

**RESEARCH ON THE MECHANISMS FOR REMOVAL  
OF SOLUBLE BOD<sub>5</sub> IN CLARIFIER SYSTEMS**

**FIRST PILOT SCALE TRIAL**

Project 3216

EPA Ref. No. R 803-119-01

Report Three

A Progress Report

to

**MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY**

August 18, 1975

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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## TABLE OF CONTENTS

|  | Page |
|--|------|
| SUMMARY AND CONCLUSIONS                              | 1    |
| OBJECTIVES   | 3    |
| INTRODUCTION   | 4    |
| LABORATORY WORK                                      | 6    |
| Sampling and Analytical Procedures                   | 6    |
| Jar Tests  | 7    |
| Concentration of the Waste Stream                    | 14   |
| Evaluation of Separate Mill Sewers                   | 16   |
| Trial of Pilot Clarifier Under Laboratory Conditions | 18   |
| PILOT SCALE CLARIFIER STUDIES AT MOSINEE             | 24   |
| Equipment and Basic Operation                        | 24   |
| Sampling   | 25   |
| Testing Schedule                                     | 30   |
| Results and Discussion                               | 31   |
| PRELIMINARY EVALUATION OF COMPARATIVE ECONOMICS      | 36   |
| LITERATURE CITED                                     | 41   |
| APPENDIX I. DATA FROM PILOT SCALE FIELD TRIALS       | 42   |
| APPENDIX II. SUPPORTING MILLS OF GROUP PROJECT 3216  | 57   |

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RESEARCH ON THE MECHANISMS FOR REMOVAL OF SOLUBLE BOD<sub>5</sub>  
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FIRST PILOT SCALE TRIAL

SUMMARY AND CONCLUSIONS

Laboratory Jar tests were used to evaluate various flocculating agents and primary/polymer flocculating agent combinations for the optimum removal of the 5-day biochemical oxygen demand (BOD<sub>5</sub>) constituents from the total mill effluent of the Mosinee Paper Corporation of Mosinee, Wisconsin.

The best procedures developed during these tests were then used in a two months, on-site trial of a small (114-gallon) clarifier operating in parallel with the two commercial clarifiers at the mill. These included clarification with a polymer (Hercofloc 812.3 at 0.75 mg/liter) alone, as practiced by the mill, and the use of alum, ferric chloride and ferric sulfate in conjunction with the polymer, as well as short trials with ferrous sulfate and sulfuric acid with the polymer.

The field tests substantiated the laboratory findings, that:

1. When the clarifiers were all operated with the polymer alone, the two systems were equivalent in the removal of suspended solids and BOD<sub>5</sub>.
2. Additional suspended solids and BOD<sub>5</sub> removal, as well as marked reduction in effluent color, could be achieved with the addition of the ferric ion, in the form of either the chloride or sulfate salt, along with the Hercofloc 812.3 to promote flocculation and clarification.
3. Alum (aluminum sulfate) and polymer did not increase the removal of BOD<sub>5</sub>, but did enhance the removal of suspended solids and color over that for the polymer alone.

4. The presence of black liquor in the effluent stream, either from spills or the mill washing procedures, markedly reduced the efficiency of both clarifier systems. This would greatly increase the chemicals required and the cost of clarification for adequate effluent quality. Additional work is being done to determine more completely the effects of these components upon the overall clarifier system.

### OBJECTIVES

Laboratory trials under the Phase I studies of pulp and paper process water clarification systems served to confirm evidence that small but significant quantities of soluble components, responsible for a portion of the total biochemical oxygen demand, could be removed under favorable conditions of physicochemical treatment. Those results justified Phase II extension of the project to employ small-scale, pilot plant equipment operating parallel to representative commercial-scale mill clarifiers with the following objectives:

1. To develop an improved technology for increasing the capabilities for removal of BOD<sub>5</sub> components during primary clarification, over and above that achieved in standard mill practices.
2. To develop a better understanding of the physicochemical mechanisms involved in achieving increased BOD<sub>5</sub> removal in the clarifier.
3. To explore physicochemical systems of in-plant treatment of manufacturing process water flows, and particularly of those flows being recycled within the process, in such manner as to achieve substantial reduction in the BOD<sub>5</sub> loading of out-plant treatment systems.
4. To collate available data which could develop the base for preliminary evaluation of the comparative economics of achieving improved levels of BOD<sub>5</sub> removal by physicochemical clarification systems as compared to BOD removal in secondary biological treatment systems.

Objectives 1 and 4 are discussed in this report. The second and third objectives are subjects for continuing studies to be described in a later report.

## INTRODUCTION

Phase I of this research evaluated the significance and extent to which the constituents responsible for biochemical oxygen demand (BOD) in pulp and paper mill effluents may be removed in a first step of primary clarification. Surveys of mill waste flows and of clarifier effluents were conducted at mills of eleven companies. Data summarizing the prevailing levels of both total and soluble BOD<sub>5</sub> components are given in Progress Report One dated July 25, 1974. Means for removal of these components under laboratory conditions are detailed in Progress Report Two dated October 18, 1974. Those Phase I studies were undertaken as a jointly financed research effort of some pulp and paper mills (see list in Appendix II), of the U.S. Environmental Protection Agency (Grant No. R803 119 01) and of the Wisconsin Department of Natural Resources (Ref. No. 8100).

A secondary program (Phase II) of study using small-scale automated pilot equipment in on-site comparative studies, paralleling commercial clarifiers operating at two mill sites representing broad segments of the industry, were undertaken with funds supplied jointly by the U.S. Environmental Protection Agency and The Institute of Paper Chemistry (under Funded Formal Plan). This report summarizes data obtained in a 2-month field trial at the unbleached kraft pulp and paper mill of the Mosinee Paper Corporation in Mosinee, Wisconsin during the early months of 1975.

This mill, situated on the Wisconsin River, produces 230 tons per day in six batch-type digesters using the kraft pulping process. The unbleached pulp is washed on five countercurrent washers, with part of the fifth stage wash water being sewerred. The water from the paper machines, the fifth stage washer, and the high density sewer are combined with discharges from the pulp mill and evaporator condensates to produce a 16-18 million gallon daily waste discharge to the treatment plant.

The Phase II field studies were directed to development of means for reduction of BOD<sub>5</sub> in the primary clarifier. Improved primary treatment might serve to relieve the BOD<sub>5</sub> loading and increase color removal efficiency of secondary treatment systems now being designed. Elucidation of the physical or chemical mechanisms involved is an important second objective to be developed in these studies. It is also desired to achieve a preliminary evaluation of the economics for the reduction of BOD<sub>5</sub> by these means.

A following report covers the second field demonstration at a relatively new chemimechanical pulp mill producing bleached pulp and paper.



#### LABORATORY WORK

In the first two reports for Project 3216, "soluble" was defined as that portion of the solids passing with the liquid through a 0.45  $\mu\text{m}$  Gelman filter (Gelman Industries of Ann Arbor, Michigan) under 100 psig nitrogen pressure. This concept has been continued throughout this report.

#### SAMPLING AND ANALYTICAL PROCEDURES

Samples of mill effluent were taken under both "grab" and 24-hour composite conditions and transported to our Appleton laboratories with as little delay as possible. These were used to determine the ranges which could be expected in suspended solids, chemical oxygen demand (COD), total and soluble biochemical oxygen demand (BOD<sub>5</sub>), pH, total organic carbon (TOC), and color. These effluents were also used for the jar tests described later in this report.

The analytical procedures were basically those of the 13th Edition of the Standard Methods of the American Public Health Association (1) and the color method of the National Council for Air and Stream Improvement (2). In determining the dissolved oxygen in the BOD test, a Weston & Stack Model 350 DO Analyzer was used. The chemical oxygen demand was determined by the dichromate-sulfuric acid oxidation procedure, color was read with either a Beckman DU or DK-2A spectrophotometer against the No. 500 APHA Platinum-cobalt color standard. A Beckman pH meter was used for both the determination of sample pH and for pH adjustment during the color development prior to filtration. Total organic carbon was done with a Beckman Process Carbonaceous Analyzer.

#### JAR TESTS

In order to establish the correct parameters for the operation of the pilot-scale clarifier on the waste from Mosinee Paper, samples were taken of the total mill waste going to the treatment plant and treated in the laboratory using standard jar tests.

These were done with a six-position Phipps & Bird flocculator, with the various flocculating agents, or combinations, added under carefully standardized conditions of chemical addition, rapid mixing, flocculation mixing, settling and sampling. Briefly these can be described as:

1. The treatment of 1.0 or 1.5 liters of waste in 3-liter jars;
2. The addition of the primary flocculant, followed by one minute of mixing at 100 rpm;
3. If the second agent (polymer, etc.) was added, the addition was followed by a second rapid mix of one-half minute at 100 rpm; otherwise
4. The paddle speed was reduced to 20 rpm for 20 minutes to provide time for flocculation. The flocculation step was used after the final addition of chemical agents, no matter how many additives were involved.
5. At the end of the flocculation period, the jars were removed from the unit and the floc allowed to settle for one hour without disturbance.
6. At the end of the settling period, samples were withdrawn into 250-ml bottles under slight vacuum, with the tip of the sample tube one-half inch under the surface of the liquid in the jar.

An untreated jar of the waste was carried through the entire test from rapid mix to sampling and all "removal" data are based on the comparison of the treated samples with the analyses of this (control) sample.

If sludge volumes were to be determined, separate jars containing 1 liter of the waste were treated and carried through the test up to the beginning of the "settling" period. The contents of the jar were carefully transferred to Imhoff settling cones and the volume of the settled material was noted at the end of 30 minutes and finally at 60 minutes.

A number of tests were made with samples of the mill waste prior to the transfer of the pilot unit to Mosinee, while others were taken periodically throughout the on-site study at the mill.

Samples from these jar tests were, in some cases, subjected to complete analyses (Tables I and II) for suspended solids, total and soluble BOD<sub>5</sub>, TOC, COD and color in order to establish an estimate of the removals that might be attained under different conditions of treatment. Others (Table III) were merely used to establish flocculating characteristics and/or sludge volumes that would develop with the addition of the chemical combinations.

In the early trials, it was established that alum at 200-300 mg/liter and ferric chloride at 100 mg Fe<sup>+3</sup>/liter could be used to remove quantities of BOD on the order of 37-56% total and 12-25% soluble from the wastes in the jar tests. The addition of 0.75 mg/liter Hercofloc 812.3 appeared to provide additional removal of the soluble BOD<sub>5</sub> constituents, as indicated by an increase from 13% removal to 35% removal when added with 100 mg/liter alum and from 12% to 28% with 200 mg/liter alum (Table I). The use of the Hercofloc 812.3 polymer at 0.75-1.5 mg/liter levels, in the jar tests, appeared to markedly increase the removal of soluble BOD<sub>5</sub>; i.e., 14 and 21% removal, respectively, compared with the BOD<sub>5</sub> of the untreated (settled) control sample.

TABLE I

MOSINEE - JAR TESTS (CLARIFIER INFLUENT 11/21/74)  
 STUDY OF REMOVAL OF VARIOUS COMPONENTS  
 FROM THE WASTE

| Flocculant   |                 | Final<br>pH | % Reduction in                  |     |                      |                  | Total<br>color <sup>b</sup> |
|--|-----------------|-------------|---------------------------------|-----|----------------------|------------------|-----------------------------|
| Type   | mg/liter        |             | Total                           |     | Soluble <sup>a</sup> |                  |                             |
|  |                 |             | BOD <sub>5</sub>                | COD | TOC                  | BOD <sub>5</sub> |                             |
| FeCl <sub>3</sub>  | 50 <sup>c</sup> | 6.4         | 51                              | 71  | 31                   | 13               | 52                          |
|  | 100             | 6.0         | 37                              | 70  | 44                   | 25               | 43                          |
|  | 150             | 5.0         | 58                              | 76  | 47                   | 24               | 89                          |
| Alum   | 100             | 7.2         | 49                              | 60  | 14                   | 13               | 24                          |
|  | 200             | 7.0         | 56                              | 68  | 24                   | 12               | 43                          |
|  | 300             | 6.8         | 56                              | 73  | 31                   | 12               | 47                          |
| Lime   | 200             | 11.1        | 22                              | 52  | -13                  | -16              | 15                          |
|  | 300             | 11.6        | 39                              | 68  | -1                   | -14              | 58                          |
|  | 500             | 12.0        | 41                              | 71  | 1                    | -9               | 11                          |
| Hercofloc  |                 |             |                                 |     |                      |                  |                             |
| 812.3  | 0.75            | 8.4         | 18                              | 8   | 3                    | 14               | 0                           |
|  | 1.5             | 8.2         | 19                              | 11  | 6                    | 21               | 15                          |
| Added 0.75 mg/l Hercofloc 812.3 after 1 min mixing with primary indicated: |                 |             |                                 |     |                      |                  |                             |
| FeCl <sub>3</sub>  | 10              | 7.0         | No indication of floc formation |     |                      |                  |                             |
|  | 25              | 6.8         | No indication of floc formation |     |                      |                  |                             |
|  | 50              | 6.4         | 56                              | 72  | 30                   | 30               | 47                          |
| Alum   | 50              | 7.4         | No indication of floc formation |     |                      |                  |                             |
|  | 100             | 7.2         | 54                              | 76  | 14                   | 35               | 18                          |
|  | 200             | 7.0         | 52                              | 71  | 21                   | 28               | 32                          |

<sup>a</sup>Passing through a 0.45 µm Metrical filter.

