 | 1.87 | -- | .29 | |
| | 31 | 10.69 | 8.14 | 2.14 | 1.88 | -- | .29 | |
| 13 | Feb. 9, 1970 | 10.97 | 9.14 | 1.55 | -- | -- | .29 | .03 |
| | 10 | 10.15 | 9.05 | 1.12 | -- | -- | .29 | .02 |
| | 13 | 10.82 | 8.91 | 1.65 | -- | -- | .29 | .02 |
| | 17 | 11.49 | 9.48 | 1.72 | -- | -- | .29 | .03 |
| | 18 | 11.82 | 9.88 | 1.68 | -- | -- | .29 | .03 |
| | 19 | 11.62 | 9.65 | 1.68 | -- | -- | .29 | .03 |
| | 21 | 10.77 | 9.06 | 1.67 | -- | -- | .29 | .03 |
| | 22 | 11.67 | 9.99 | 1.63 | -- | -- | .29 | .03 |
| | 23 | 11.91 | 9.87 | 1.65 | -- | -- | .29 | .03 |
| | 24 | 11.85 | 9.89 | 1.68 | -- | -- | .29 | .03 |
| | 25 | 10.83 | 8.80 | 1.66 | -- | -- | .29 | .03 |

TABLE 4

TEMPERATURE DATA FOR FULL-SCALE COOLING TOWER OPERATION

| Period | Date | Temperature (°F) | | |
|---|---|---|---|---|
| | | To Tower | From Tower | Wet Bulb |
| 1 | May 14, 1969 | 107.3 | 78.1 | 61.5 |
| | 15 | 113.9 | 79.7 | 62.5 |
| | 16 | 115.5 | 82.3 | 65.9 |
| | 17 | 114.4 | 82.9 | 67.4 |
| | 18 | 115.9 | 82.5 | 66.6 |
| 2 | May 19, 1969 | 113.6 | 82.8 | 69.1 |
| | 20 | 112.5 | 83.9 | 69.7 |
| | 21 | 112.1 | 83.3 | 69.2 |
| | 22 | 112.0 | 83.6 | 69.1 |
| | 23 | 112.3 | 84.0 | 67.7 |
| | 24 | 111.5 | 83.9 | 69.2 |
| | 25 | 110.8 | 82.3 | 67.7 |
| 3 | May 26, 1969 | 120.2 | 85.3 | 68.3 |
| | 27 | 119.8 | 86.5 | 66.9 |
| | 28 | 119.7 | 86.1 | 65.4 |
| | 29 | 120.2 | 87.6 | 67.9 |
| | 30 | 120.1 | 87.3 | 68.0 |
| | 31 | 119.3 | 87.3 | 69.5 |
| | June 1 | 119.0 | 88.5 | 70.5 |
| 4 | June 2, 1969 | 116.0 | 86.5 | 67.7 |
| | 3 | 115.8 | 82.3 | 58.2 |
| | 4 | 116.1 | 84.4 | 61.0 |
| | 5 | 114.8 | 86.3 | 66.2 |
| | 6 | 113.4 | 84.9 | 67.1 |
| | 7 | 116.1 | 88.5 | 70.4 |
| 5 | June 9, 1969 | 114.5 | 87.4 | 71.5 |
| | 10 | 117.0 | 88.3 | 70.0 |
| | 11 | 116.7 | 89.9 | 71.8 |
| | 12 | 117.1 | 90.6 | 72.9 |
| | 14 | 120.2 | 90.4 | 74.8 |
| | 15 | 117.5 | 90.5 | 73.3 |
| | 16 | 119.9 | 88.3 | 71.1 |
| | 17 | 120.9 | 90.3 | 74.5 |
| | 18 | 119.8 | 87.3 | 72.2 |
| | 19 | 120.4 | 88.1 | 72.3 |

TABLE 4
(Continued)

| Period | Date | Temperature (°F) | | |
|--------|------|------------------|------|----------|
| | | To Tower | From Tower | Wet Bulb |
| 5 (Cont.) | June 22 | 120.2 | 90.2 | 74.7 |
| | July 3 | 124.5 | 89.5 | 76.0 |
| | 4 | 123.0 | 90.0 | 76.5 |
| | 5 | 121.0 | 90.0 | 76.0 |
| | 6 | 119.5 | 91.0 | 78.0 |
| | 7 | 117.0 | 90.0 | 77.0 |
| | 8 | 117.5 | 90.0 | 76.5 |
| | 9 | 118.5 | 90.5 | 77.5 |
| | 10 | 121.5 | 89.5 | 76.5 |
| | 11 | 121.0 | 91.0 | 78.0 |
| | 12 | 121.0 | 90.5 | 77.5 |
| | 15 | 118.5 | 91.0 | 76.0 |
| | 16 | 118.0 | 89.5 | 74.0 |
| | 17 | 118.5 | 89.0 | 74.0 |
| | 18 | 120.0 | 90.0 | 76.0 |
| 6 | July 19, 1969 | 120.0 | 90.5 | 76.0 |
| | 20 | 119.0 | 88.5 | 74.0 |
| | 21 | 119.0 | 89.0 | 74.0 |
| | 25 | 116.5 | 89.5 | 75.0 |
| | 28 | 119.2 | 89.2 | 74.5 |
| | 29 | 119.4 | 88.4 | 73.4 |
| | 30 | 118.9 | 88.4 | 72.6 |
| | 31 | 119.6 | 89.1 | 74.2 |
| | Aug. 2 | 118.2 | 89.8 | 74.4 |
| | 3 | 115.4 | 88.8 | 71.9 |
| | 5 | 107.2 | 86.5 | 70.2 |
| | 6 | 110.6 | 87.5 | 72.6 |
| | 7 | 119.1 | 90.5 | 73.8 |
| | 8 | 117.2 | 91.3 | 74.5 |
| | 11 | 118.2 | 90.0 | 73.0 |
| | 12 | 118.6 | 89.0 | 71.7 |
| | 13 | 118.9 | 88.2 | 70.9 |
| | 14 | 119.3 | 89.9 | 73.5 |
| | 15 | 118.4 | 90.9 | 74.1 |
| | 16 | 119.5 | 91.4 | 75.7 |
| | 17 | 119.2 | 92.1 | 76.1 |
| 7 | Aug. 22, 1969 | 119.4 | 87.1 | 68.0 |
| | 23 | 118.5 | 84.3 | 64.9 |
| | 24 | 117.8 | 85.1 | 65.5 |
| | 25 | 117.9 | 86.9 | 67.6 |

TABLE 4
(Continued)

| Period | Date | Temperature (°F) | | |
| --- | --- | --- | --- | --- |
| | | To Tower | From Tower | Wet Bulb |
| 7 (Cont.) | Aug. 26, 1969 | 118.7 | 88.4 | 70.2 |
| | 27 | 117.1 | 88.4 | 72.4 |
| | 28 | 113.1 | 83.6 | 66.6 |
| | 29 | 118.3 | 86.7 | 68.0 |
| | Sept. 3 | 117.5 | 91.0 | 72.2 |
| | 6 | 120.7 | 90.2 | 73.0 |
| | 7 | 120.7 | 90.5 | 73.0 |
| | 8 | 123.0 | 90.9 | 73.1 |
| 8 | Sept. 9, 1969 | 122.2 | 88.1 | 64.5 |
| | 10 | 122.3 | 86.9 | 61.5 |
| | 11 | 121.7 | 86.6 | 62.3 |
| | 12 | 121.7 | 86.8 | 60.5 |
| | 13 | 122.0 | 86.9 | 62.8 |
| | 14 | 121.9 | 86.9 | 62.8 |
| | 15 | 123.1 | 91.3 | 71.2 |
| | 16 | 123.1 | 93.0 | 73.0 |
| 9 | Sept. 18, 1969 | 120.6 | 91.7 | 69.8 |
| | 19 | 116.9 | 83.6 | 67.3 |
| | 20 | 108.8 | 83.1 | 63.8 |
| | 21 | 115.3 | 84.4 | 64.7 |
| | 22 | 115.9 | 84.4 | 64.8 |
| | 23 | 118.1 | 87.9 | 69.1 |
| | 24 | 117.5 | 87.9 | 68.2 |
| | 25 | 118.3 | 86.1 | 65.3 |
| | 26 | 117.6 | 85.4 | 64.0 |
| | 27 | 118.7 | 86.4 | 66.1 |
| | 28 | 119.2 | 87.1 | 67.4 |
| | 29 | 117.4 | 82.5 | 58.0 |
| | Oct. 1 | 113.5 | 85.6 | 70.4 |
| | 2 | 116.8 | 86.3 | 66.0 |
| 10 | Oct. 5, 1969 | 119.5 | 87.8 | 62.8 |
| | 6 | 119.0 | 88.6 | 63.3 |
| | 7 | 120.5 | 92.0 | 69.3 |
| | 8 | 121.2 | 91.4 | 68.6 |
| 11 | Oct. 10, 1969 | 116.5 | 88.4 | 66.2 |
| | 11 | 116.3 | 87.8 | 66.6 |
| | 12 | 117.3 | 88.4 | 66.5 |
| | 13 | 119.5 | 89.7 | 68.1 |
| | 15 | 115.0 | 83.3 | 62.5 |

TABLE 4
(Continued)

| Period | Date | Temperature (°F) | | |
| --- | --- | --- | --- | --- |
| | | To Tower | From Tower | Wet Bulb |
| 11 (Cont.) | Oct. 16 | 114.5 | 81.9 | 60.5 |
| | 17 | 113.4 | 75.8 | 51.8 |
| | 18 | 113.8 | 79.5 | 57.0 |
| | 20 | 118.4 | 89.3 | 72.4 |
| | 21 | 115.6 | 86.9 | 66.3 |
| | 26 | 111.6 | 85.4 | 60.0 |
| | 27 | 111.5 | 84.6 | 59.3 |
| | 28 | 111.1 | 84.0 | 52.7 |
| | Nov. 1 | 112.5 | 87.8 | 65.3 |
| | 2 | 111.8 | 83.3 | 58.9 |
| | 3 | 105.0 | 78.8 | 50.4 |
| | 5 | 101.2 | 76.4 | 44.7 |
| 12 | Nov. 6, 1969 | 101.1 | 78.6 | 50.0 |
| | 7 | 103.7 | 80.1 | 52.6 |
| | 8 | 103.9 | 80.0 | 50.3 |
| | 11 | 104.8 | 81.3 | 60.0 |
| | 12 | 107.5 | 81.7 | 54.0 |
| | 13 | 107.4 | 77.9 | 47.4 |
| | 18 | 113.6 | 87.3 | 63.7 |
| | 24 | 110.9 | 83.3 | 59.5 |
| | 25 | 111.5 | 83.7 | 59.3 |
| | 26 | 109.5 | 80.7 | 53.9 |
| | 29 | 105.9 | 76.8 | 49.5 |
| | 30 | 106.4 | 78.4 | 41.2 |
| | Dec. 10 | 105.4 | 80.2 | 48.7 |
| | 12 | 107.6 | 79.2 | 41.4 |
| | 14 | 109.2 | 79.3 | 45.4 |
| | 15 | 105.0 | 77.1 | 41.2 |
| | 16 | 105.4 | 78.0 | 40.1 |
| | 28 | 105.5 | 78.9 | 44.1 |
| | 29 | 108.7 | 84.0 | 58.5 |
| | 30 | 109.1 | 84.7 | 60.8 |
| | 31 | 104.4 | 77.1 | 43.3 |

# SELECTED PAPERS, PART I

## 32a    MEASUREMENT OF THE RELATIVE VOLATILIZATION RATES OF THE WATER-MISCIBLE FRACTIONS IN AN AQUEOUS EFFLUENT

L. J. Thibodeaux, University of Arkansas
Fayetteville, Arkansas
R. B. Estridge and B. G. Turner, Georgia Kraft Company
Rome, Georgia

SIXTY-NINTH NATIONAL MEETING
Cincinnati, Ohio
May 16-19, 1971

## Introduction

Aqueous effluents from industrial sources contain a broad spectrum of pollutant constituents, and there are several standard measuring techniques by which the wastewater can be analyzed and categorized. The dissolved constituents in wastewater can be of varied nature and new measurement techniques are continually needed to provide effective assessment of complex treatment processes. Of the total portion of dissolved components in a wastewater, a further sub-classification into a portion which is volatile and a non-volatile portion is needed. The volatile portion of the dissolved constituents in an aqueous effluent is that portion which can be transferred to the air sphere by the mere contact of the phases, i.e., contact of the aqueous phase and gas (air) phase. Interphase mass-transfer of dissolved constituents will occur when the partial pressure of a constituent in the gas phase is less than the equilibrium partial pressure of the constituent in the aqueous phase.