<sup>b</sup>Co-Pt units at 465 nm (NCASI Method)

<sup>c</sup>As Fe<sup>+3</sup>.

Initial values: Total COD = 711 mg/l  
 (Control) BOD = 215 mg/l  
 Color = 109 units  
 Soluble TOC = 87 mg/l  
 BOD = 122 mg/l

TABLE II

JAR TESTS - MOSINEE (CLARIFIER INFLUENT 12/12/74)  
STUDY OF PRIMARY AND VARIOUS ADDITIVES  
AS FLOCCULATING AGENTS

| Flocculant                          |                 |                    |        | Final<br>pH | % Reduction in   |      |         |                  |       |
|-------------------------------------|-----------------|--------------------|--------|-------------|------------------|------|---------|------------------|-------|
| Primary                             |                 | Polymer            |        |             | Total            |      | Soluble |                  | Color |
| Type                                | mg/l            | Type               | mg/l   |             | BOD <sub>5</sub> | COD  | TOC     | BOD <sub>5</sub> |       |
| Analytical Grade Primary Chemicals: |                 |                    |        |             |                  |      |         |                  |       |
| FeCl <sub>3</sub>                   | 50 <sup>a</sup> | --                 | --     | 5.8         | 38               | 56   | 49      | 29               | 88    |
|                                     |                 | Herc. <sup>b</sup> | 0.75   | 5.8         | 37               | 57   | 51      | 27               | 89    |
|                                     |                 |                    | 1.5    | 5.8         | 38               | 58   | 51      | 27               | 90    |
| Alum                                | 50              | --                 | --     | 7.4         | 11               | -0.7 | 20      | 9                | 39    |
|                                     |                 | Herc. <sup>b</sup> | 0.75   | 7.5         | 10               | -0.7 | 21      | 15               | 47    |
|                                     |                 |                    | 1.5    | 7.7         | 6                | 0.7  | 14      | 10               | 45    |
|                                     | 100             | Act.Si             | 10     | 7.7         | 5                | 4    | 24      | 4                | 40    |
|                                     |                 | Herc. <sup>b</sup> | --     | 7.1         | 13               | 3    | 34      | 5                | 69    |
|                                     |                 |                    | 0.75   | 6.8         | 15               | 16   | 33      | 8                | 69    |
|                                     | 200             | Herc. <sup>b</sup> | 1.5    | 7.1         | 10               | 3    | 34      | 16               | 72    |
|                                     |                 |                    | Act.Si | 10          | 7.4              | 11   | 4       | 29               | 12    |
|                                     |                 | Herc. <sup>b</sup> | --     | 7.4         | 23               | 54   | 42      | 8                | 86    |
| 0.75                                | 7.2             |                    | 23     | 54          | 40               | 4    | 88      |                  |       |
| 1.5                                 | 7.0             |                    | 21     | 47          | 39               | 4    | 87      |                  |       |
| Act.Si                              | 10              | 6.9                | 23     | 57          | 39               | 4    | 84      |                  |       |
| Commercial Grade Primary Chemicals: |                 |                    |        |             |                  |      |         |                  |       |
| FeCl <sub>3</sub>                   | 50 <sup>a</sup> | Herc. <sup>b</sup> | 0.75   | 5.5         | 32               | 50   | --      | 28               | --    |
| Alum                                | 100             | Herc. <sup>b</sup> | 0.75   | 6.5         | 20               | 9    | --      | 13               | --    |

<sup>a</sup>In terms of Fe<sup>+3</sup>.

<sup>b</sup>Hercofloc 812.3.

Initial values (for untreated influent control):

Total COD = 711 mg/l  
BOD = 215 mg/l  
Color = 109 Pt-Co units  
Soluble TOC = 87 mg/l  
BOD = 122 mg/l.

TABLE III

JAR TESTS - MOSINEE (CLARIFIER INFLUENTS AT VARIOUS TIMES)  
 STUDY OF FLOCCULATING CHARACTERISTICS

| Type              | Flocculant |           | From 1/16/75 |                      | From 3/5/75 |                      | From 3/11/75 |                      |    |
|-------------------|------------|-----------|--------------|----------------------|-------------|----------------------|--------------|----------------------|----|
|                   | Primary    | Polymer   | pH           | Clarity <sup>a</sup> | pH          | Clarity <sup>a</sup> | pH           | Clarity <sup>a</sup> |    |
|                   | mg/l       | Type mg/l |              |                      |             |                      |              |                      |    |
| Fe <sup>+3</sup>  | 25         | --        | --           | --                   | --          | --                   | 6.8          | 0                    |    |
|                   | 50         | --        | 6.6          | 0                    | 6.9         | 0                    | 5.9          | 5                    |    |
|                   |            | Herc.     | 0.75         | 6.8                  | 0           | 6.6                  | 0            | --                   | -- |
|                   | 100        | --        | 5.0          | 0                    | 5.7         | 4                    | 4.2          | 4                    |    |
|                   |            | Herc.     | 0.75         | 5.6                  | 3           | 5.6                  | 4            | 4.3                  | 4  |
|                   | 150        | --        | --           | --                   | 4.5         | 1                    | 3.4          | 3                    |    |
|                   | Herc.      | 0.75      | --           | --                   | 4.3         | 1                    | 3.4          | 3                    |    |
| Alum <sup>b</sup> | 100        | --        | --           | --                   | 9.0         | 0                    | --           | --                   |    |
|                   |            | Herc.     | 0.75         | --                   | 8.6         | 0                    | --           | --                   |    |
|                   | 200        | --        | --           | --                   | 8.4         | 1                    | --           | --                   |    |
|                   | 300        | --        | --           | --                   | 7.2         | 4                    | --           | --                   |    |
| Alum <sup>c</sup> | 200        | --        | 7.4          | 1                    | --          | --                   | --           | --                   |    |
|                   | 300        | --        | 7.1          | 5                    | --          | --                   | --           | --                   |    |
|                   | 400        | --        | 6.5          | 4                    | --          | --                   | --           | --                   |    |
| Alum <sup>d</sup> | 200        | --        | 7.0          | 1                    | --          | --                   | --           | --                   |    |
|                   | 300        | --        | 6.9          | 5                    | --          | --                   | --           | --                   |    |
|                   | 400        | --        | 6.5          | 4                    | --          | --                   | --           | --                   |    |

<sup>a</sup>Clarity rated as 0 = untreated control, 1-5 = partial to complete clearing of the supernatant after settling one hour.

<sup>b</sup>Alum is analytical grade.

<sup>c</sup>Alum is commercial grade with precipitate in suspension.

<sup>d</sup>Alum is the commercial grade decanted to remove the precipitate.

Lime as a primary flocculating agent and activated silica as an additive appeared to be relatively ineffective in the removal of soluble BOD<sub>5</sub> from the waste from the Mosinee mill (Table II).

Of great interest in these studies was the high removal of COD, color and BOD<sub>5</sub> that could be achieved with ferric ion and alum from the Mosinee clarifier effluent (Table IV). Twenty-five to forty percent removal of soluble BOD<sub>5</sub> components was obtained with these primary flocculants added to either the north or south clarifier effluents. Lime and "additional" Hercofloc 812.3 did not produce

enhancement of the "solubles" removal, but did provide added reductions in total BOD<sub>5</sub>, COD and color.

TABLE IV  
JAR TESTS - MOSINEE (EFFLUENT FROM 11/21/74)  
STUDY OF THE REDUCTION OF CONTAMINANTS IN CLARIFIER EFFLUENTS

| Flocculant            |                 | pH                         | % Reduction in             |     |       | Soluble BOD <sub>5</sub> |
|-----------------------|-----------------|----------------------------|----------------------------|-----|-------|--------------------------|
| Type                  | mg/l            |                            | BOD <sub>5</sub>           | COD | Color |                          |
| From North Clarifier: |                 |                            |                            |     |       |                          |
| FeCl <sub>3</sub>     | 50 <sup>a</sup> | 5.1                        | 61                         | 72  | 65    | 39                       |
|                       | 100             | 3.4                        | 63                         | 72  | 79    | 40                       |
|                       | 150             | 3.0                        | 64                         | 68  | 85    | 38                       |
| Alum                  | 100             | 6.0                        | 43                         | 56  | 42    | 26                       |
|                       | 200             | 6.2                        | 61                         | 70  | 65    | 25                       |
|                       | 300             | 6.2                        | 61                         | 70  | 68    | 26                       |
| Lime                  | 200             | 9.9                        | 25                         | 32  | 28    | -14                      |
|                       | 300             | 11.1                       | 33                         | 48  | 42    | -19                      |
|                       | 500             | 11.6                       | 41                         | 55  | 42    | 0.8                      |
| Hercofloc             |                 |                            |                            |     |       |                          |
| 812.3                 | 0.75            | 8.8                        | 12                         | 4   | 7     | -6                       |
|                       | 1.5             | 8.6                        | 15                         | 11  | 4     | 3                        |
| From South Clarifier: |                 |                            |                            |     |       |                          |
| FeCl <sub>3</sub>     | 50 <sup>a</sup> | 5.7                        | 63                         | 68  | 46    | 38                       |
|                       | 100             | 3.8                        | 65                         | 70  | 70    | 39                       |
|                       | 150             | 3.1                        | 59                         | 64  | 75    | 38                       |
| Alum                  | 100             | 6.9                        | No apparent floc formation |     |       |                          |
|                       | 200             | 6.5                        | 60                         | 64  | 27    | 31                       |
|                       | 300             | 5.6                        | 62                         | 66  | 46    | 26                       |
| Lime                  | 200             | 11.3                       | No apparent floc formation |     |       |                          |
|                       | 300             | 11.6                       | 43                         | 44  | 2     | -13                      |
|                       | 500             | 12.0                       | 43                         | 50  | 11    | 3                        |
| Hercofloc             |                 |                            |                            |     |       |                          |
| 812.3                 | 0.75 & 1.5      | No apparent floc formation |                            |     |       |                          |

<sup>a</sup>In terms of Fe<sup>+3</sup>.

|                              |   |  |
|------------------------------|---|--|
| Initial Values:<br>(Control) | { | Soluble BOD (mg/l) North=124 South=130 |
|                              |   | Total BOD (mg/l) North=214 South=240   |
|                              |   | COD (mg/l) North=628 South=612         |
|                              |   | Color (units) North=108 South=63       |

Periodic checks of the formation of flocs and the chemical analyses of the supernatant fluid from the jar tests led to the following interesting observations.

The presence of black liquor, in relatively low concentrations, in the waste stream resulted in almost complete failure of both floc formation and the reduction of any of the parameters under study, except for the suspended solids. Since good floc characteristics could be restored by removal of the liquor contamination from the waste stream, careful control of spills, leaks and other sources of liquor discharge into the sewers (now under study by the engineering firm doing work at the mill) should greatly reduce this problem area.

Adjustment of the pH from the initial 11 or higher, to 8 with sulfuric acid prior to the addition of the chemical flocculating agents, markedly increased the amount of suspended solids removed, but had only slight effect on the amount of remaining BOD<sub>5</sub> in solution (Table V).

Incomplete flocculation, as evidenced by the presence of colloidal material and the Tyndall effect, in the jar tests almost invariably resulted in low removal of soluble BOD<sub>5</sub>. This may account for the increased removal of the soluble BOD<sub>5</sub> when polymer was used in conjunction with the primary, since the addition of the polymer in many cases did result in increased "removal" and also less turbid supernatant fluid in the jars.

The ferric ion was equally effective as the sulfate or chloride salt, as long as the concentration of the Fe<sup>+3</sup> ion was maintained and the pH of the influent was not too high. The chloride form appeared to have a wider pH range for adequate floc formation.