Air-water contact operations on both domestic (municipal) and industrial aqueous effluents is common practice, as a treatment operation in itself or as a means of obtaining molecular oxygen. Aqueous phase biochemical oxidation of the dissolved organic constituents is a universally employed treatment process which can be performed most economically by employing intimate phase contact with air as the source of molecular oxygen (Eckenfelder, 1953). The auto-oxidation of hydrocarbons by molecular oxygen is a recent innovation which employs air-water contact ( Prather, 1970  ). The use of large volumes of air in a deliberate attempt to take advantage of interphase mass-transfer phenomena for the removal of dissolved volatile constituents from an aqueous effluent is currently receiving much attention. The removal of dissolved organics from industrial wastewater (Cohn and Tonn, 1967; Mohler, Elkin and Kummick, 1964; Smathers and Frady, 1969; Estridge, Turner, Smathers,

and Thibodeaux, 1970; Burns and Eckenfelder, 1965), and the removal of ammonia from domestic sewage (Slechta and Culp, 1967) account for bulk of air-water operations other than oxidation. Although these processes involving air-water contact are in current use, there remains a need for a method of evaluating what fraction of the dissolved constituents is amenable to interphase mass transfer and the rate at which this transfer can be undertaken.

The ever-growing role of organics in the air sphere and their involvement with photochemical smog formation will necessitate that all sources be pin-pointed and examined as possible contributors. The increase in the number of air-water contact operations which employ large volumes of air, in a once through operation, with any of several wastewater treatment techniques, and the current increase in wastewater treatment activities may usher in another important source of air pollution. The gross effect is solving, or partially solving, a water pollution problem and inadvertantly creating an air pollution problem. There is a need for a method of assaying whether or not an aqueous effluent is a potential air pollution source if the effluent is employed in one of many air-water contact treatment schemes.

## Volatilization Measurement Devices

Interphase mass-transfer devices are employed on a large scale in the chemical process industries. The theory and design procedures for transfer of known components in a continuous process are well established (Treybal, 1968). These devices consist of vertical towers, either cylinderical or rectangular in shape, packed with appropriate material that provide large interfacial area for enhancement of interphase mass-transfer and are usually operated in a countercurrent flow arrangement. The removal of volatile constituents from an aqueous phase is commonly referred to as "stripping." A device incorporating the essential features of the above mentioned full scale devices is necessary for obtaining relative volatilization rates of dissolved volatile components.

On the surface it seems that one could air sparge a given amount of wastewater in a laboratory graduate and obtain the necessary information. Although the total volatile fraction could be easily established by this simple apparatus information concerning the volatilization rates is usually masked by the transient behavior of this batch process with respect to the interfacial area for mass transfer. Figure No. 1 reveals the nature of the problem for simple batch sparging. The transient nature of this operation is due to the simultaneous vaporization of water, the most abundant volatile component, and hence a reduction in interfacial area due to a reduction in total volume. Foaming frequently occurs when air is introduced into wastewater so that it becomes the dispersed phase.

The device shown in Figure No. 2 is capable of producing experimental data on the result of air-water contact operations involving almost any aqueous effluent. This apparatus arrangement will allow one to evaluate the total fraction of the dissolved constituents which are volatile, plus it will allow him to evaluate the rate of removal of any portion of this volatile
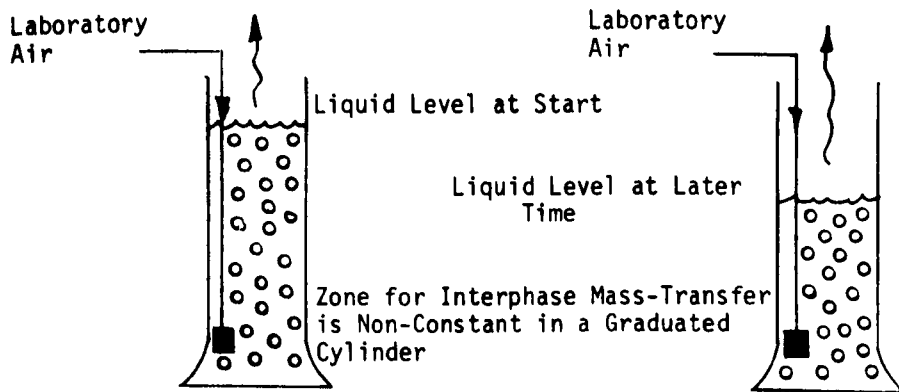
FIGURE NO. 1: SIMPLE BATCH AIR SPARGING
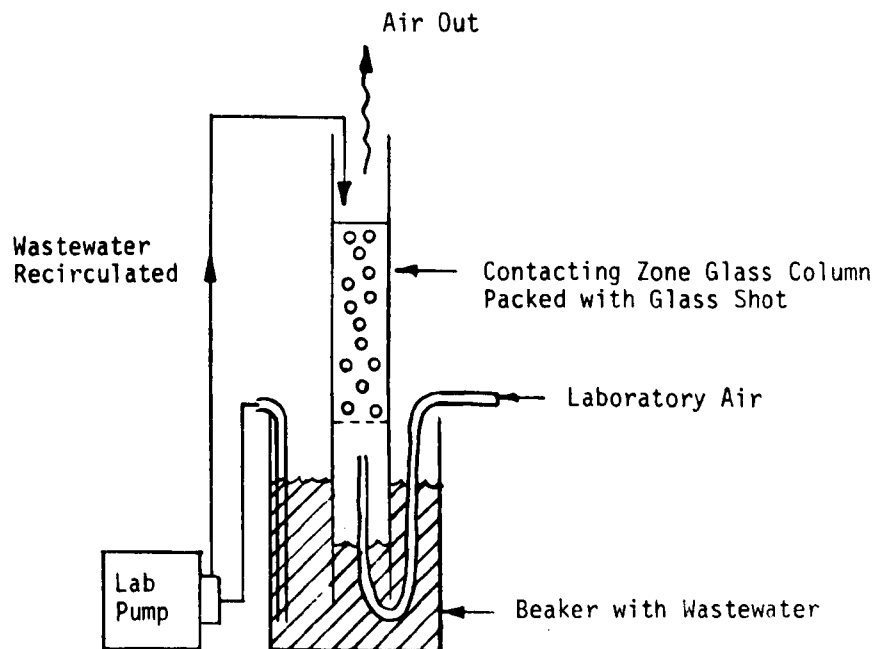


FIGURE NO. 2: BATCH, RECIRCULATING AIR-WATER CONTACTOR

fraction. This device also employs a fixed quantity of wastewater but is independent of the quantity remaining since the mass-transfer operation is performed continuously in a separate device by the use of a recirculating pump and a small section of glass tubing packed with an appropriate material (i.e., glass beads). This arrangement maintains a constant amount of interfacial area and also forces the air to become a continuous phase thus eliminating foaming problems.

## Continuous Volatilization of Single Components

In order for the proposed volatilization measuring device to be of general utility a straight forward method of analyzing the experimental results is required. Due to the transient nature of the air-volatilization operation and the usual complexities associated with time varying systems a simple method of analysis seemed unlikely. However, a simplistic linearized view of the overall process coupled with a simple mathematical analysis yielded an equation from which the air volatilization rate could be determined accurately and quickly.

The schematic of the air-volatilization operation shown in Figure No. 3 is helpful in visualizing the simple model used in the mathematical analysis. This model assumes that for a constant air rate, air wet bulb temperature, water recycle rate and water temperature that the amount of a volatile component removed is a constant multiple of the quantity of this component entering the tower. This constant is denoted by $K_i$ and is defined as the specific volatilization rate for component i in the column:

$$K_i \equiv (L_{mi}x_{ii} - L_{mo}x_{io})/L_{mi}x_{ii} \qquad (1)$$

where $L_{mi}$ and $L_{mo}$ are the volumetric flows (volume/time .area) to and from the column,

$x_{ii}$ and $x_{io}$ are the concentrations of component i entering and leaving the packed column.

Definition of the remaining quantities in the schematic are:

a – specific volatilization rate for water in the column. This quantity is constant once the aqueous phase has cooled to the air wet bulb temperature.

M – volumetric quantity of liquid in the device. The initial quantity charged is $M_o$.

$x_i, x_o$ – concentration of water in the recycled liquid and the column outlet.

t – experiment run time.

The relative volatilization rate is defined as the ratio of the specific
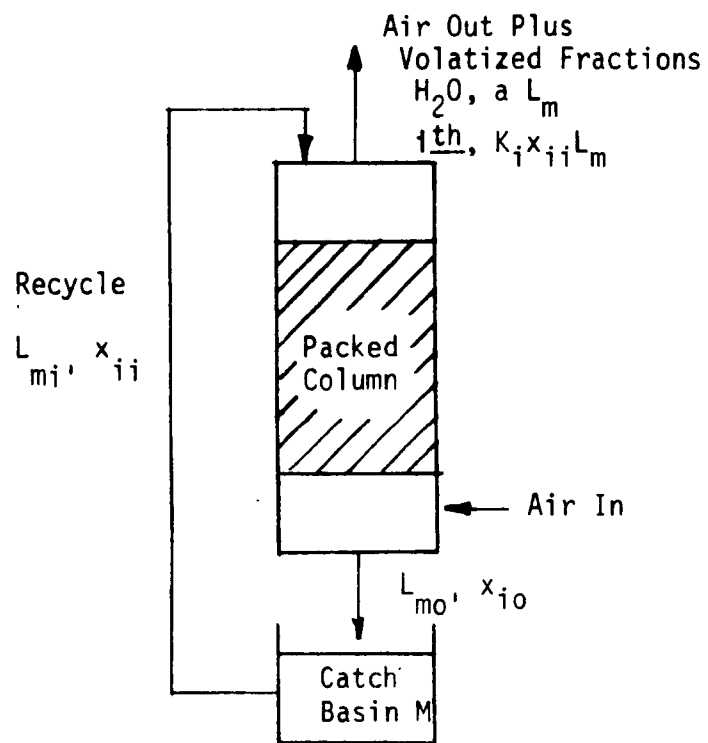
FIGURE NO. 3: SCHEMATIC OF VOLATILIZATION DEVICE

volatilization rate of component i to the specific volatilization rate for water (i.e., $K_i/a$).