TABLE V  
JAR TESTS -- MOSINEE  
EFFECT OF BLACK LIQUOR CONTENT ON FLOCCULATION

| Flocculant  |      | Final<br>pH | % BOD <sub>5</sub> reduction |         | % Reduction in<br>suspended solids |
|---|------|-------------|------------------------------|---------|------------------------------------|
| Primary   | mg/l |             | Total                        | Soluble |                                    |
| Influent (2/11/75): pH = 11.2   |      |             |                              |         |                                    |
| Fe <sup>+3</sup>  | 50   | 10.7        | -3                           | -5      | 22                                 |
|   | 100  | 10.3        | -5                           | -3      | 55                                 |
|   | 150  | 9.9         | 1                            | 6       | 72                                 |
|   | 200  | 9.4         | --                           | 8       | 50                                 |
| Alum  | 200  | 10.8        | -0.2                         | 1       | 35                                 |
|   | 300  | 10.6        | -7                           | 4       | 18                                 |
|   | 400  | 10.4        | 4                            | 12      | 2                                  |
|   | 500  | 10.2        | 2                            | 7       | 15                                 |
|   | 600  | 10.1        | 2                            | 5       | 30                                 |
| Influent (2/11/75) adjusted to pH 8 with sulfuric acid prior to jar test: |      |             |                              |         |                                    |
| Fe <sup>+3</sup>  | 50   | 7.2         | 6                            | 11      | 75                                 |
|   | 100  | 6.8         | 6                            | 4       | 72                                 |
| Alum  | 200  | 7.5         | -9                           | 5       | 76                                 |
|   | 300  | 7.3         | -5                           | -7      | 84                                 |
|   | 400  | 7.1         | -8                           | 20      | 80                                 |

Sludge volumes were also markedly reduced by the addition of the polymer in the jar tests (Table VI) and for this reason alone, it was incorporated in all but one of the pilot studies.

#### CONCENTRATION OF THE WASTE STREAM

In order to study the flocculation and BOD<sub>5</sub> removal characteristics of a more concentrated waste, that might become available for treatment if the total water use in the mill was reduced through recycling, we concentrated a sample of the total mill effluent (clarifier influent) by reverse osmosis.

TABLE VI  
JAR TESTS - MOSINEE  
SLUDGE VOLUME MEASUREMENTS

| Primary   | Flocculant |                    | mg/1 | Sludge volume,<br>ml/1 | Final<br>pH | Clarity <sup>a</sup><br>0-5 |
|---|------------|--------------------|------|------------------------|-------------|-----------------------------|
|   | mg/1       | Polymer            |      |                        |             |                             |
| Influent 12/21/74:  |            |                    |      |                        |             |                             |
| Fe <sup>+3</sup>  | 50         | None               | --   | 122                    | 5.4         | 4                           |
|   | 50         | Hercofloc<br>812.3 | 0.75 | 115                    | 5.5         | 5                           |
| Alum  | 100        | None               | --   | 64                     | 6.2         | 2                           |
|   | 100        | Herc.              | 0.75 | 54                     | 6.5         | 2                           |
| Influent 12/31/74:  |            |                    |      |                        |             |                             |
| Fe <sup>+3</sup><br>A.R. FeCl <sub>3</sub> <sup>b</sup>         | 50         | None               | --   | 92                     | 6.3         | 4                           |
|   | 50         | Herc.              | 0.75 | 80                     | 6.2         | 5                           |
| Fe <sup>+3</sup> commer-<br>cial FeCl <sub>3</sub> <sup>c</sup> | 50         | None               | --   | 96                     | 6.3         | 5                           |
|   | 50         | Herc.              | 0.75 | 85                     | 6.3         | 5                           |
| Influent 1/16/75:   |            |                    |      |                        |             |                             |
| Fe <sup>+3</sup>  | 50         | None               | --   | 36                     | 6.6         | 0                           |
|   | 50         | Herc.              | 0.75 | 30                     | 6.8         | 0                           |
|   | 100        | None               | --   | 48                     | 5.0         | 0                           |
|   | 100        | Herc.              | 0.75 | 60                     | 5.6         | 3                           |
| Alum  | 300        | None               | --   | 96                     | 6.3         | 4                           |
|   | 300        | Herc.              | 0.75 | 80                     | 6.3         | 5                           |

<sup>a</sup>Clarity: 0 = control (no apparent flocculation)  
5 = completely clear supernatant (no apparent suspended solids).

<sup>b</sup>Analytical Reagent Grade.

<sup>c</sup>Commerical Grade 42°Be.

The concentrated material from the RO process, representing a 4:1 v/v concentration, was used to prepare samples equivalent to 1:1, 2:1 and 3:1 concentrations by diluting with the permeate from the RO process. In this way a better sample could be attained, than would have been the case if tap or distilled water were used for dilution.

Jar tests were made with all concentrations and the samples were analyzed, before and after treatment with ferric chloride:polymer and alum:polymer combinations, for suspended solids, total and soluble BOD<sub>5</sub> and color (Figure 1).

Treatment with ferric ion at 100 mg/liter with 0.75 mg/liter Hercofloc 812.3 could produce an acceptable effluent for discharge, in terms of suspended solids and BOD<sub>5</sub>, up to a concentration of approximately 3:1 and still gain on both hydraulic and gravimetric loading. However, over this range of concentration, the flocculating agents did not prove effective in producing an adequate effluent.

While this was a rough study and could be subject to several objections in terms of improved processing techniques such as spill control and their relationship to concentration by water reuse within the mill, as well as economics, it certainly indicates that wastes could be successfully treated at higher concentrations.

#### EVALUATION OF SEPARATE MILL SEWERS

One of the basic problems encountered at the Mosinee mill, and probably a problem in many treatment plants, was the high variability of the waste stream, in terms of hydraulic flows and in content of solids and BOD<sub>5</sub> loading. If some of the streams entering the waste treatment line could be segregated before they were diluted (or contaminated), they might individually prove more amenable to

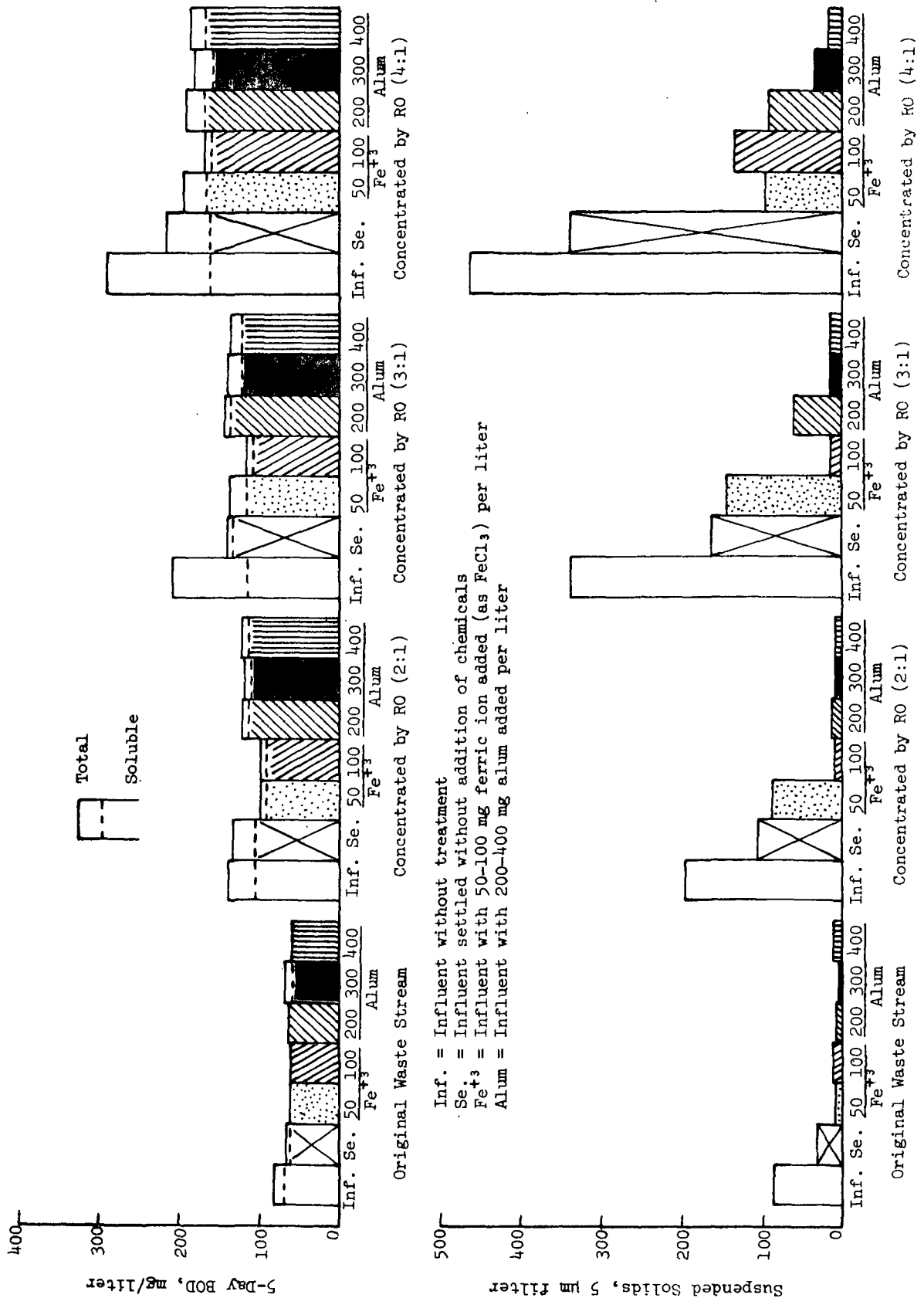


Figure 1. Jar Tests with Mosinee Influent Concentrated by RO

simpler processes of treatment and also improved clarifier performance, the heavy slugs and spills of lignin-containing pulp liquors are of particular concern in reducing clarifier performance.

Samples of seven sewers were obtained, along with a sample of clarifier influent, and analyzed for BOD<sub>5</sub>, COD, TOC, color and suspended solids (Table VII). Three had high biochemical oxygen demands, the pulp mill sewer, the soda recovery sewer and the fifth stage of the brownstock washer. These comprised only 600,000, 280,000 and 35,000 gallons/day, respectively, of the total mill discharge of 16-18 million gallons/day.

If one or more of these relatively low volume, high BOD<sub>5</sub> streams could be treated separately by flocculation, reverse osmosis, ultrafiltration or some other process, so as to remove this load from the treatment plant, a marked improvement should be noted in the overall efficiency of the treatment plant, as well as delivering a reduced load to the secondary treatment facility and a greater potential for water reuse.

This phase of the laboratory work promised a potentially valuable approach to the treatment of the wastes discharged by the unbleached kraft pulping industry as well as specifically to the conditions prevailing at the Mosinee mill.

#### TRIAL OF PILOT CLARIFIER UNDER LABORATORY CONDITIONS

Three thousand gallons of Mosinee clarifier influent were delivered by truck to the Institute early in January 1975 and used to check the operation of the pilot-scale clarifier (Figure 2), without the samplers or the submersible pump (P-1), prior to the transfer of the complete test unit to the mill at Mosinee, Wisconsin.

TABLE VII  
ANALYSIS OF MOSINEE PAPER COMPANY SAMPLES

| Source                               | pH   | Total, mg/l |                  | Soluble, mg/l <sup>a</sup> |                  | Color <sup>b</sup> | Suspended solids |      |
|--------------------------------------|------|-------------|------------------|----------------------------|------------------|--------------------|------------------|------|
|                                      |      | COD         | BOD <sub>5</sub> | TOC                        | BOD <sub>5</sub> |                    | 0.45 μm          | 5 μm |
| A. Digester sewer                    | 11.8 | 2971        | 635              | 741                        | 775              | 4000               | 239              | 98.5 |
| B. Pulp mill sewer                   | 11.2 | 4460        | 1624             | 1099                       | 1074             | 4880               | 260              | 71   |
| C. 5th Stage Brownstock washer       | 10.7 | 4865        | 1349             | 1402                       | 1156             | 4150               | 130              | 94   |
| D. High density sewer                | 9.7  | 553         | 158              | 138                        | 144              | 920                | 120              | 26   |
| E. Foul evaporator condensate        | 8.5  | 871         | 762              | 197                        | 624              | 100                | 22               | 34   |
| F. Digester blowdown foul condensate | 8.2  | 1485        | 964              | 389                        | 953              | 562                | 2                | 15   |
| G. Soda recovery sewer               | 10.1 | 8328        | 4162             | 2077                       | 3705             | 4200               | 636              | 184  |
| H. Clarifier influent                | 8.0  | 920         | 181              | 74                         | 106              | 92                 | 1004             | 686  |

<sup>a</sup>Passing through a 0.45 μm Metrical filter.

<sup>b</sup>Co-Pt units at 465 nm (NCASI Method).

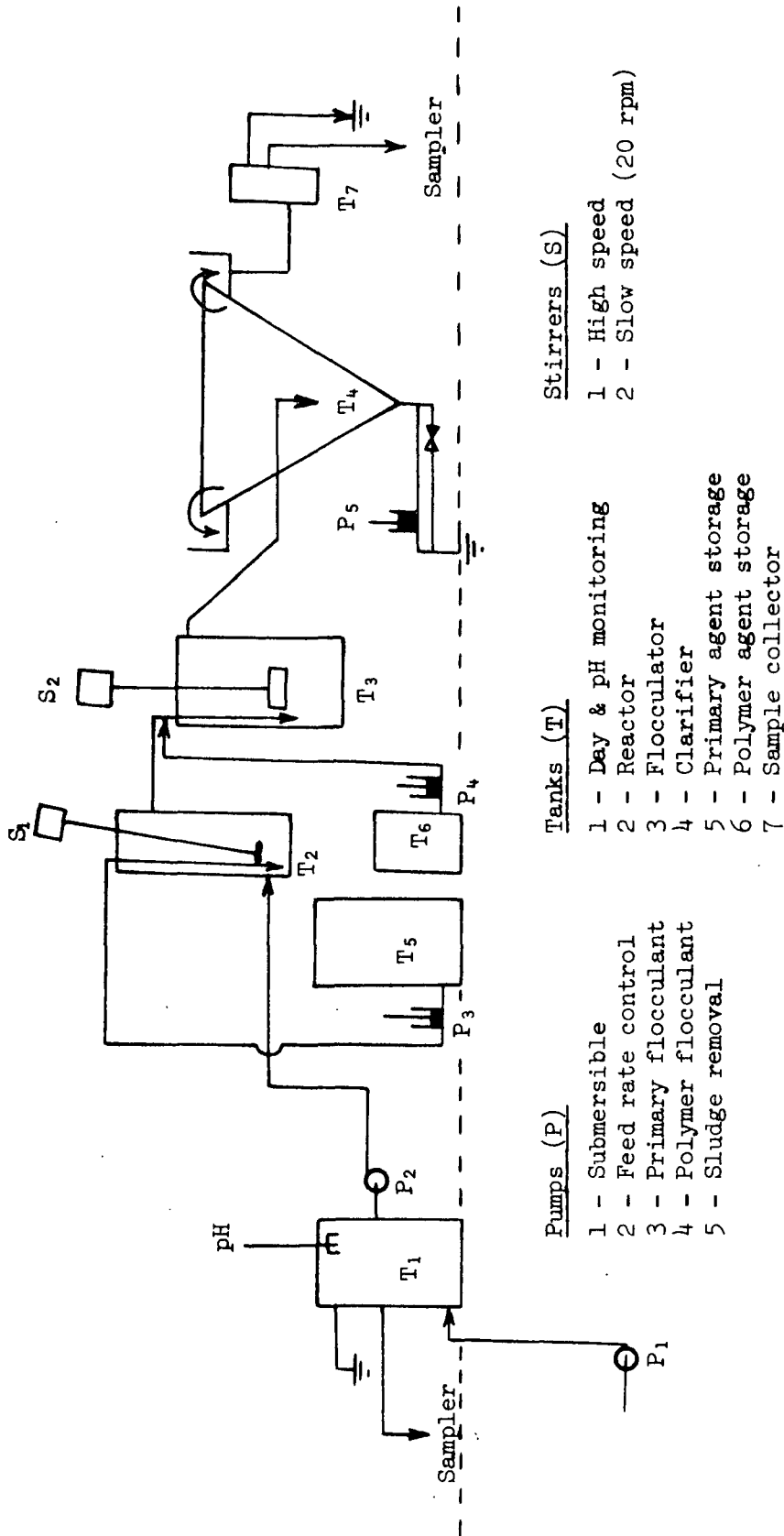


Figure 2. Schematic for Pilot-Scale Clarifier

The system consisted of the following items and arrangement:

1. A tank (T-1) provided a constant supply of the waste to be treated.
2. The Feed Control pump (P-2) maintained a constant feed rate.
3. A 3-gallon Reactor tank (T-2) with a high-speed mixer provided rapid mixing of the waste with the primary flocculating agent and gravity flow to the balance of the system.
4. The flow from the Reactor tank was into an open pipe extending to the bottom of the Flocculator tank (T-3). If polymer were to be added, it was introduced at the top of this open pipe, into a quiescent zone approximately one-quarter of the distance down the pipe in order to provide adequate mixing without excessive turbulence or floc dispersion. A slow speed (20 rpm = 1.6 fps peripheral velocity) paddle was mounted in the center of this tank to provide mixing without excessive shear.
5. The overflow from the reactor tank passed downflow into the clarifier (T-4). This clarifier had been developed at The Institute of Paper Chemistry under Project 3029, jointly sponsored by the pulp and paper industry, the Environmental Control Technology Corporation (ENCOTEC) and the Upper Great Lakes Regional Commission and was constructed of stainless steel. The inlet was downflow through a 2-inch stainless steel pipe with an opening 1.25 feet from the bottom of the cone-shaped tank. The center height was 4.25 feet and the diameter was 3.5 feet. It was equipped with flow-over weirs which discharged into a 2-inch trough around the entire circumference of the top. The flow from this trough was from one side into a small sampling pot (T-7) and then to the sewer.
6. In the laboratory studies the sludge was removed from the bottom of the clarifier by gravity flow through a vented overflow pipe (not shown) that could be raised and lowered to control the rate. Both gravity flow and a pumping system were used in the field trials and are discussed later.



7. The flocculating agents were stored in small tanks (T-5, T-6) and were metered into the system with tubing pumps (P-3, P-4).

Using this system, a brief study was made of the effects of waste flow and sludge removal rates, at a constant level of flocculating agent(s), on the quality of discharge produced.

An excellent quality discharge (Table VIII) appeared to be produced if the waste feed and sludge discharge rates resulted in an overflow rate of 400-425 gallons/sq ft/day (gsfd). The removal also appeared to be dependent upon the type of sludge blanket developed in the clarifier. Best results were obtained with the level at least two inches from the top to prevent floc carry-over, but not less than three feet from the bottom (two feet above the waste inlet). The latter was assumed to promote the development of larger floc particles and a particle entrapment effect to markedly enhance the quality of the discharge.

These parameters of flow rate and sludge level were, therefore, selected for the operation of the unit during the field trials.

TABLE VIII  
 LABORATORY EVALUATION OF PILOT  
 SCALE CLARIFIER

| Over-<br>flow<br>rate <sup>a</sup> | Sludge<br>removal,<br>% | Flocculant, mg/l            |                    | % Removal of        |       |                  |         |
|------------------------------------|-------------------------|-----------------------------|--------------------|---------------------|-------|------------------|---------|
|                                    |                         | Primary<br>Fe <sup>+3</sup> | Polymer<br>H 812.3 | Suspended<br>solids | Color | BOD <sub>5</sub> |         |
|                                    |                         |                             |                    |                     |       | Total            | Soluble |
| 369                                | 20                      | 87                          | 1.3                | 99                  | 55    | 24               | 8       |
| 395                                | 13                      | 64                          | 0.78               | 99                  | 79    | 34               | 17      |
| 406                                | 10                      | 61                          | 0.77               | 99                  | --    | 29               | 9       |
| 425                                | 10                      | 52                          | 0.77               | 97                  | 46    | 36               | 10      |
| 526                                | 15                      | 51                          | 0.77               | 19                  | 49    | 19               | 13      |
| 579                                | 12                      | 51                          | 0.77               | -52                 | 49    | 5                | 16      |
| 587                                | 10                      | 50                          | 0.77               | -29                 | 48    | 0                | 0       |
| 632                                | 14                      | 50                          | 0.75               | -35                 | 49    | 9                | 9       |

<sup>a</sup>Overflow in gallons/square foot/day based on surface area of clarifier.

Initial Values: Suspended solids = 234 mg/l  
 (Control) BOD<sub>5</sub>, total = 134 mg/l  
 BOD<sub>5</sub>, soluble = 114 mg/l  
 Color = 130 units.

## PILOT SCALE CLARIFIER STUDIES AT MOSINEE

The information gained during the early part of the laboratory studies with jar tests of the Mosinee mill effluent was used to prepare a scheme for the treatment of this mill effluent with the pilot scale clarifier described in the previous section.

This part of the report will cover the work done on-site at the mill in Mosinee, Wisconsin from January 15 to April 4, 1975 and will deal with the problems encountered and with some of the solutions developed for these problems, the removal rates for suspended solids, color and total/soluble biochemical oxygen demand as well as a rough estimate of the chemical costs involved in the various treatment schemes.

### EQUIPMENT AND BASIC OPERATION

The IPC system was to be operated in parallel with the two mill clarifiers and was, therefore, installed in the waste treatment plant. This concrete building was immediately adjacent to the two clarifiers and was unheated, except for the heat from the incoming waste stream.

Due to the arrangement of the waste treatment flow system, it was necessary to use a submersible pump (P-1 in Figure 2), mounted in the waste trench immediately downstream from the bar and travelling screens, to lift the waste to floor level (6-8 feet) at a rate of 5 to 8 gallons per minute.

The flow from the submersible pump was directed into the bottom of a 50-gallon tank (T-1) for supplying a centrifugal Feed Control pump (P-2) with the excess overflowing to the sewer near the influent sampler. This tank also contained pH recording equipment.

The Feed pump (P-2), fitted with an orifice, maintained a waste flow of 3 gpm into the Reactor tank (T-2) and the only other modification of the system, over that described under Laboratory Evaluation in the preceding section, was the installation of a pump in the sludge removal line during some of the trials.

#### SAMPLING

During the early part of the mill study, influent and effluent samples were taken with two refrigerated Sigmamotor samplers, set to take individual samples hourly around the clock. In order to reduce the analytical load, these were composited into twelve-hour samples daily.

It soon became apparent that the rapid changes in the mill discharge (Table 9 and Figure 3) would not permit such an infrequent sampling scheme. A third sampler, a CVE refrigerated unit capable of taking small samples at short intervals (1-60 minutes) for compositing in a 1-gallon jug, was placed in the influent stream. This unit was set to take 40-ml samples at 15-minute intervals and the twelve-hour composites obtained were compared with those from the Sigmamotor unit taking hourly 400-ml aliquots from the same influent source.

Poor correlation was noted (Table 10) and a second trial was made. This was with four samplers in the following arrangement:

- a. The two Sigmamotor samplers on the influent and effluent streams set at 30-minute intervals to take twenty-four samples in twelve hours,
- b. The CVE sampler on the influent taking 40-ml samples every ten minutes,
- c. A Polystaltic tubing pump, set to take 9 ml/min continuously, was used on the effluent line.

TABLE IX  
ANALYSIS OF INDIVIDUAL SAMPLES  
TO ESTABLISH RANGE

| No.   | pH    | Milligrams/liter |                        |                          |
|---|-------|------------------|------------------------|--------------------------|
|   |       | Suspended solids | Total BOD <sub>5</sub> | Soluble BOD <sub>5</sub> |
| Samples taken at hourly intervals (start 10 a.m. 1/16/75) |       |                  |                        |                          |
| 1   | 10.12 | 210              | 241                    | 203                      |
| 2   | 10.07 | 628              | 206                    | 178                      |
| 3   | 9.57  | 494              | 166                    | 138                      |
| 4   | 9.63  | 145              | 155                    | 138                      |
| 5   | 9.11  | 85               | 129                    | 116                      |
| 6   | 9.48  | 144              | 135                    | 114                      |
| 7   | 8.86  | 265              | 143                    | 140                      |
| 8   | 9.40  | 152              | 163                    | 140                      |
| 9   | 9.19  | 97               | 148                    | 140                      |
| 10  | 9.30  | 76               | 127                    | 117                      |
| 11  | 9.78  | 94               | 138                    | 135                      |
| 12  | 9.60  | 115              | 132                    | 124                      |
| 13  | 9.59  | 267              | 148                    | 118                      |

Analytical comparisons (Table 11) were excellent and indicated that the Sigmamotor samplers could be used to take representative samples, if the 30-minute cycle was used.