By assuming the catch basin is completely mixed at all times, $X_{H_2O} >>> x_i$ and the temperature of the aqueous phase remains constant a series of differential component balances plus overall balances yields upon integration the concentration of component i as a function of run time and the other pertinent system variables:

$$x = x_i^0 \left[ 1 - \frac{aL_m t}{M_o} \right]^{\left( \frac{K_i - a}{a} \right)} \tag{2}$$

for all $aL_m t \leq M_o$. Detailed derivation of this equation is presented in the appendix. Equation (2) shows that as run time progresses the concentration of component i, where i is any component other than water, declines from its initial value of $x_i^0$. The quantity a is computed from the experimental data by:

$$a = (M_o - M_F)/t_F L_m \tag{3}$$

where $M_o$ and $M_F$ is the volumetric quantity of material at the start (t = 0) and finish of the experiment $(t_F)$. It should be noted that mass or molar quantities can be used in equations (2) and (3) without any loss of generality.

The important utility of equation (2) is obtaining $K_i$ from experimental run data. Performing a logarithmic transformation yields

$$\log x = \log x_i^0 + \left( \frac{K_i - a}{a} \right) \log \left[ 1 - aL_m t / M_o \right] \tag{4}$$

It can be seen at this point that if a log-log plot of x vs. $\left[ 1 - aL_m t / M_o \right]$ results in a straight line its slope will be $(K_i - a)/a$ from which $K_i$ can be extracted. The absolute rate of volatilization of component i is $L_m x_i K_i$, and the relative volatilization rate of component i with respect to water is $(x_i K_i / a) \times 10^{-6}$.

## The Concentration Independence of $K_i$

The interphase mass-transfer phenomena occuring in the packed column is of a transient nature but the specific voltalization rate of component i, $K_i$, is independent of the concentration of this component in the column. This occurence is essential for use of equation (4) to evaluate $K_i$.

The steady state flow operation of a packed column for interphase mass-transfer of low concentration constituents being transferred to a gas phase is given by (Treybal, 1968)

$$\frac{Z_T \, K_y a_i}{G_m} = \int_{y_{io}=0}^{y_{ii}} \frac{dy_i}{y_i^* - y_i},$$  (5)

where $Z_T$ is the height of a packed section,

$K_y a_i$ is the overall mass-transfer coefficient for component i in the gas phase,

$G_m$ is the molar gas flux rate, and

$y_i$ is the mole fraction of component i in the gas phase.

Since most volatile components in a wastewater stream are of low concentration Henry's Law is sufficient for expressing the phase equilibria for isothermal operation:

$$y_i^* = H_i x_i.$$  (6)

An i$\underline{th}$ component balance over any arbitrary section of the packed column yields:

$$y_i = \frac{L_m}{G_m} (x_i - x_{io}).$$  (7)

Relations (6) and (7) are sufficient to transform the integral in (5) to one of liquid phase concentrations. After this transformation is completed the indicated integration operation is performed and rearrangement yields:

$$x_{ii} = x_{io} \left\{ (S_{Ri}-2) \text{ EXP} \left[ Z_T \frac{K_y a_i}{G_m} (S_{Ri}-1) \right] \right\} / (S_{Ri}-1), \qquad (8)$$

where $S_{Ri} = \frac{H_i G_m}{L_m}$ . Now if this expression is employed with the definition of $K_i$ and assuming $L_{ii} = L_{io}$, a result showing that $K_i$ is independent of concentration is obtained, i.e.,

$$K_i = 1 - \frac{(S_{Ri}-1)}{(S_{Ri}-2) \text{ EXP} \left[ Z_T \frac{K_y a_i}{G_m} (S_{Ri}-1) \right] + 1} . \qquad (9)$$

The final result showing $K_i$ to be independent of concentration of i also suggest that this equation can also be used to compute $K_i$ apriori. All terms are easily obtained from experimental data except for $K_y a_i$. This term can be estimated by the use of published correlations (Perry, 1963), however ideal systems consisting of binary components with no extraneous interferences are typically employed in obtaining the correlated $K_y a$ data. Even under these conditions regression techniques are needed to correlate the resulting data. The presence of trace components at or near the interface is known to invalidate a literature value of $K_y a$. Due to the heterogeneous nature of most wastewater an experimentally determined $K_i$ is most likely advantageous. Equation (9) should be used as an estimate of $K_i$ only. $K_i$ is also independent of concentration for non-isothermal operations however equation (9) does not apply since $H_i$ is strongly temperature dependent.

## Continuous Volatilization of Multiple Components

It is common practice to measure organic pollutants in wastewater by gross measures such as biochemical oxygen demand (B.O.D.), chemical oxygen demand (C.O.D.), and total organic carbon (T.O.C.), etc. Although these gross measures indicate the concentrations of the combined volatile and non-volatile components and not single constituents, much information concerning the relative amounts of these two factions can be learned from these tests combined with a volatilization experiment. The gross concentration measure can be expressed as the sum of the concentrations of the volatile and non-volatile fractions thus:

$$c^o = c_i^o + c_j^o \tag{10}$$

where $c^o$ is a gross concentration measure (such as BOD, COD, TOC, etc.)
   of the original wastewater, and

$c_i^o$ is the sum of the concentrations of all the volatile components in
   equivalent measure as C, and

$c_j^o$ is the sum of the concentrations of all the non-volatile components
   in equivalent measure as C.

The concentrations $c_i^o$ and $c_j^o$ and hence the total fraction consisting of volatiles plus the relative volatilization rate (reference to water) can be obtained from a single air-volatilization experiment.

The concentration behavior of any single volatile component during an air-volatilization experiment is given by equation (2), where the specific volatilization rate, $K_i$, is greater than zero. For non-volatile constituents $K_j = 0$, implying none of these components are removed in the packed column, so that equation (2) becomes

$$x_j = x_j^o \bigg/ \left[ 1 - \frac{aL_m t}{M_o} \right] \tag{11}$$

Just as equation (2) shows that the concentration of the volatiles decrease with time equation (11) shows the concentration of non-volatiles to increase with time. The quantity of wastewater in the device is related to run time by

$$M = M_o \left( 1 - \frac{aL_m t}{M_o} \right) \tag{12}$$

By analogy to equation (10) the gross mass quantity of constituents in the intial wastewater aliquot is

$$c^o M_o = c_i^o M_o + c_j^o M_o \tag{13}$$

At any time during the experiment the quantity of constituents in the wastewater is

$$CM = C_i M + C_j M \tag{14}$$

Since the concentration of the volatile and non-volatile constituent at any time during the experiment is $\sum\limits_{i=1}^{n} x_i$ and $\sum\limits_{j=1}^{m} x_j$ respectively, equation (14) becomes, upon substituting (2), (11), (12) and summing over all constituents,

$$CM = M_o \sum_{i=1}^{n} x_i^o \left[ 1 - \theta \right]^{\frac{K_i}{a}} + M_o \sum_{j=1}^{m} x_j^o \tag{15}$$

where n is the number of volatile components other than water,

m is the number of non-volatile components, and

$\theta \equiv aL_m t/M_o$ is a dimensionless run time.

A more useful form of the above expression is obtained by dividing equation (15) by $c^o M_o$:

$$F = \sum_{i=1}^{n} F_i^o \left[ 1 - \theta \right]^{\frac{K_i}{a}} + \sum_{j=1}^{m} F_j^o \tag{16}$$

where $F \equiv CM/c^o M_o$ and is the fraction of the total amount of the gross constituents remaining in the wastewater,

$F_i^o \equiv x_i^o/c^o$ is the original fraction of volatile component i in the waste-

water, and

$F_j^o \equiv x_j^o/c^o$ is the original fraction of non-volatile component j in the

wastewater.

Equation (16) shows much about the behavior of the wastewater constituents

with experiment run time. As run time increases $\Theta \to 1.0$ the fraction of

material remaining is all non-volatile, i.e.,

$$F_{\Theta=1} \equiv \sum_{j=1}^{m} F_j^o \tag{17}$$

At this point it is obvious that $c_i^o = (1-F_{\Theta=1}) \; c^o$ and $c_j^o = (F_{\Theta=1}) \; c^o$.

Although a gross concentration measure cannot single out individual

constituents, a slight change in the form of equation (16) allows further

study of the volatile fraction. If the volatile fraction is assumed to be

made of a single pseudo volatile component equation (16) is re-interpreted as

$$F = F_s^o \left[ 1 - \Theta \right]^{\frac{K_s}{a}} + F_{\Theta=1} \tag{18}$$

where $F_s^o$ is the total fraction of the pseudo component and $K_s$ is the specific

volatilization rate of this component.

Now due to the above $F_s^o + F_{\Theta=1} = 1$. Employing equation (17), $F_s^o = 1 - F_{\Theta=1}$,

and performing a logarithmic transformation results in

$$\log \; \phi = \frac{K_s}{a} \; \log \left[ 1 - \Theta \right] \tag{19}$$

where $\phi \equiv (F-F_{\Theta=1})/(1-F_{\Theta=1})$. Now a log-log plot of $\phi$ vs $(1-\Theta)$ data yields $K_s$ for

the volatile fractions. The absolute rate of volatilization of $\phi \times 100\%$ of the

volatile fraction is $L_m \; (1-F_{\Theta=1}) \; c^o \; K_s$.

## Experimental Materials and Methods

Kraft mill evaporator condensates are known to contain a broad array of volatile organic compounds plus non-volatile organics and provide an excellent wastewater for volatilization experiments. Kraft mill decker filtrate was studied also. The following six volatile compounds have been identified in the condensates: methyl mercaptan, methyl sulfide, acetone, methanol, α-pinene and methyl disulfide. Methanol is the major volatile component. The static vapor-liquid equilibrium method (Turner and Van Horn, 1969), and a gas chromatograph were used for identification and analysis.

The static vapor-liquid equilibrium method is quite simple for use with gas-chromatography. A liquid sample is placed in a 500 ml. flask, the flask is sealed with a serum cap, and then the flask and its contents are placed in a constant temperature bath at $55^{\circ}$C. After sufficient time is allowed for vapor-liquid equilibrium to be established, usually 30 to 60 minutes, a vapor sample is removed by inserting a syringe needle through the cap, and the sample is injected into the chromatograph. This method has been found to give very reproducible results, and once peaks on the chromatogram are identified, calibration curves can be prepared from pure compounds and quantitative results obtained.

A second method which was found to be satisfactory for quantitative analysis of the more concentrated components involved direct injection of a known volume of liquid condensate sample into the chromatograph. Concentrations can be determined by comparing the measured peak area of the chromatogram to previously determined calibration curves.

The identification and analysis equipment used throughout this study consisted of a Perkin-Elmer Model 881 Gas Chromatograph equipped with a flame ionization detector, a recorder, and an Infotronic CRS-104 Integrator. Separations were made on a six foot, 1/8" column of 15 percent Carbowax

20M on 100-120 mesh Chromosorb W operated at 70°C with a helium flow of 30 cc/minute.

A relatively large batch, recirculating air-water contactor was employed in this study since experiments relating to cooling were also studied, however the simple apparatus shown in Figure No. 2 is capable of the same general performance. This device was a countercurrent flow, columnar, gas-liquid contactor of ¼ square foot cross-sectional area (6"x6") of Plexiglas construction. Overall height was approximately twelve feet, ten of which was packed with Poly-Grid media stacked on 1½ inches centers. The Poly-Grid is a plastic material of high void volume consisting of 1½ inch sections meshed with 2"x2" square openings. Air for contacting the wastewater was drawn through the tower (induced draft) by two turbine-type fans located atop the column. Liquid flow is via a positive displacement, squeeze-action type pump. Auxiliary equipment included a heat exchanger for re-heating the cooled recycle liquid plus rotameter, thermometers, manometers for air flow measurement, rheostats and sample ports.

As was described briefly in a previous section, volatilization experiments were performed by placing a known volume of wastewater into the tower catch basin. The volume charged was normally 10 to 12 liters. One extended run was performed with a charge of 30 liters. A total of ninteen experiments were performed, eighteen with evaporator condensates and one run with a simulated wastewater consisting of methanol and tap water.

After charging the basin with the test wastewater the blowers were started and ambient air was drawn upward through the tower. Air velocity (apparent) in the tower ranged from 200 to 600 feet per minute. The waste-water recirculating pump was started and flow was adjusted and maintained constant throughout the run. Liquid loading rates ranged from 2.00 to 8.00 gallons per minute per square foot of column area. Simultaneously to starting

the liquid flow, steam was admitted to the heat exchanger to maintain a liquid temperature of $125°F$ at the top of the column. This temperature could be controlled (manually) to $\pm 3°F$. This top temperature was maintained constant for all runs. No attempt was made at trying to control the basin temperature or the temperature and humidity of the entering air. The air was accepted as found in the laboratory. The air temperature was approximately $75°F$ (dry bulb) but the relative humidity varied from 50 to 90%.

Experimental data obtained from the column during the volatilization operation was: initial charge volume, liquid flow rate, air flow rate, final charge volume, total duration of run, GC analysis and/or $BOD_5$ concentration with run time. All samples were withdrawn from the catch basin.

## Behavior of Selected Organic Compounds During Volatilization

By employing the above analysis techniques it was possible to study the effects of volatilization by observing the remaining organic compounds in the water. Each sample injected into the chromatograph provided a point value or the "signature" of the remaining flame ionizable material. By recording the wastewater's signature with time it was possible to observe which compounds were being removed and obtain some indication of their relative rates of removal (qualitatively) Figures No. 4 and No. 5 show the effects of volatilization of two kraft mill wastewaters.

Evaporator condensates chromatograms are shown in Figure No. 4. This wastewater has a large portion of volatile organics and their removal via volatilization is shown by the disappearance of individual peaks or the reduction in size of these peaks between the start and at some time later in the run. Identified constituents being volatilized are methanol, acetone, methyl mercaptan, and methyl sulfide. The compounds are known to be very volatile and methanol is the predominant volatile constituent. The other peaks have not been identified.

Decker filtrate chromatograms are shown in Figure No. 5. This wastewater has only a small portion of its dissolved organics that are readily volatilized. These chromatograms also show the decline in concentration of the more volatile constituents, but there remains a predominance of relatively non-volatile organics which are not easily volatilized. α-Pinene has been identified as one such compound. Notice the relative unchanged nature of the prominant peaks after volatilization for 20 minutes.
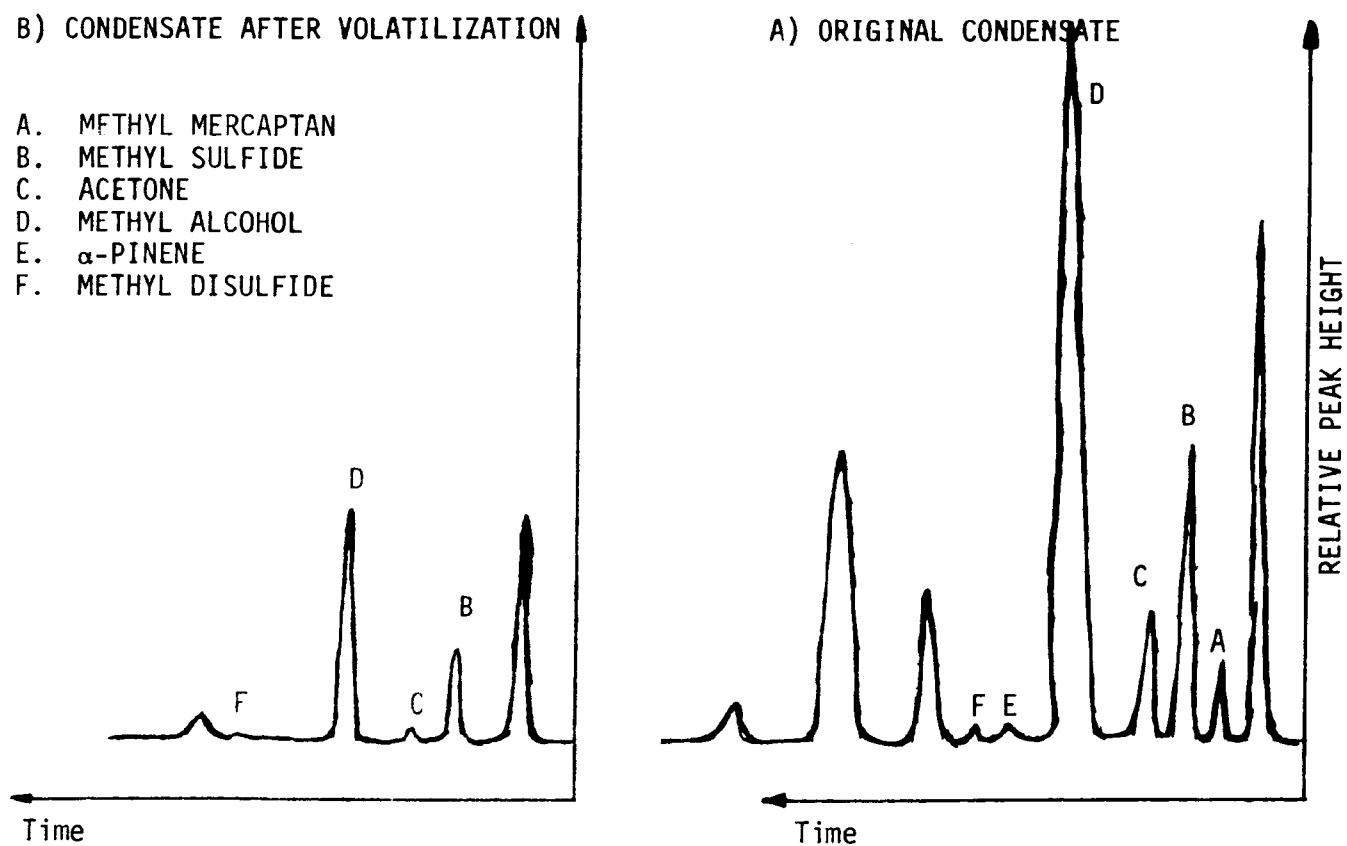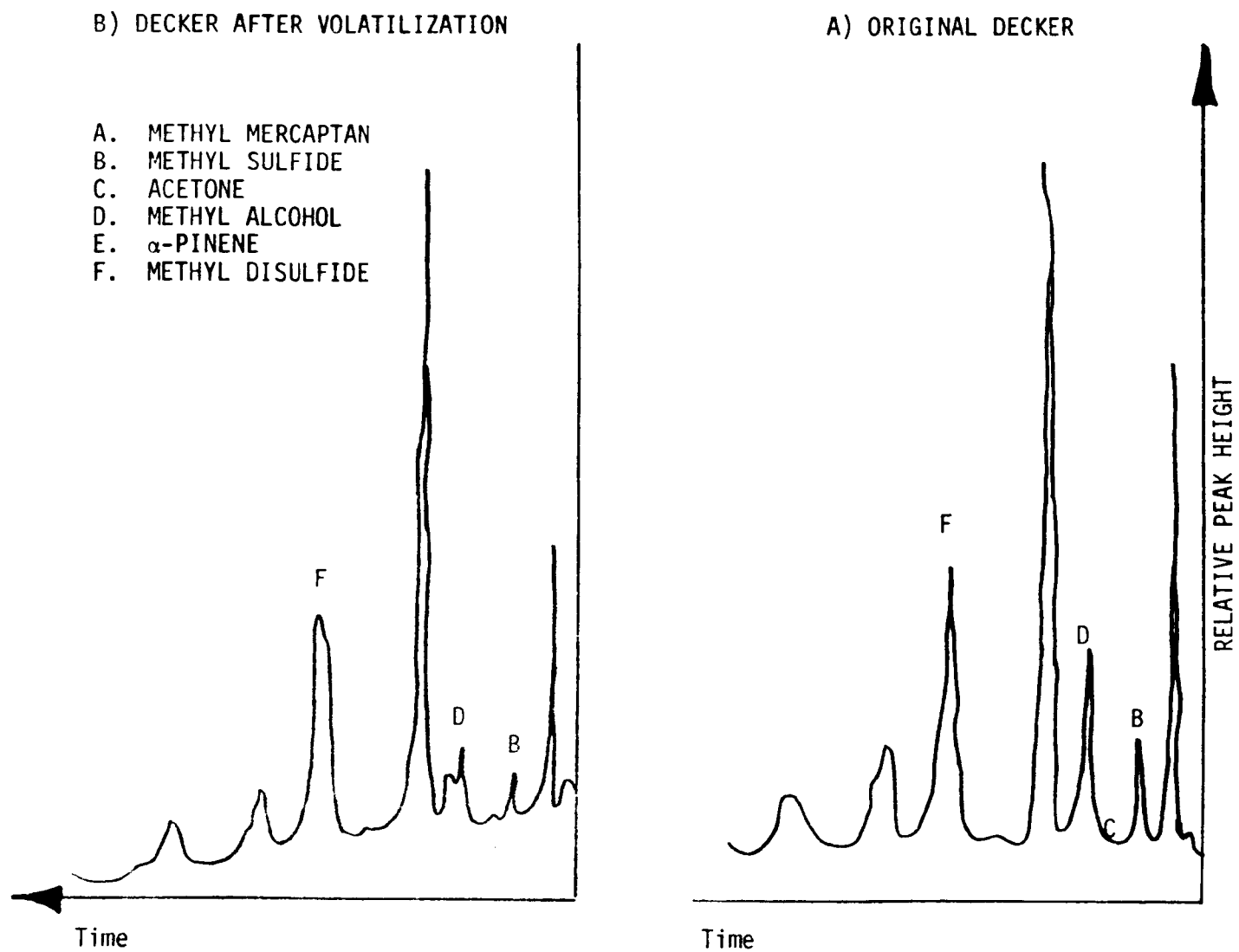
FIGURE NO. 4:   CHROMATOGRAM OF EVAPORATOR CONDENSATE

FIGURE NO. 5: CHROMATOGRAM OF DECKER FILTRATE

## Volatilization Rates of Single Components

Methanol was by far the most prominent volatile compound of concern in the evaporator condensates. Table No. 1 shows typical average concentrations of the identified constituents in this wastewater. Due to its obvious importants with respect to the volatiles in this wastewater, methanol was used as the key component for detailed studies of the volatilization mechanism. Methanol concentration was obtained with run time as was described above. This experimental data was then analyzed to obtain the relative rate of methanol volatilization to that for water (i.e., $K_{CH_3OH}/a$).