In order to compensate for the "system holding time" of 90 minutes, the compositing of the individual influent and effluent samples from the Sigmamotor samplers were adjusted to obtain representative samples from the same twelve-hour test period. This was easily accomplished by compositing the numbered bottles in groups so that those for the effluent were three bottles "back" of those for the influent.

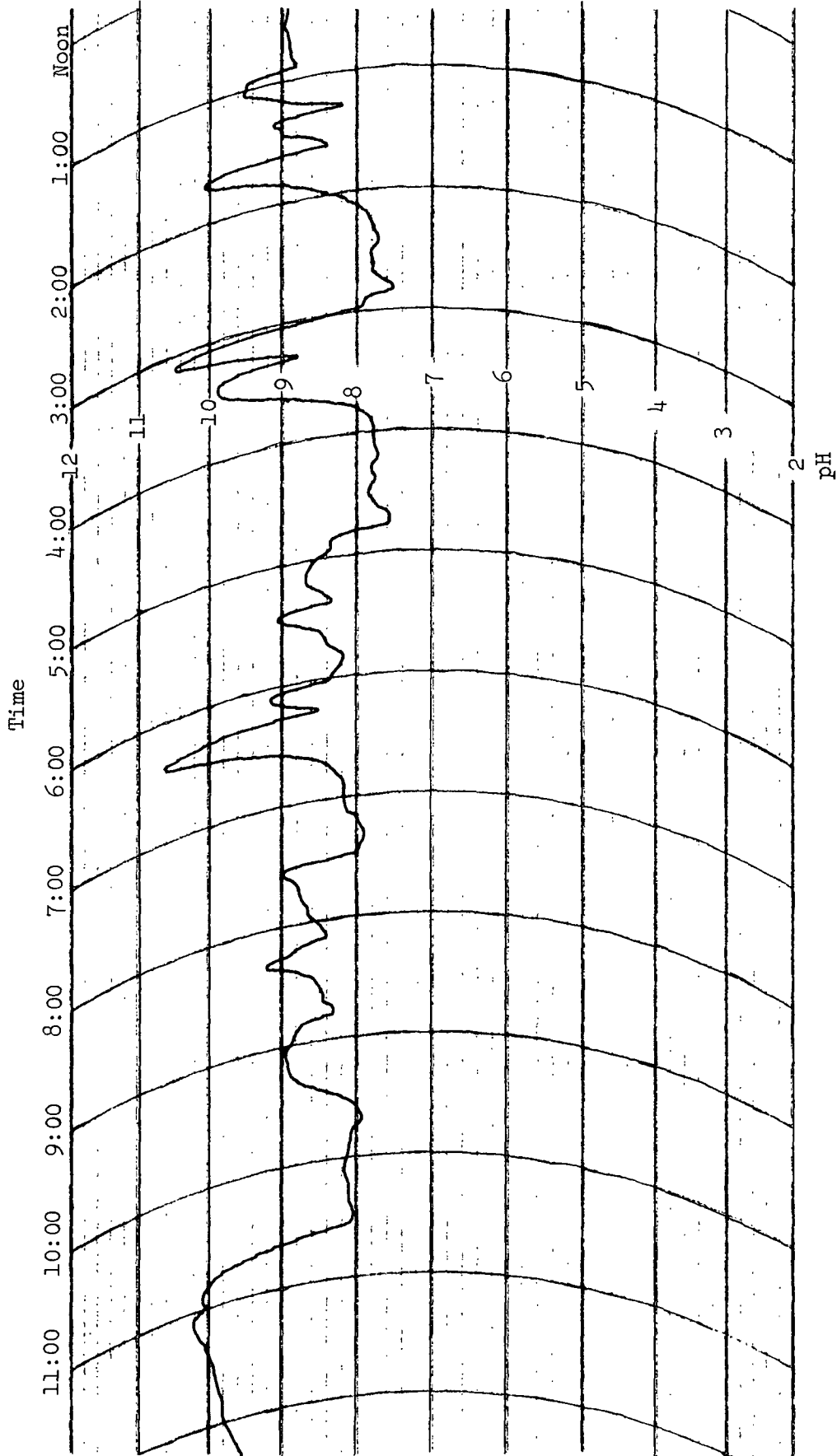


Figure 3. Clarifier Study - Mosinee Paper Corporation  
pH of Influent to IPC Clarifier

TABLE X  
CLARIFIER STUDY - MOSINEE PAPER CORPORATION  
COMPARISON OF SAMPLERS AND TIMING - TRIAL NO. 1

| No. | PH      |         | Mg/l             |         |                        |         | Pt-Co Color |         |
|-----|---------|---------|------------------|---------|------------------------|---------|-------------|---------|
|     | Special | Regular | Suspended Solids |         | Total BOD <sub>5</sub> |         | Special     | Regular |
|     |         |         | Special          | Regular | Special                | Regular | Special     | Regular |
| 1   | 7.22    | 7.85    | 219              | 189     | 162                    | 190     | 38          | 78      |
| 2   | 7.82    | 8.75    | 182              | 136     | 177                    | 244     | 115         | 130     |
| 3   | 8.05    | 7.73    | 221              | 126     | 130                    | 128     | 119         | 133     |
| 4   | 8.40    | 8.51    | 210              | 199     | 124                    | 158     | 170         | 204     |
| 5   | 7.48    | 8.40    | 257              | 240     | 104                    | 140     | 67          | 168     |
| 6   | 7.35    | 7.61    | 213              | 169     | 98                     | 142     | 45          | 74      |
| 7   | 7.35    | 7.11    | 213              | 198     | 120                    | 88      | 60          | 82      |

Special samples taken with CVE Sampler at 15-minute intervals.

Regular samples taken with Sigmamotor Sampler (24/24 hours - Composited in sets of 12).

TABLE XI  
CLARIFIER STUDY - MOSINEE PAPER CORPORATION  
COMPARISON OF SAMPLERS AND TIMING - TRIAL NO. 2

| Sample No. | PH      |         | Total BOD <sub>5</sub> , mg/l |         | Soluble BOD <sub>5</sub> , mg/l |         | Color (Pt-Co Units) |         |
|------------|---------|---------|-------------------------------|---------|---------------------------------|---------|---------------------|---------|
|            | Special | Regular | Special                       | Regular | Special                         | Regular | Special             | Regular |
| AA-1       | 8.08    | 8.09    | 197                           | 180     | 162                             | 148     | 268                 | 273     |
| AA-2       | 7.41    | 7.22    | 174                           | 173     | 120                             | 124     | 95                  | 145     |
| BB-1       | 4.41    | 4.67    | 128                           | 122     | 116                             | 107     | 42                  | 45      |
| BB-2       | 3.69    | 3.61    | 94                            | 86      | 90                              | 83      | 65                  | 52      |
| AA-3       | 7.61    | 7.40    | 183                           | 165     | 142                             | 135     | 120                 | 122     |
| AA-4       | 7.19    | 7.20    | 140                           | 139     | 110                             | 104     | 50                  | 68      |
| BB-3       | 3.99    | 3.96    | 111                           | 106     | 101                             | 98      | 22                  | 55      |
| BB-4       | 3.30    | 3.32    | 95                            | 89      | 90                              | 86      | 50                  | 70      |

Samples: (All Composited on 12-hour Basis)

A and B - With Sigmamotor Samplers at 30-minute intervals on Influent and Effluent

AA - With CVE Sampler at 10-minute intervals on Influent

BB - With Polystatic Pump at 9 Ml/minute continuously on Effluent

No. 1 & 3 - 7:00 AM to 7:00 PM

No. 2 & 4 - 7:00 PM to 7:00 AM

Mill - 7:30 AM Composite



Samples of the mill clarifier influent and effluent were taken at 7:30 a.m. daily by the mill staff and analyzed by both mill and IPC personnel.

Prior to analysis, all samples for BOD<sub>5</sub> were stored at 4°C, others were maintained at room temperature, but not allowed to freeze.

#### TESTING SCHEDULE

In order to establish a comparison between the mill and IPC clarifiers, the first trial was the operation of the pilot unit under conditions as near those of mill as practical. This "base line" was developed by operating the small unit with Hercofloc 812.3 at 0.75 mg/liter and with a waste flow of 3 gpm. If a 10% sludge withdraw could be maintained, the clarifier overflow would be 400 gsfd, approximately one-half of that of the larger unit.

Since we were not attempting to develop optimum clarification at high hydraulic loadings, but merely to study the increased removal of BOD<sub>5</sub> components from the waste stream while operating under different chemical treatment conditions, it was not necessary to show that we could duplicate mill operation. Rather, it was more important to show that, while operating under our planned trial conditions, we did not achieve the increased removal merely through the design of the system. Then, if later trials with the additional chemical treatment resulted in increased BOD<sub>5</sub> removal, over that realized in the mill clarifier during the same test period, this increase should be attributable to the chemical treatment.

Following the development of this base line, other chemical treatment schemes based on the laboratory studies were also tested:

- A. Base line using 0.75 mg/liter Hercofloc 812.3
- B. Alum at 200 mg/liter plus 0.75 mg/liter Hercofloc 812.3

- C. Ferric chloride (100 mg  $\text{Fe}^{+3}/\text{l}$ ) plus Hercofloc at 0.75 mg/liter
- D. Ferric sulfate (50-100 mg/l  $\text{Fe}^{+3}$ ) without polymer
- E. A second base-line study with 0.75 mg/liter Hercofloc 812.3
- F. Sulfuric acid for pH adjustment alone
- G. Sulfuric acid for pH adjustment plus 0.75 mg/liter Hercofloc 812.3
- H. Ferrous sulfate (100 mg  $\text{Fe}^{+2}/\text{l}$ ) plus 0.75 mg/liter Hercofloc 812.3.

Original planning was to have tests of two weeks duration. Unfortunately, we encountered several periods of problem/solution development early in the trial period, which delayed the program and resulted in shortened test periods (F, G, H) near the end of the study. Also, throughout almost the entire trial period, the mill was on a reduced work week (4 days) which limited the number of samples per week.

#### RESULTS AND DISCUSSION

In our first attempt to establish the base line, we immediately encountered three problems. The submersible, centrifugal sump pump installed in the waste trench had a small (1 inch) inlet hole in the baseplate and due to the high fluid velocity in the waste trench, an "aspirator" effect developed across the inlet when the pump was vertically mounted and we were unable to pump sufficient waste. Mounting the pump at a  $90^\circ$  angle pointed downstream increased the aspiration effect, while mounting it pointed upstream resulted in rapid plugging of the inlet hole with pitch and debris not removed by the bar or travelling screens. This problem also extended to the centrifugal pump used for feed control.

Due to the high solids content of the Mosinee waste, a centrifugal pump was the only available pump that was considered suitable for control of the flow at the 3 gpm rate. A one-half-inch Eastern centrifugal pump was, therefore, used

to control the rate of waste fed to the clarifier unit and at first the rate was controlled with a 1/2-inch valve on the pressure side of the pump. This rapidly plugged with pitch and fibers and resulted in erratic flow patterns.

The third problem developed in the gravity sludge removal system. Settling of the high solids content of the Mosinee waste rapidly overwhelmed the available space in the clarifier and resulted in solids carryover, even in the absence of chemical agents other than the Hercofloc 812.3.

In order to reduce these problems:

- 1) A conical screen (20 mesh), 18 inches long by 7 inches in diameter, was installed on the submersible pump. When installed with the apex of the cone mounted upstream, the pumping action was excellent and the cone was somewhat self-cleaning. When mounted with downstream orientation, which should increase the self-cleaning aspect of the cone shape, the flow was reduced below acceptable levels. Periodic cleaning, with high pressure water, was required to maintain an adequate supply to the system.

- 2) The centrifugal feed pump was fitted with a smooth-bore orifice plate for flow control and with periodic cleaning this provided better flow control.

- 3) A multihead tubing pump (Brosites) was installed in place of the gravity system for sludge removal.

Although none of these worked perfectly and problems were encountered from time to time, failure of the system could be minimized by careful cleaning and operation procedures.

Data for the trials with the various flocculating agents and for the base lines are summarized in Table 12, the more detailed analysis of the individual samples are in the Appendix (Figures 4-13; Tables 14-18).