The experimental data was transformed as suggested by equation (4), namely $M_o - aL_m t$ , the volume of wastewater remaining vs. $x_{CH_3OH}$, the concentration of methanol remaining. The former is the independent variable. Once these two variables are obtained a log-log plot can be made. Figure 6 shows typical data for three runs.

This plot shows several aspects of the nature of trace component removal by volatilization. First the plot shows that as run time increases (i.e., as system volume decreases) the concentration of methanol decreases. Also the functional relationship between these variables is logarithmic, as predicted by the trace component volatilization model, provided K and a are constant. This is proved to be correct as shown by the straight line correlation of the data. All nineteen runs were displayed on a plot of this type and all resulted in a straight line. This straight line indicates that for approximately three cycles of methanol concentration the slope is constant. Equation (4) reveals that:

$$slope = \frac{K_{CH_3OH} - a}{a} \qquad (20)$$

By experiment design a is constant, therefore $K_{CH_3OH}$ must be constant also and can be obtained from equation (20).

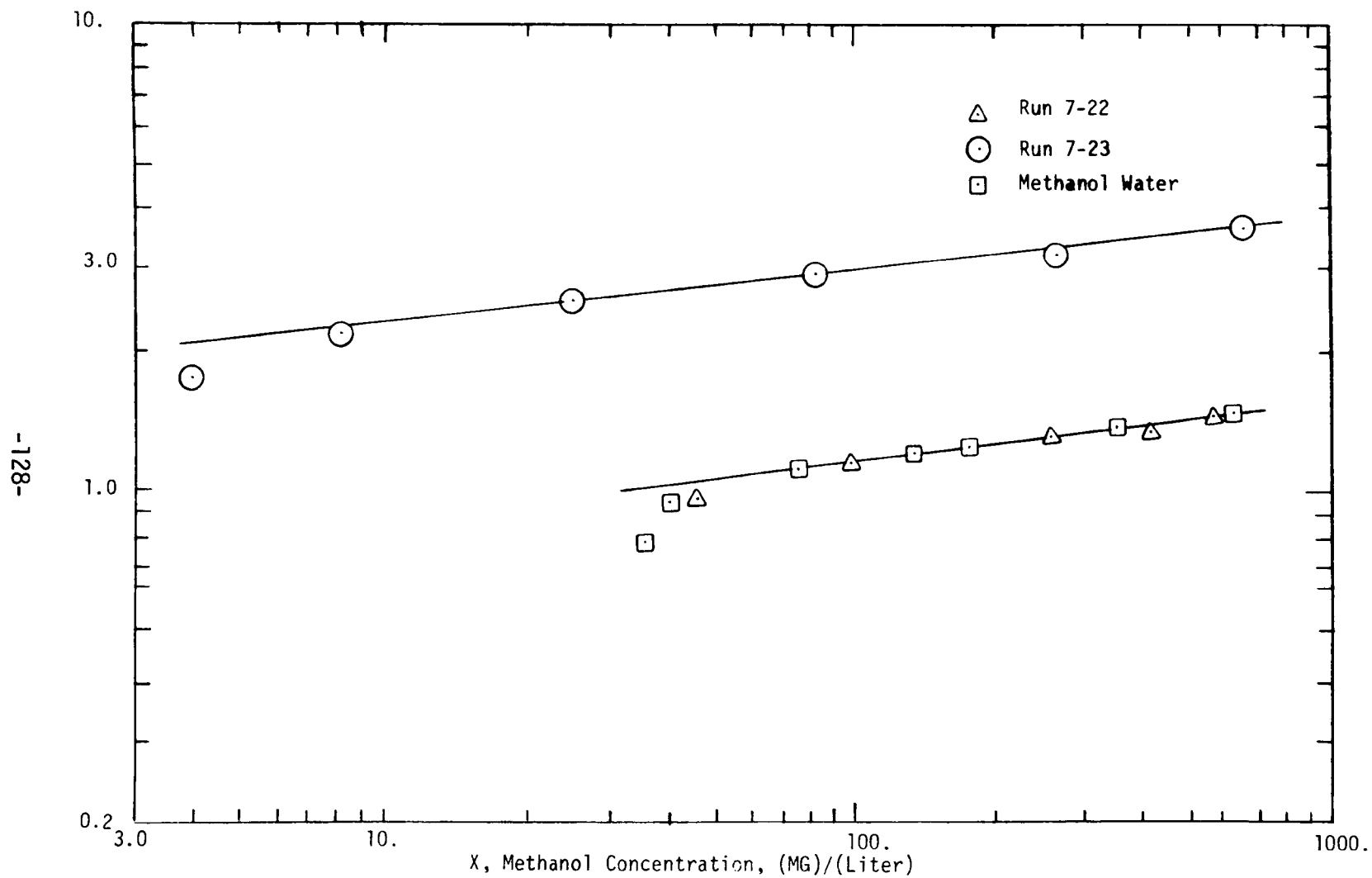Table No. 2 shows the values of $K_{CH_3OH}$ and a obtained on the nineteen

FIGURE NO. 6: METHANOL VOLATILIZATION, CONDENSATE SAMPLE 7-15-68

## Table No. 1

## Concentration of Volatile Organics is Kraft Condensates

(Turner and Van Horn, 1969)

|                  | (mg)/(l) |
|------------------|----------|
| methanol         | 1100     |
| methyl disulfide | 6.5      |
| acetone          | 3.       |
| α-pinene         | 1.4      |
| methyl sulfide   | .2       |
| methyl mercaptan | Trace    |

## Table No. 2

### Specific Volatilization Rates of Methanol and Water

| $K_{CH_3OH}$ | a | L/G* |
|---|---|---|
| .250 | .0256 | 1.32 |
| .268 | .0504 | 1.55 |
| .452 | .0423 | 1.35 |
| .448 | .0732 | 1.59 |
| .304 | .0350 | 1.52 |
| .324 | .0373 | 1.35 |
| .269 | .0275 | 1.36 |
| .260 | .0400 | 1.35 |
| .186 | .0238 | 2.85 |
| ]232 | .0238 | 5.01 |
| .351 | .0245 | 2.02 |
| .268 | .0270 | 2.45 |
| .411 | .0401 | 1.06 |
| .176 | .0392 | 1.27 |
| .481 | .0381 | 0.623 |
| .594 | .0470 | 0.506 |
| .112 | .0150 | 5.17 |
| .484 | .0433 | 0.516 |
| .336 | .0402 | 1.32 |

| ave. | 0.327 | .0364 | ---- |
|---|---|---|---|
| S | 0.12 | | ---- |

*Air wet bulb temperature also varied from run to run but was not
recorded.

experiments. There is a strong variation in $K_{CH_3OH}$ and a with the liquid to air flow rates and temperature in the column. These effects are predicted by equation (9). The average value of $(K_{CH_3OH}/a)$ was 9.18 (S = 2.57) indicating that the specific rate of methanol volatilization is approximately nine times more rapid than that for water volatilization. Table No. 3 is helpful in interpreting the significance of the magnitude of the relative volatilization rate.

Table No. 3

Interpretation of the Relative Volatilization Rate

| $K_i/a$ | Character of Constituents |
|---|---|
| >1 | Specific volatilization rate is greater than water and hence i can be removed from the water phase by air contact. |
| =1 | specific volatilization rate is the same as water and i cannot be removed from the water phase by air contact. |
| <1 | specific volatilization rate of i is less than that of water and air water contact will result in the concentration of this constituent in the aqueous phase. |

## The Volatile Fraction of Gross Pollutant Measures

It was shown above that these kraft mill wastewaters contain components which are relatively non-volatile. The quantitative amount of the volatiles that can be removed from a wastewater by volatilization is an important piece of information that can be obtained from this experiment. Measuring the concentration of the gross pollutants remaining in the basin can be performed on the same sample employed for single component analysis. These gross concentration measures can be: $BOD_5$, COD, TOC, etc. The $BOD_5$ of the wastewater was employed in a series of volatilization experiments in this study.