TABLE XII

CLARIFIER STUDY - MOSINEE PAPER CORPORATION  
AVERAGE EFFLUENT QUALITY AND REMOVAL  
VALUES FOR IPC AND MILL UNITS

| Clarifier Unit   | Effluent Quality       |                  |               |                  | % Removal        |         |       |    |
|--|------------------------|------------------|---------------|------------------|------------------|---------|-------|----|
|  | Suspended solids, mg/l | BOD <sub>5</sub> |               | Suspended solids | BOD <sub>5</sub> |         | Color |    |
|  |                        | Total, mg/l      | Soluble, mg/l |                  | Total            | Soluble |       |    |
| A. Both units with Hercofloc 812.3 at 0.75 mg/l:   |                        |                  |               |                  |                  |         |       |    |
| IPC  | 86                     | 146              | 129           | 76               | 70               | 17      | 14    | 28 |
| Mill   | 58                     | 137              | 129           | 74               | 80               | 14      | 13    | 28 |
| B. IPC unit with 200 mg/l alum + Hercofloc 812.3 at 0.75 mg/l -- mill using Hercofloc 812.3 at 0.75 mg/l:  |                        |                  |               |                  |                  |         |       |    |
| IPC  | 22                     | 96               | 92            | 21               | 88               | 19      | 18    | 81 |
| Mill   | 59                     | 98               | 85            | 89               | 72               | 18      | 17    | 46 |
| C. IPC unit with ferric chloride (100 mg/l Fe <sup>+3</sup> ) and Hercofloc -- mill with Hercofloc only:   |                        |                  |               |                  |                  |         |       |    |
| IPC  | 16                     | 89               | 80            | 80               | 90               | 34      | 23    | 71 |
| Mill   | 62                     | 111              | 91            | 102              | 72               | 22      | 8     | 30 |
| D. IPC unit with ferric sulfate (50-100 mg/l Fe <sup>+3</sup> ) and Hercofloc -- mill with Hercofloc only: |                        |                  |               |                  |                  |         |       |    |
| IPC  | 44                     | 105              | 94            | 48               | 78               | 34      | 24    | 68 |
| Mill   | 66                     | 133              | 116           | 156              | 66               | 26      | 10    | 2  |
| E. Second base line with both units using Hercofloc 812.3 at 0.75 mg/l:                                    |                        |                  |               |                  |                  |         |       |    |
| IPC  | 40                     | 137              | 118           | 157              | 80               | 13      | 8     | 7  |
| Mill   | 56                     | 116              | 103           | 118              | 78               | 29      | 10    | 13 |

E, G, & H. Insufficient data to provide good comparisons.

The base-line operations, both the initial and final trials (A & E), with 0.75 mg/liter Hercofloc 812.3 indicated that the IPC unit was equal to or slightly less efficient than the mill clarifiers in removing suspended solids, soluble BOD<sub>5</sub> and color. The reason for the marked difference noted in the total BOD<sub>5</sub> reductions for the mill clarifier during the second base-line trial are unknown, but there had been a slow, progressive increase in the mill clarifier efficiency for BOD<sub>5</sub> removal throughout the study period, i.e., from 14 to 35% between Trials A and H. This was not readily traceable to changes in the concentration of BOD<sub>5</sub> going to the clarifiers during this period, since these were on the average 161, 120, 138, 181, 161, 211, 114, and 178 mg/liter for Trials A to H, respectively.

Alum with polymer and without pH adjustment, as predicted by the laboratory trials, did not increase the removal of the BOD<sub>5</sub> components, but did markedly increase the efficiency for suspended solids and color removals.

The ferric ion, both as chloride and sulfate salts, was an excellent flocculating agent for removing BOD<sub>5</sub>, the ferric chloride being more effective for suspended solids. The latter could have been due to the development of final pH levels, with the three chloride ions, nearer to the optimum for the Fe<sup>+3</sup> produced flocs (pH 4-5).

Ferrous ions, at the level of 100 mg soluble Fe<sup>+2</sup>/l, appeared to reduce the efficiency of the system, even with the addition of polymer during the short trial made on the Mosinee waste. While this level of ion was below that which would be theoretically required by the Schulze-Hardy rule, which states that the concentration of the counterion required to collapse the double layer and produce rapid flocculation is inversely proportional to the 6th power of the valence, it was the highest level practical during our trials due to the low solubility

of the commercial grade ferrous sulfate. Based on the effectiveness of the ferric ion at 100 mg/liter, the level of ferrous ion theoretically required would have been on the order of approximately 1200 mg/liter.

The use of sulfuric acid to decrease the pH level and to remove some of the components from the waste stream was one process under consideration by the mill for use in the large clarifiers. A trial was, therefore, designed to test this procedure in the small system, but due to the mechanical difficulties we had encountered earlier in the trial period, only a short period was available near the end of the study. The data were insufficient to provide reliable comparison with mill operation, but laboratory studies have shown that pH reduction to below 4.5 resulted in marked reduction in suspended solids and total BOD<sub>5</sub>, with little effect on the soluble BOD<sub>5</sub> level in the effluent.

These trials, with ferric, ferrous and aluminum ions, and especially with the iron salts, have shown that a 25-30% increase in clarifier efficiency could be attained with the Mosinee waste. The sulfate form might be preferable to the chloride, from the standpoint of corrosion, particularly if the sludge were ultimately to be burned.

### PRELIMINARY EVALUATION OF COMPARATIVE ECONOMICS

The field studies at the Mosinee mill as described in this report confirm the capability of clarifiers operating at pulp and paper mills to accomplish appreciable and possibly important reductions in the BOD<sub>5</sub> of the dilute spent liquors and wash waters being processed. The practical significance of these findings will be largely dependent upon development of an adequate understanding of the mechanisms involved in removing BOD<sub>5</sub> in the clarifier, such that the reactions can be advanced and controlled reliably at reasonable cost, and preferably at cost levels improving upon BOD reduction by other methods. These continuing studies of the mechanisms of soluble BOD<sub>5</sub> removal are advancing in studies to be reviewed in following reports. However, it becomes increasingly necessary to determine the economic significance of the work so far completed in terms of whether further studies can be economically advantageous, such as to justify further expenditures of research man power and funding toward development of practical design and operating parameters.

The studies reviewed in this report were not originally designed to develop economic criteria. Practical observations and indicators arising from actual field experience do point to probable areas for improving the degree of BOD removal.

One of the principal, practical observations in the field study at this mill related to visual as well as analytical and other evidence that heavy slugs and spills of strong, digester room spent liquors and washes, some of which were of several hours duration, adversely affected clarifier performance. A single program of grab sample collection was undertaken to help indicate the sources of strong process waters. The analytical data from study of that one set of grab samples are summarized in Table VII, previously described, and showed the relative strength of the various soluble materials contained in these samples. The

significance of that data was further developed by developing the estimate of daily loadings which might be expected to prevail from each individual process flow. The mill staff provided estimates of the probable daily flows from each source.

These estimated levels of loading are shown in Table XIII, with the obvious qualifications to be expected in use of data from single grab samples and estimated rather than carefully metered flows. Some degree of reliability (or of unreliability of the estimations in each category) for the grab sample of the clarifier influent loading can be determined from comparison with the averages for 28 to 29 samples carefully collected in 24-hour composites of the clarifier influents over the period of the entire field study program at this mill.

The data in Table XIII indicate that a large proportion of the suspended solids going to the clarifier derive from the paper machine sewer and, although the data are less conclusive for the COD components, we would expect that the fiber and fines losses in the paper machine white water probably also are the source of much of the COD.

Total BOD<sub>5</sub>, soluble BOD<sub>5</sub>, total organic carbon and color apparently come chiefly from the pulp mill sewer, soda recovery sewer and the high density sewer. These data would seem to indicate that at least 50% and as much as 90% or more of the BOD<sub>5</sub> loading to the clarifier at this mill derives from just two of the several sewers. The pulp mill sewer and the soda recovery sewer together account for less than 1/10 of the total flow, and the obvious prevalence of heavy slugs and spills at times could indicate that even smaller volumes may be carrying a very large proportion of the total load.



TABLE XIII  
PRELIMINARY ESTIMATION OF SEWER LOADINGS BY VARIOUS MOSINEE PROCESS WATERS  
(Grab Samples from First Trial - Data from Table VII)

|                              | Gal/Day<br>Volume<br>Estimates<br>by Mosinee | Total (Lbs/Day) |                  | Soluble (Lbs/Day) |                  | (Unit Lb/Day)<br>Color | Suspended Solids |        |
|------------------------------|--|-----------------|------------------|-------------------|------------------|------------------------|------------------|--------|
|                              |  | COD             | BOD <sub>5</sub> | TOC               | BOD <sub>5</sub> |                        | 0.45 um          | um 5   |
| High Density Sewer           | 1,500,000                                    | 6,922           | 1,978            | 1,724             | 1,803            | 11,516                 | 1,503            | 326    |
| Pulp Mill Sewer              | 600,000                                      | 22,331          | 8,131            | 5,502             | 5,378            | 24,431                 | 5,011            | 356    |
| Foul Evap. Cond.             | 300,000                                      | 2,181           | 1,908            | 493               | 1,562            | 250                    | 55               | 85     |
| Soda Recovery Sewer          | 280,000                                      | 19,459          | 9,725            | 4,853             | 8,657            | 9,814                  | 1,487            | 430    |
| Digester Blow Down Cond.     | 70,000                                       | 868             | 563              | 227               | 568              | 328                    | 1                | 9      |
| Digester Room Sewer          | 50,000                                       | 1,240           | 265              | 309               | 323              | 1,169                  | 98               | 41     |
| 5th Stage Brown Stock Washer | 35,000                                       | 1,421           | 394              | 410               | 338              | 1,212                  | 38               | 28     |
| Sub Total                    | 2,835,000                                    | 54,422          | 22,964           | 13,518            | 18,629           | 48,723                 | 8,193            | 1,275  |
| Paper Machine Sewer          | Est. (IPC)<br>10,000,000                     | -               | -                | -                 | -                | -                      | 13,529           | 10,857 |
| Sub Total                    | 12,835,000                                   | -               | -                | -                 | -                | -                      | 21,722           | 12,132 |
| Clarifier Influent           | 14,500,000                                   |                 |                  |                   |                  |                        |                  |        |
| "                            | Single Grab                                  | 111,322         | 21,901           | 8,954             | 12,826           | 11,132                 | 121,580          | 83,072 |
| "                            | 24 hr composites Average*                    | -               | 17,787           | -                 | 13,784           | 23,354                 | -                | 29,767 |

\*Average of 28 to 29 samples

Internal measures for environmental quality control at many mills are showing obvious advantage from development of comprehensive programs for reducing the flow of the stronger wash waters, and particularly of spills through installation of spill collection systems to return the stronger flows to the pulp mill recovery system. It is understood that a comprehensive program of internal quality control is under way at Mosinee and presumably much improvement is in prospect.

Although evidence of a principal area of improvement in internal environmental quality control is an obvious result from study of Table XIII, the attainment of objectives for this project in terms of improving BOD removal in the clarifier may also be anticipated. Heavy discharges and spills of lignin organics from the pulping operations are well recognized as disruptive to performance of clarifiers. These materials act as dispersants and inhibitors to effective flocculation and sedimentation in clarifiers. Effective reductions of spills and wastage of these strong lignin flows should greatly enhance the capability of the clarifier to promote the reactions resulting in removal of the BOD within the clarifier and greatly reduce the costs of effective clarification in categories other than BOD removal.

It is, therefore, logical to expect that reagent costs to promote the BOD removal and clarification reactions developed in this study would be substantially less with better internal practices of effluent quality control than were prevailing during the course of this study. It is also likely that the quantities of BOD remaining in a well controlled system would be more effectively absorbed and removed with the flocs developed under conditions better adapted to effective clarification (i.e., with lowered levels of dispersant activity).

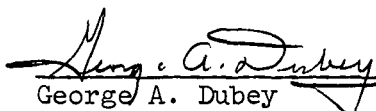
A study to better assess these capabilities for improving the performance and the economics of BOD removal is under way as a result of studying the data available in Tables VII and XI. This study will utilize the jar test procedure to determine the clarification characteristics of the individual sewer streams going to the Mosinee clarifier, as well as mixtures of these streams to measure the effect of each on the efficiency of clarification.


It may then be possible to develop cost data evaluations on a more exact and better controlled data base than are available from the data developed in this first field study.