Equation (16) suggest that a plot of F vs. $\Theta$ may be profitable since the fraction of the total amount of the gross constituent measure which is non-volatile can be obtained at the limit $\Theta = 1$. A total of fourteen volatilization runs were analyzed for $BOD_5$ on two separate samples of evaporator condensate. The results of these runs appear in Figures No. 7 and No. 8. Both figures show that as $\Theta$ increases (i.e., run time increases) the fraction of biodegradable organic material remaining decreases rapidly at first and then more slowly for larger $\Theta$ values and finally becoming invariant for $\Theta = 0.5$. The constant F section of the curve is significant for it shows that fraction of the original $BOD_5$ that is not readily volatilized. Figure 7 shows that approximately 25% of the original $BOD_5$ of this particular sample of condensate is non-volatile and hence cannot be removed by air contact. Conversely 75% can be removed by air contact. The sample represented by the data in Figure No. 8 is approximately 14% non-volatile. Obviously evaporator condensates contain constituents that are volatile and which accounts for 75 to 86% of the original $BOD_5$ of this wastewater.
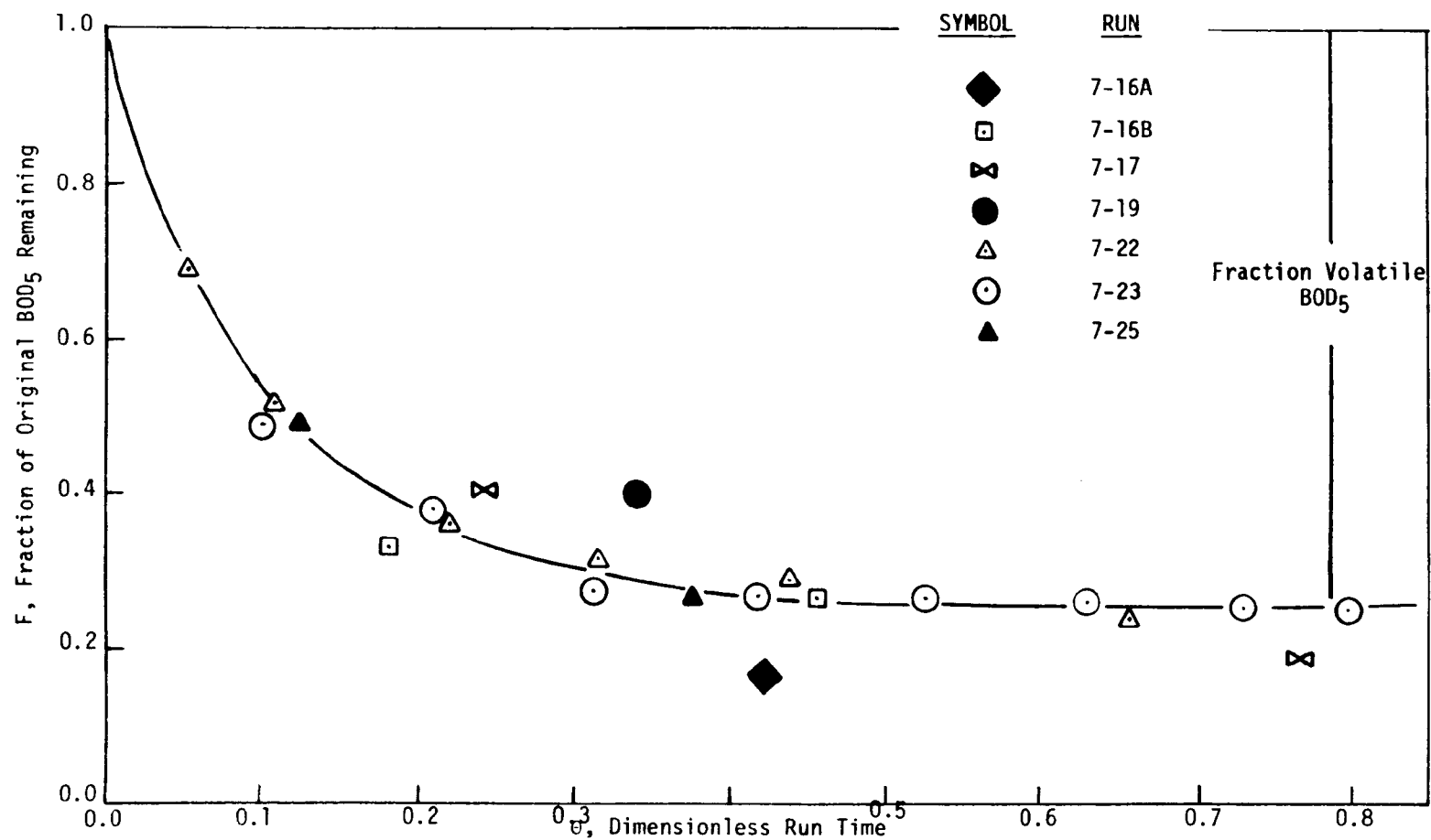
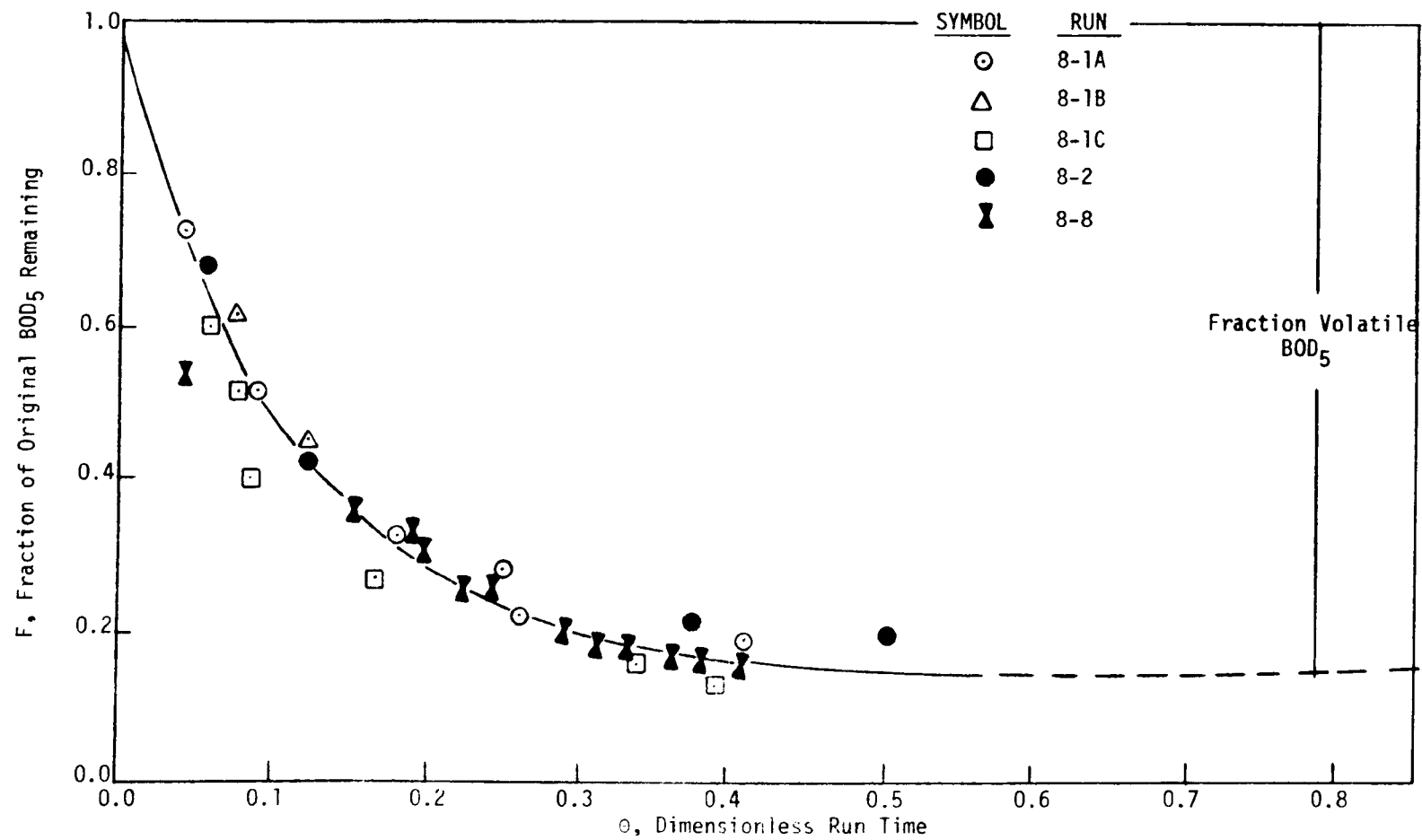FIGURE NO. 7:   VOLATILE FRACTION OF EVAPORATOR CONDENSATE, SAMPLE 7-15-68

FIGURE NO. 8:   VOLATILE FRACTION OF EVAPORATOR CONDENSATE SAMPLE, 8-1-68

## Volatilization Rates of Combined Components

The data presented in Figures 7 and 8 can be transformed to $\phi$ vs $1-\theta$ by equation (19) once $F_{\theta=1}$ has been obtained. This has been done for the two evaporator condensate samples and the results appear in Figure 9 and 10. A perfunctory examination of these figures indicates that the data does not correlate in a linear fashion and hence $K_s$ is not a constant. This is not surprising when it is realized that the wastewater has a spectrum of volatile constituents which display a spectrum of relative volatilization rates. As the experiment approaches complete removal of easily volatilizable components the less volatilizables remain and therefore display lower relative volatilization rates and a reduced magnitude of slope.

Extracting the slope at various points on the figures reveals some interesting aspects about the volatile fractions of the $BOD_5$ of this evaporator condensate. The slope on Figure 9 for $0.1 \leq \phi \leq 1.0$ is 8.47 with corresponding $K_s = 0.284$ while the slope for $.01 \leq \phi \leq 0.1$ is approximately 4.53 giving $K_s = 0.152$. Note that the average value of $K_m$ for methanol reported in Table No. 2 (0.327) is similar to that of the first volatile constituents to be removed. The last fraction of volatiles to be removed is approximately half as easy to volatilize as methanol. The slope in Figure 8 is computed to be 7.94 resulting in a value of $K_s = 0.253$, again of the order of the specific volatilization rate of methanol. It is also interesting to note the relative volatilization rates for the most volatile fraction as computed from $BOD_5$ measurements vs. those computed from methanol concentration measurements:

| | |
|---|---|
| methanol analysis (several samples) | 8.98 |
| $BOD_5$ analysis (sample 7-15-68) | 8.47 |
| $BOD_5$ analysis (sample 8-1-68) | 7.94 |

These relative rates of volatilization obtained from $BOD_5$ analysis suggest that the bulk fraction of the volatile $BOD_5$ consist of methanol or constituents of comparable volatilization nature.
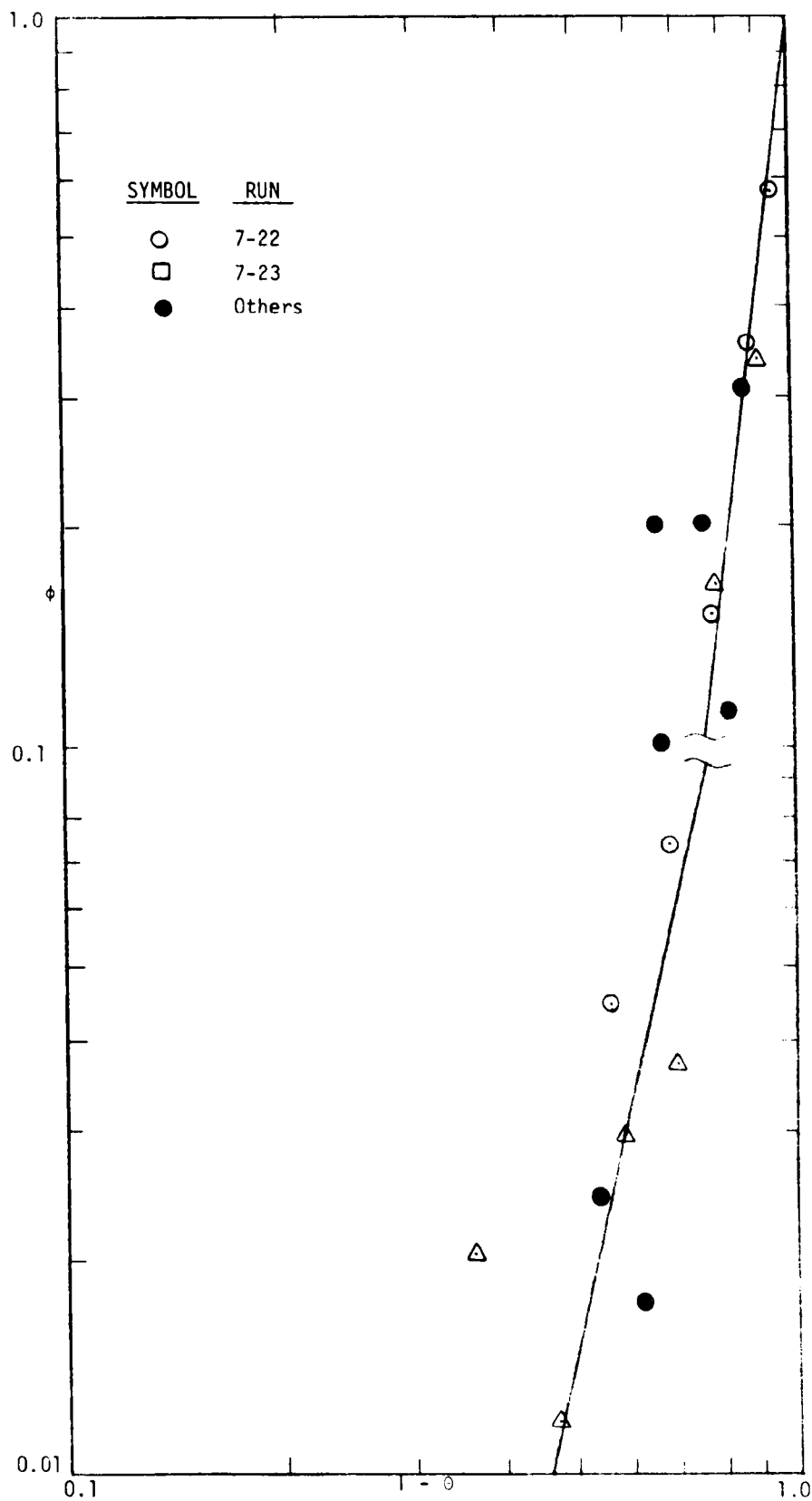
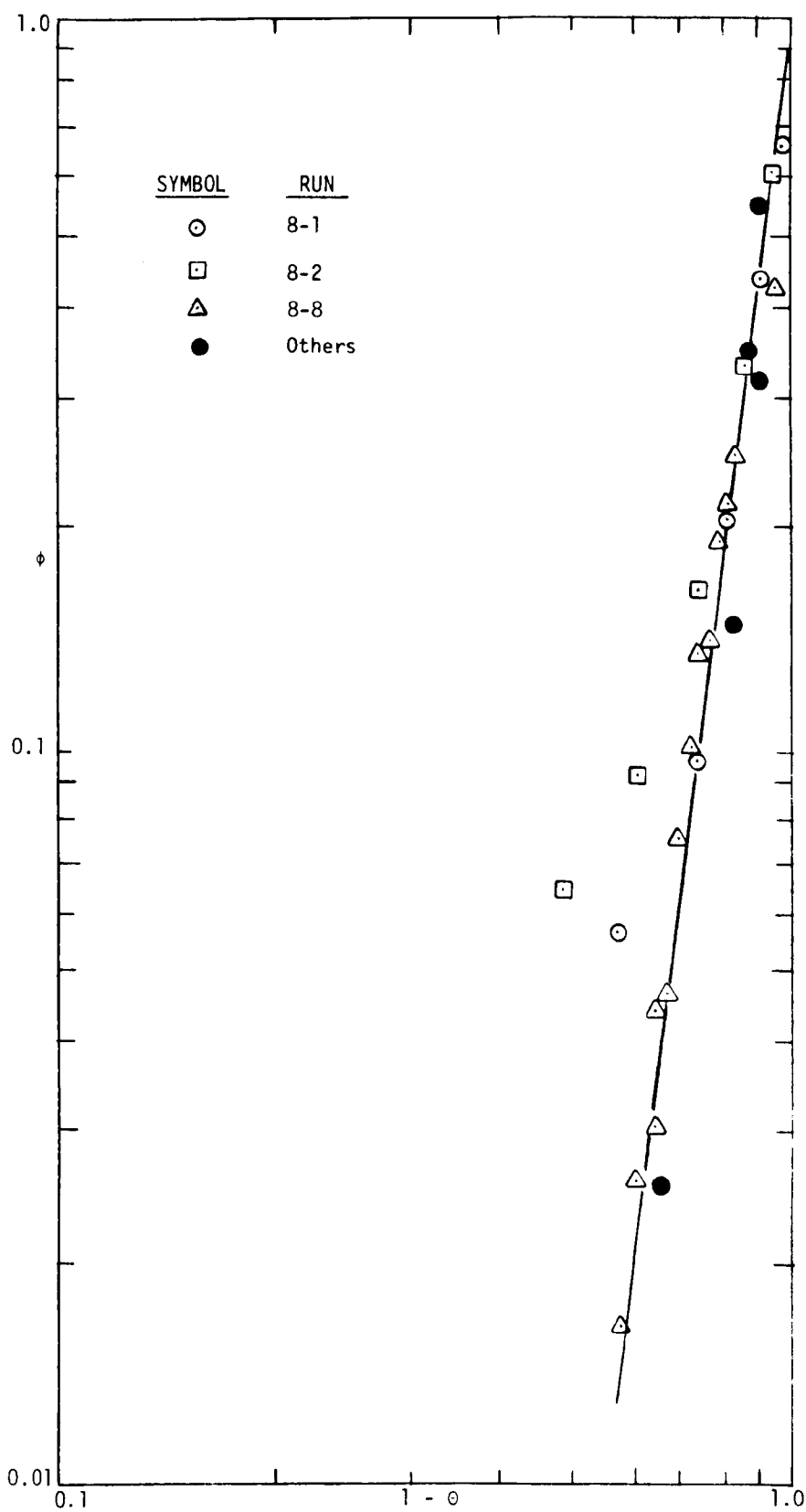FIGURE NO. 9:   GROSS CONSTITUENT VOLATILIZATION CHARACTERISTICS, SAMPLE 7-15-68