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APPENDIX I

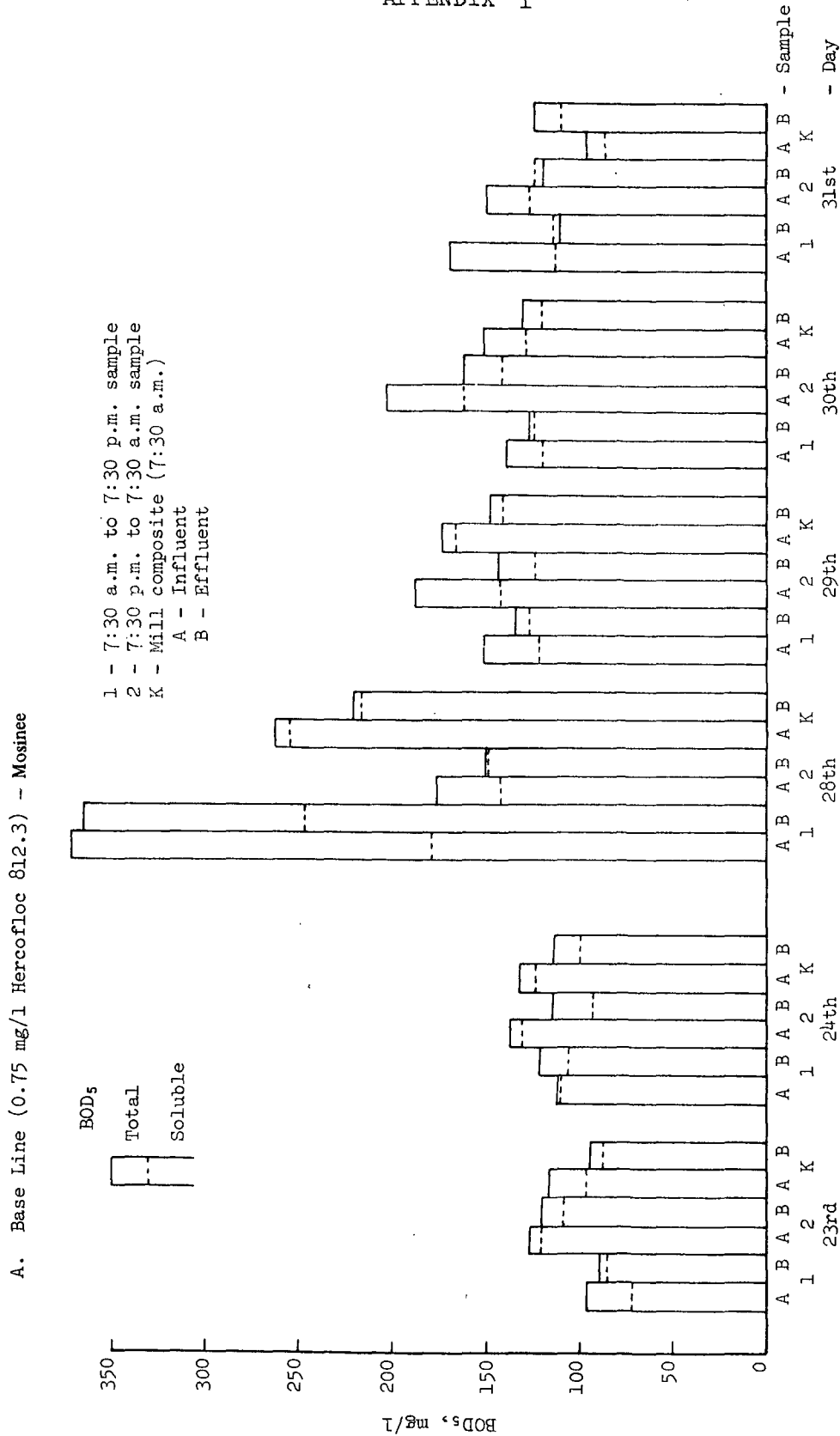


Figure 4. BOD<sub>5</sub> Reduction During Clarification

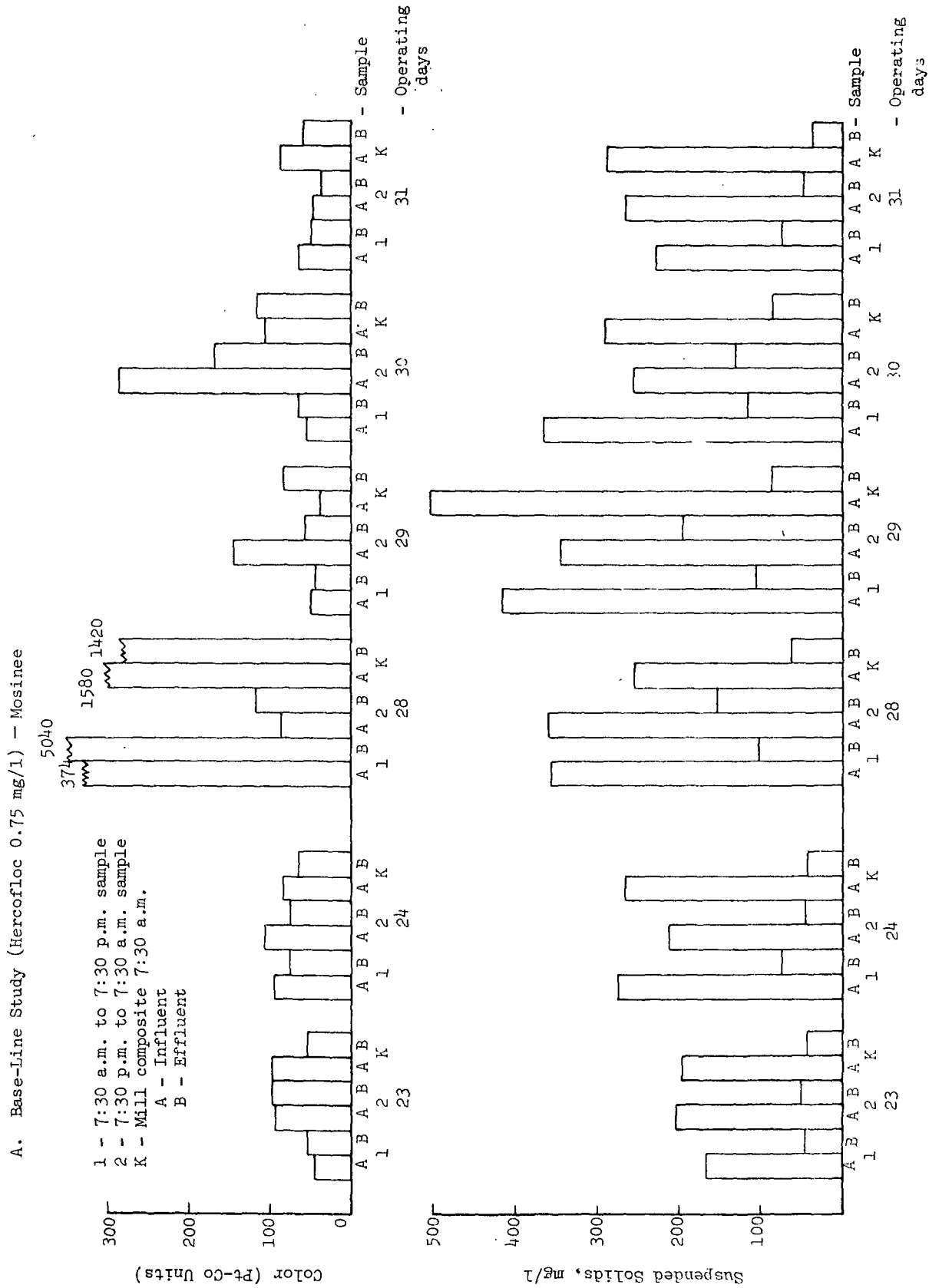


Figure 5. Color and Suspended Solids Reduction During Clarification

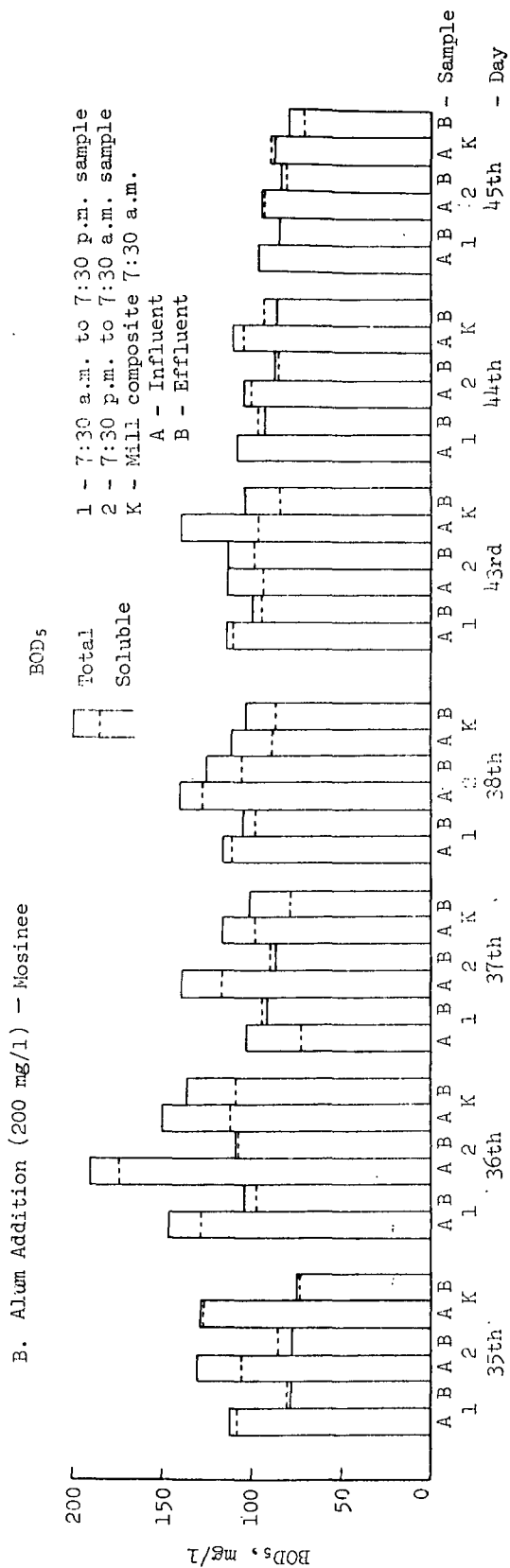


Figure 6. BOD<sub>5</sub> Reduction During Clarification

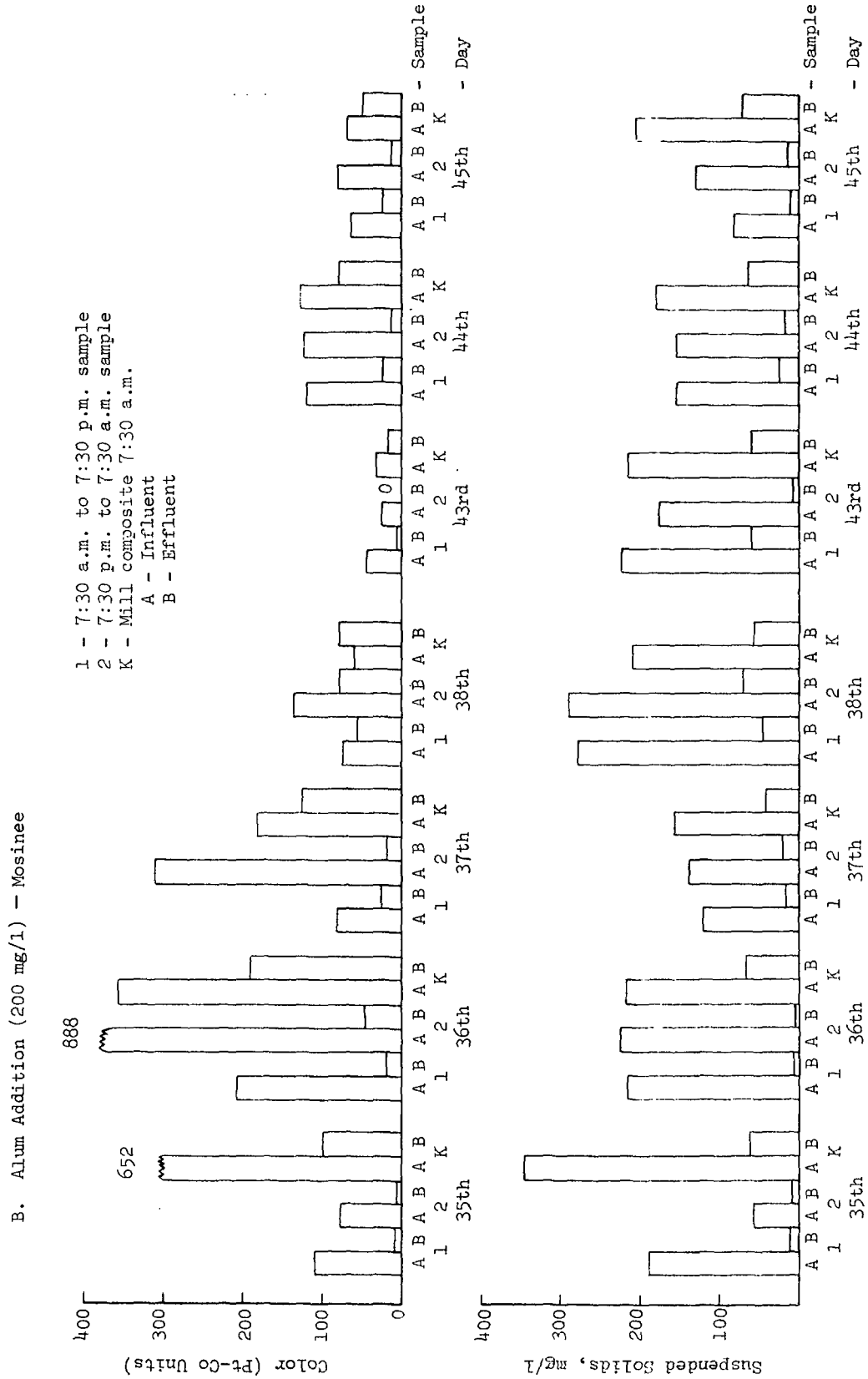


Figure 7. Color and Suspended Solids Reduction During Clarification