FIGURE NO. 10: GROSS CONSTITUENT VOLATILIZATION CHARACTERISTICS, SAMPLE 8-1-68

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## Conclusions

A method of studying the volatile character of the dissolved constituents in an aqueous effluent has been presented both from theoretical and experimental points of view. The following list includes the major findings:

1. An experimental apparatus for volatilization studies was presented which was void of the transient operation problem associated with the volatilization of water.

2. By the use of this apparatus one can find whether or not a wastewater contains volatile constituents.

3. The fraction of the original gross pollutant measure (i.e., $BOD_5$, COD, TOC, etc.) which is non-volatile can be determined experimentally.

4. The specific and relative volatilization rates of individual volatile constituents can be determined.

5. The specific and relative volatilization rates of the combined volatile constituents can be determined.

6. A method of interpretation is presented by which one can predict the consequences of air-water contact operations on the volatile constituents. This can be done by inspecting the magnitude of the relative volatilization rate.

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## Nomenclature

$K_i$ — Specific volatilization rate for component i

$L_m$ — volumetric or molar flux rate of aqueous phase ($\ell$/sec.cm$^2$)

$x_i$ — concentration of component i in aqueous phase (mg/$\ell$)

a — specific volatilization rate for water

M — volumetric quantity of liquid in the device ($\ell$)

t — experiment run time (min)

$y_i$ — concentration of component i in gas phase (mg/$\ell$)

$Z_T$ — height of column packed section (cm)

$K_y a_i$ — overall mass-transfer coefficient for component i (g-moles/sec.cm$^3$)

$G_m$ — molar flux rate of gas phase in column (g-moles/sec.cm$^2$)

C — a gross pollutant concentration measure (mg/$\ell$)

$\Theta$ — a dimensionless run time

n — total number of volatile components in aqueous phase

m — total number of non-volatile components in aqueous phase

F — fraction of the gross pollutant constituents remaining in the aqueous phase

$\phi$ — fraction of the gross volatile pollutant constituents remaining in the aqueous phase

## Subscripts

s — a pseudo component

i — inlet of column when double subscripts appear

o — outlet of column when double subscripts appear

i — denotes a volatile constituent

j — denotes a non-volatile constituent

## Superscripts

o — indicates initial condition (i.e. t = 0)

# APPENDIX H

## MICROBIOLOGICAL REPORT ON KRAFT MILL COOLING TOWER WATERS

Submitted September 10, 1969

Donald G. Ahearn, Ph.D.
Associate Professor Microbiology
Georgia State College
Atlanta, Georgia

Wood pulp processing waters flowing through the experimental cooling tower at the kraft mill in Macon, Georgia were examined for their microbial flora. Waters leading to and from the tower as well as those flowing over the plastic trickling filters were examined. On July 28, 1969, the first collection day, waters were plated onto bacterial and fungal isolation media at the site of collection. Control media were exposed to the environment during the collection period to determine the aerial flora. Isolation media included potato dextrose agar (PDA), malt extract-yeast extract-peptone agar with chloramphenicol and lactic acid (M-12), nutrient agar (NA) and blood agar (BA). Samples were collected in sterile bottles and appropriate alliquots were innoculated onto the isolation media by spread plate technique. Triplicate plates were prepared of each sample; incubation temperatures of 24 and 43°C were employed. Samples collected on August 7 and September 3, 1969, were diluted in sterile deionized water prior to plating.

The sites of collection are listed below.

| Code No. | Site |
|---|---|
| K0 | Tower base (sump) |
| K1 | Lower plastic grid, N.E. Corner |
| K2 | Lower plastic grid, N.E. Corner |
| K3 | Sump, adjacent to pump |
| K4 | Top of tower, sprinkler |
| K5 | Composite sample (to tower) |
| K6 | Decker filtrate |
| K7 | Tower effluent for recycling |
| K8 | Heavy liquor effluent |
| K9 | Total composite mill effluent |

## Results

Bacteria were the predominant organisms isolated from all samples. Average bacterial numbers are given in Table I. The low populations obtained on July 28 may be in part due to alteration of techniques. The predominant species obtained on July 28 included representatives of the genera

Bacillus, Flavobacterium, Pseudomonas, Serratia, and Aerobacter. On August 7, the relative concentrations of the Flavobacterium-Pseudomonas complex and Serratia groups appeared to increase. This latter species pattern was also found on September 3, 1969. The bacterial populations were markedly higher in samples collected on September 3, 1969. Special attempts were made to obtain yeasts and other fungi from the samples. No yeasts or other fungi were isolated on July 28. Only a few filamentous fungal colonies were obtained on August 7. The effluents collected on September 3 failed to yield fungi; however, two separate redwood samples from the cooling tower frame gave Trichoderma viride, a known cellulolitic fungus. The wood samples on collection showed no visual evidence of decomposition. Tricoderma viride is common in the papermill environment and its culturing from the wood samples may have been fortuitous. The red-wood frame should be carefully cultured and visually examined during the next few months.

Slime material was collected on all three collection trips from the top of the tower (41°C) and from the base of the tower (34°C). Samples from both sites contained about 5 nematodes per microscopic field (ca. 200 sq μ) on each collection trip. Mature worms were found in slime from the top, whereas immature specimens predominated in lower samples. On July 27, the slime was composed of wood cells interlaced with a large gram positive rod (Bacillus?) embedded in a matrix of gram negative rods. The nematodes, bacterial predators, were feeding on the slime. The slime was similar on August 7, 1969, except for the presence of motile algae or protozoan in the lower slime sample. On September 3, 1969, the slime at the base of the tower had turned reddish in hue and contained numerous filaments of algae or fungi and profuse numbers of rotifers. Since the filamentous slime did not yield fungi on culture, the filaments were most probably algal. No filaments were observed in the upper slime sample.

## Comments

Determination of accurate bacterial densities in "activated sludge" or in organically enriched waters containing particulate matter is beyond present technology. Low bacterial densities may not reflect low activity, but rather, the presence of increasing numbers of predators. The numbers of bacteria and bacterial predators have progressively increased during the sampling period. Following enrichment, the total biologic component of the tower showed a significant increase. There is insufficient data to evaluate the influence of the closing of operations for the Labor Day holiday on this increase. It was noted that the total mill sample, aside from its higher bacterial population, was visually clearer on September 3, 1969, and was of a lower pH (pH 6 versus pH 7 on August 7).

Bacterial densities reported for sites K5 to K7 should be evaluated with consideration of the sample source. The process waters were obtained from composite sample tanks. The temperature of water in these tanks is at least 10°C below that of the cycling water and the water has been static for varying periods prior to sampling.

The low numbers of fungi obtained may be partially due to the high pH (pH 8-9) of most of the process waters. Further redwood samples should be obtained to monitor the possible development of wood rot fungi. The occurrence of _Trichoderma viride_ is interesting, but is of no immediate concern.

## Questions

Is there a method of removing sludge from the sump at the base of the tower?

Has addition of enrichment with a readily assimilated carbon source been examined? This may permit co-oxidation of the more recalcitrant sulfur derivatives.

### TABLE I

### Bacterial Densities in Mill Process Waters

| Collection Site | July 28 | August 7 | September 3 |
|---|---|---|---|
| K0 | -- [1] | $1.8 \times 10^5$ | $1.6 \times 10^7$ |
| K1 | $3 \times 10^5$ [2] | $7.5 \times 10^5$ | $3.5 \times 10^6$ |
| K2 | "    " | -- | -- |
| K3 | "    " | -- | -- |
| K4 | "    " | $3.5 \times 10^5$ | $2.5 \times 10^6$ |
| K5 | $5 \times 10^5$ | $5.3 \times 10^6$ | $2.4 \times 10^7$ |
| K6 | "    " | $4.1 \times 10^7$ | $1.8 \times 10^6$ |
| K7 | "    " | $3.2 \times 10^6$ | $1.5 \times 10^7$ |
| K8 | 25-50 | -- | -- |
| K9 | -- | $1.9 \times 10^6$ | $3.5 \times 10^7$ |

[1] -- not sampled.
[2] Average numbers.

MICROBIOLOGICAL REPORT ON KRAFT MILL COOLING TOWERS

Report No. 2 Submitted October 11

Donald G. Ahearn, Ph.D.
Associate Professor of Microbiology
Georgia State University
Atlanta, Georgia

See Report of September 10, 1969.

The fourth microbiological testing of the process waters of the kraft mill at Macon, Georgia was performed on September 23, 1969. The collection stations and the culturable bacterial counts are presented in Table I. The bacterial numbers were markedly increased over those reported for September 3, 1969. Fungi, almost exclusively Ceotrichum candidum, were observed in significant numbers for the first time. At the time of sampling, water from the upper lake with high microbial populations was being passed through the tower. The presence of high numbers of fungi in the process waters and the increased bacterial numbers appear, at least in part, related to use of the water from the upper lake. The bacterial densities in the decker filtrate are probably more accurate than those of the previous report. Samples on September 23 were taken directly from the line rather than from the sampling tank.

Slime samples were collected from the upper and lower tower. Slime from the open lower portion of the tower was reddish brown, upper slime samples from the enclosed portion of the tower were dark brown. Nematodes were observed in both samples. On September 3, 1969, it was noted that the lower slime sample had turned reddish and that it contained numerous filaments of a possible alga and small motile protozoa-like organisms. The filaments and the motile forms respectively are representatives of the genera Beggiatoa and Chromatium. These are sulfur bacteria which obtain their energy by oxidizing sulfides or $H_2S$. The genus Chromatium is composed of purple photosynthetic bacteria which store inorganic sulfur internally. They are frequently considered anerobic, but recent evidence indicates that they require, at least, low levels of oxygen. The motile chromatia and large spirilla of the genus Spirulina are responsible for the reddish hue of the slime. As our isolation media lacks $H_2S$, these sulfur bacteria have not been cultured. Direct counts indicate that their numbers are in excess of $2x10^6$ cells/ml of slime. It should be noted that bacterial counts of slime material are inaccurate. The sulfur bacteria may be of significance in the reduction of odor.

Four redwood samples were collected from the tower frame. All samples yielded fungi, _Fusarium_ sp. _Pestalotia_ sp. and _Trichoderma virde_. Only the latter species is established to be celluloytic. In previous wood testings, _T. virde_ was isolated. I did not visually observe wood determination, however, the repeated isolation of fungi from the wood frame suggests that the preservative has leached out from the wood surface.

## TABLE I

### BACTERIAL AND FUNGAL DENSITIES IN
### MILL PROCESS WATERS ON SEPTEMBER 29, 1969

| Stations | No./ml | |
|---|---|---|
| | Bacteria | Fungi |
| KO  Tower base (sump) | $>/\times10^9$ | 310 |
| K4  Top of tower (sprinkler | $3.5\times10^5$ | 60 |
| K3  Sump (pump valve) | $3.5\times10^7$ | 200 |
| K5  Composite sample (line valve | $5.5\times10^5$ | 0 |
| K6  Decker filtrate (sample tank) | $1.5\times10^3$ | 0 |
| K6  Decker filtrate (line valve) | $1.5\times10^3$ | 0 |
| K9  Total composite mill effluent | $2.8\times10^8$ | 22 |
| K10 Upper Lake | $>1\times10^9$ | 367 |

# GEORGIA STATE UNIVERSITY

33 GILMER STREET, S. E. • ATLANTA, GEORGIA 30303

January 9, 1970
Department of Biology

Mr. Billy G. Turner
Project Manager
Research and Development Center
Georgia Kraft Company
Krannert Road
Rome, Georgia 30161

Dear Billy:

The enclosed material presents the characteristics of representative
bacteria isolated from the Macon plant. These bacteria are mainly
motile, gram negative rods of the Pseudomonas complex. These we
have attempted to fully characterize. In addition to the pseudomonads,
several other bacteria were common. The general characteristics of
these bacteria also are given.

The photomicrograph illustrates the sulfur bacteria, Chromatium sp. (large
cigar shaped rod with internal refractile sulfur globules) and Spirulina
sp. (corkscrew rod). See my second report submitted October 11, 1969.
The nematode species has not been identified; due to expense I have not
pursued this effort.

This report concludes our studies of the last sampling trip (September
23, 1969). An itemized bill for our services is attached. If I can be
of help in preparing your reports on the cooling tower please call.

Regards,

Donald G. Ahearn, Ph.D.
Associate Professor of Microbiology

DGA:am
Enclosures

# CHARACTERIZATION OF PSEUDOMONAD-LIKE BACTERIA FROM PROCESSING WATERS

|  | 5K-6 | 6K-6 | 7K-6 | 8K-6 | 9K-5 | 10K-5 | HO65 | 13K-2 |
|---|---|---|---|---|---|---|---|---|
| **Assimilation** | | | | | | | | |
| Glucose | - | - | A | - | - | A | A | - |
| Xylose | - | - | A | - | - | - | A | - |
| Mannitol | - | - | A | - | - | - | WA | - |
| Lactose | - | - | -- | - | - | - | - | - |
| Sucrose | - | - | A | - | - | - | - | - |
| Maltose | - | - | A | - | - | - | WA | - |
| **Fermentation** | | | | | | | | |
| Glucose | - | - | A | - | - | - | - | - |
| Xylose | - | - | A | - | - | - | - | - |
| Mannitol | - | - | - | - | - | - | - | - |
| Lactose | - | - | - | - | - | - | - | - |
| Sucrose | - | - | - | - | - | - | - | - |
| **Maltose** | - | - | - | - | - | - | - | - |
| Urea | - | - | + | - | W | W | W | - |
| $NO_3$ | + | - | - | - | + | + | - | + |
| Indole | - | - | - | - | - | - | - | - |
| M.R. | - | - | - | - | - | - | - | - |
| V.P. | - | - | - | - | - | - | - | - |
| Gelatin | - | - | - | - | - | - | - | - |
| Litmus Milk | Alk | Alk | W | Alk | NC | Red | NC | Red |
| 10% Glucose | Alk | Alk | A | Alk | Alk | A | A | Alk |
| 10% Lactose | Alk | Alk | Alk | Alk | Alk | Alk | Alk | Alk |
| Catalase | + | + | + | + | + | + | + | + |
| Oxidase | + | + | + | + | + | + | - | + |
| Nutrient Broth | + | + | W | + | + | + | W | + |
| MacConkey | + | + | + | + | + | + | + | + |
| SS agar | W | + | W | + | - | - | - | W |
| Citrate | - | W | + | + | + | + | + | + |
| Cetrimide | + | + | + | + | - | - | - | + |
| Colony Pigment | - | Brw/Sol | - | Brw/Sol | Green | Buff | Yellow | Buff |
| Flouracin | - | - | W | Brown | - | - | - | Lt.Brw. |
| Pyocyanin | - | - | - | Brown | - | - | - | Lt.Brw. |
| HIT | Brown | Yel.Brw | Brown | " | Brown | Brw/Sol | W/Yel | Brown |
| **Growth in T6Y** | | | | | | | | |
| 5°C | - | - | - | - | - | W | - | - |
| 25 | + | + | + | + | + | + | + | + |
| 37 | + | + | + | + | + | + | + | + |
| 42 | + | + | + | + | + | + | - | + |
| Motility 37 | - | - | + | - | - | - | - | - |
| "      25 | - | + | + | + | - | + | + | + |

|            | 5K-6 | 6K-6 | 7K-6 | 8K-6 | 9K-5 | 10K-5 | H065 | 13K-2 |
|------------|------|------|------|------|------|-------|------|-------|
| Sellers    | - - - - - - - - - - - - -Blu/Grn - - - - - - - - - - - - - | | | | | | | |
| TSI Slant  | Alk  | Alk  | NC   | Alk  | Alk  | NC    | Alk  | Alk   |
| Butt       | NC   | NC   | NC   | NC   | NC   | NC    | NC   | NC    |
| H2S        | -    | -    | -    | -    | -    | -     | -    | -     |
| Gas        | -    | -    | -    | -    | -    | -     | -    | -     |

---

W = weak; NC = No Change; AC = acid; Alk = Alkaline.

Species designations:

5-K6    Pseudomonas sp (similar to Alcaligenes faecalis)

6-K6    Pseudomonas sp.(similar to P. diminuta)

7-K6    ? Aeromonos sp.

8-K6    Pseudomonas aeruginosa

9-K5    Pseudomonas sp.

10-K5   Pseudomonas sp. (similar to P. stuzeri)

H-065   Pseudomonas stutzari

13-K2   Pseudomonas sp. (see 5-K6)

Non Pseudomonad bacteria:

K-8-14   Large gram positive, pink pigmented non-spore forming rod.

K-8-15   Diphtheroid-like, gram positive, non-spore forming, orange pigmented rod.

K-8-16   Bacillus sp. Aerobic, gram positive, spore forming rod. Survived heat shock (80°C for seven days).

| 1 | Accession Number | 2 | Subject Field & Group 05D | SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM |

| 5 | Organization |

Georgia Kraft Company, Rome, Georgia
Research and Development Center

| 6 | Title |

TREATMENT OF SELECTED INTERNAL KRAFT MILL WASTES IN A COOLING TOWER,

| 10 | Author(s) |

McAlister, J. A.
Turner, B. G.
Estridge, R. B.

| 22 | Citation |

| 23 | Descriptors (Starred First) |

Pulp Wastes*, Cooling Towers,* Waste Treatment, Water Reuse*, Pollution
Abatement, Pilot Plants, Analytical Techniques, Biochemical Oxygen Demand

| 25 | Identifiers (Starred First) |

Evaporators, Effluents, Condensates, Filtrates, Methanol, Stripping,
Volatilization, Liquefiers

| 27 | Abstract |

Selected waste streams from a kraft linerboard mill have been successfully treated in a conventional cooling tower. These waste streams, along with condenser waters from a barometric type evaporator condenser, were cooled in the tower and reused. This process accomplished BOD removals of about 10,000 lbs per day and an 8-10 MGD reduction in overall mill water needs. Theoretical, laboratory, and pilot investigations of BOD removal mechanisms involved proved the predominant mechanism was stripping of volatile components. During laboratory studies a procedure called the static vapor-liquid equilibrium method was developed for analyzing low concentration volatile components in waste water. Mathematical relationships were developed, allowing translation of study findings to other waste water treatment applications. Primary factors controlling BOD removals were blowdown rate, liquid-gas ratio, and average temperature. For a blowdown rate of 15-20% of tower influent, treatment efficiencies averaged 55-65% for sixth effect condensate, 45-55% for combined condensate and turpentine decanter underflow, and 25-35% for decker filtrate.

BOD reductions were believed due primarily to methanol stripping. Some biological activity was evident, however, and nutrient additions resulted in a 5-10% improvement in BOD removal. The system has several advantages over conventional surface condenser systems. Both operating and capital costs compare favorably with other waste treatment methods. (This report contains 16 references.)

| Abstractor B. G. Turner | Institution Georgia Kraft Company |