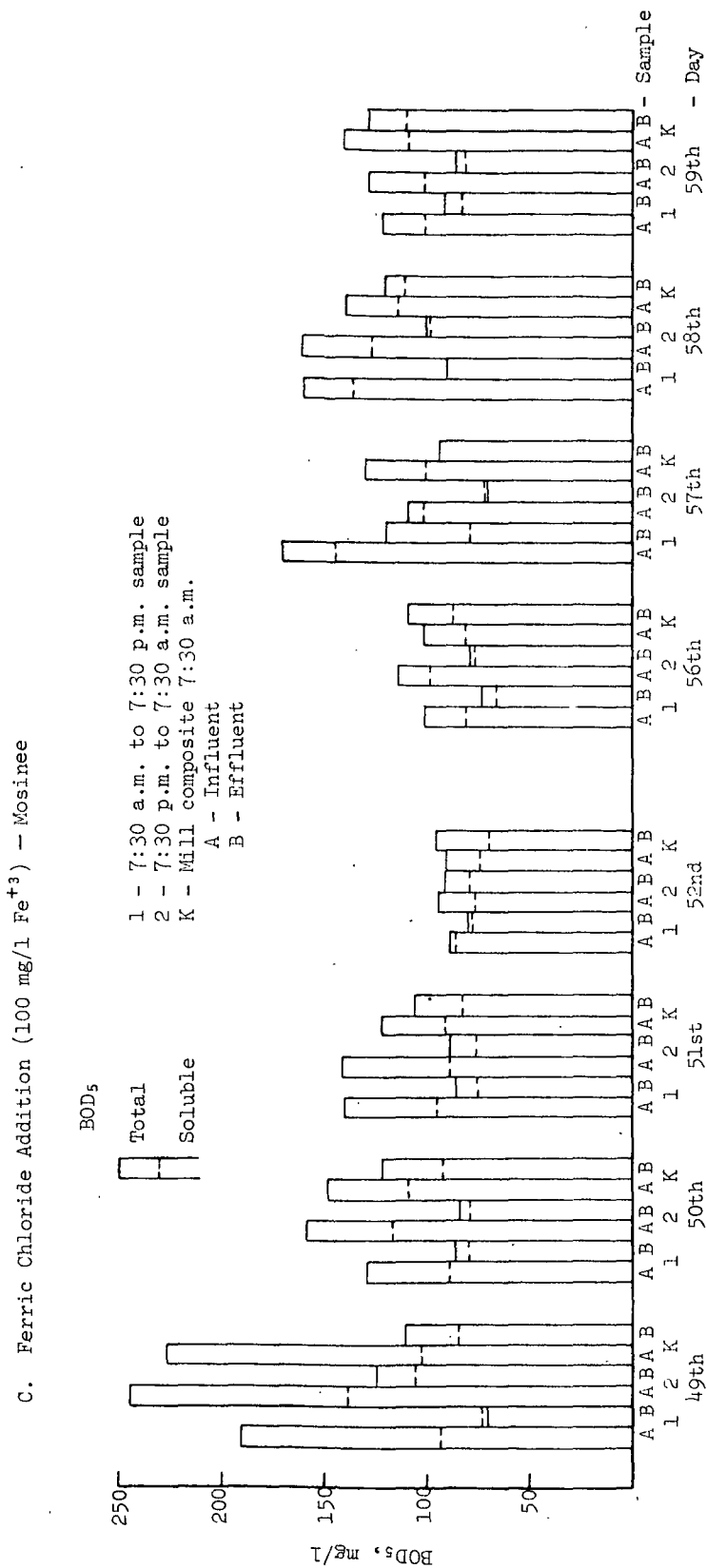


Figure 8. BOD<sub>5</sub> Reduction During Clarification

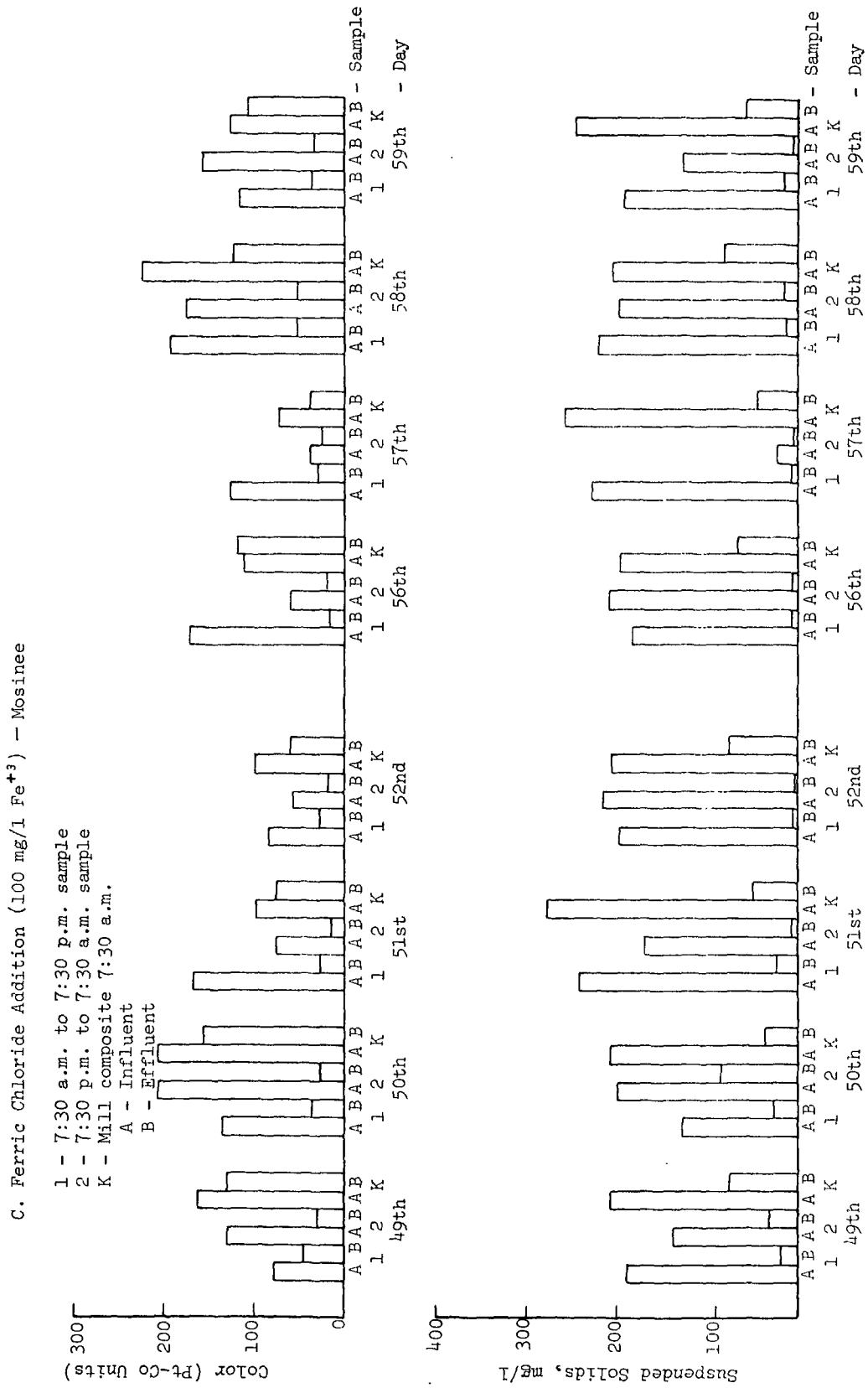


Figure 9. Color and Suspended Solids Reduction During Clarification

E. Base Line (0.75 mg/l Hercofloc 812.3)

D. Ferric Sulfate Addition - Mosinee  
(100 mg Fe<sub>2</sub>S<sub>3</sub>/l)

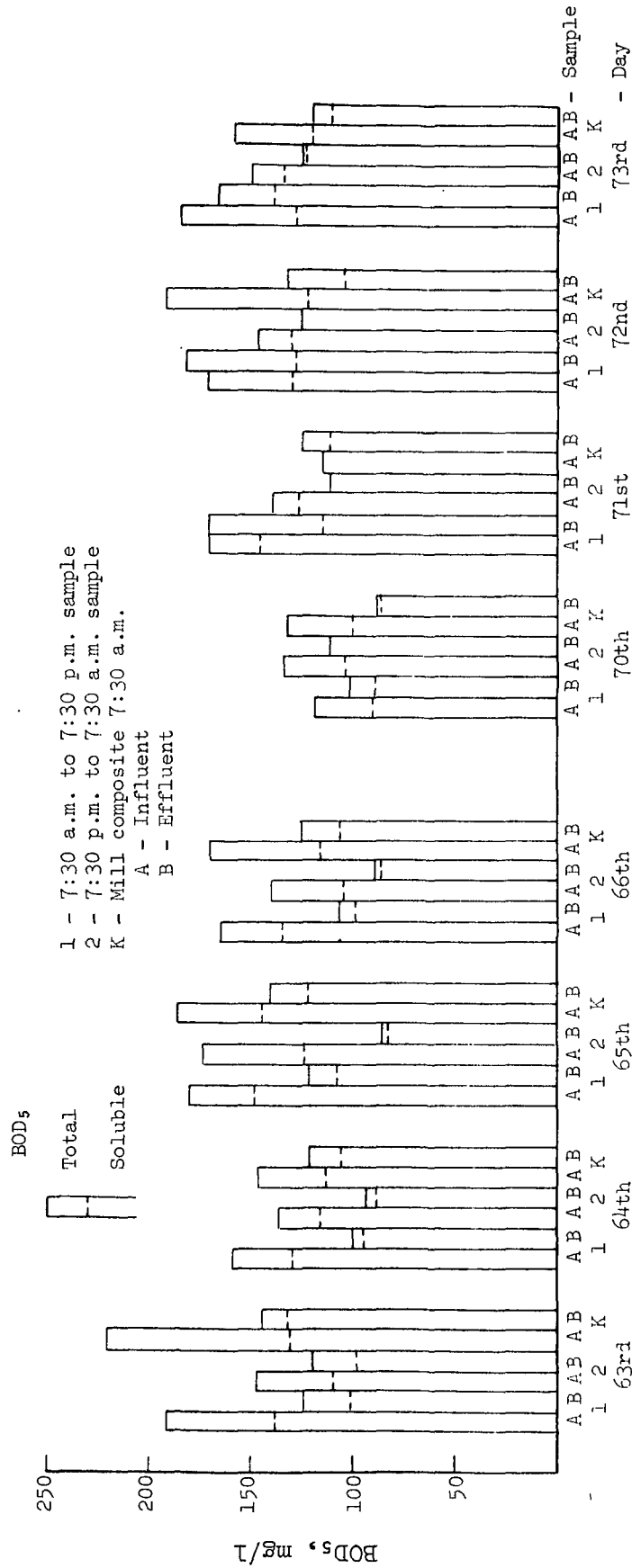


Figure 10. BOD<sub>5</sub> Reduction During Clarification

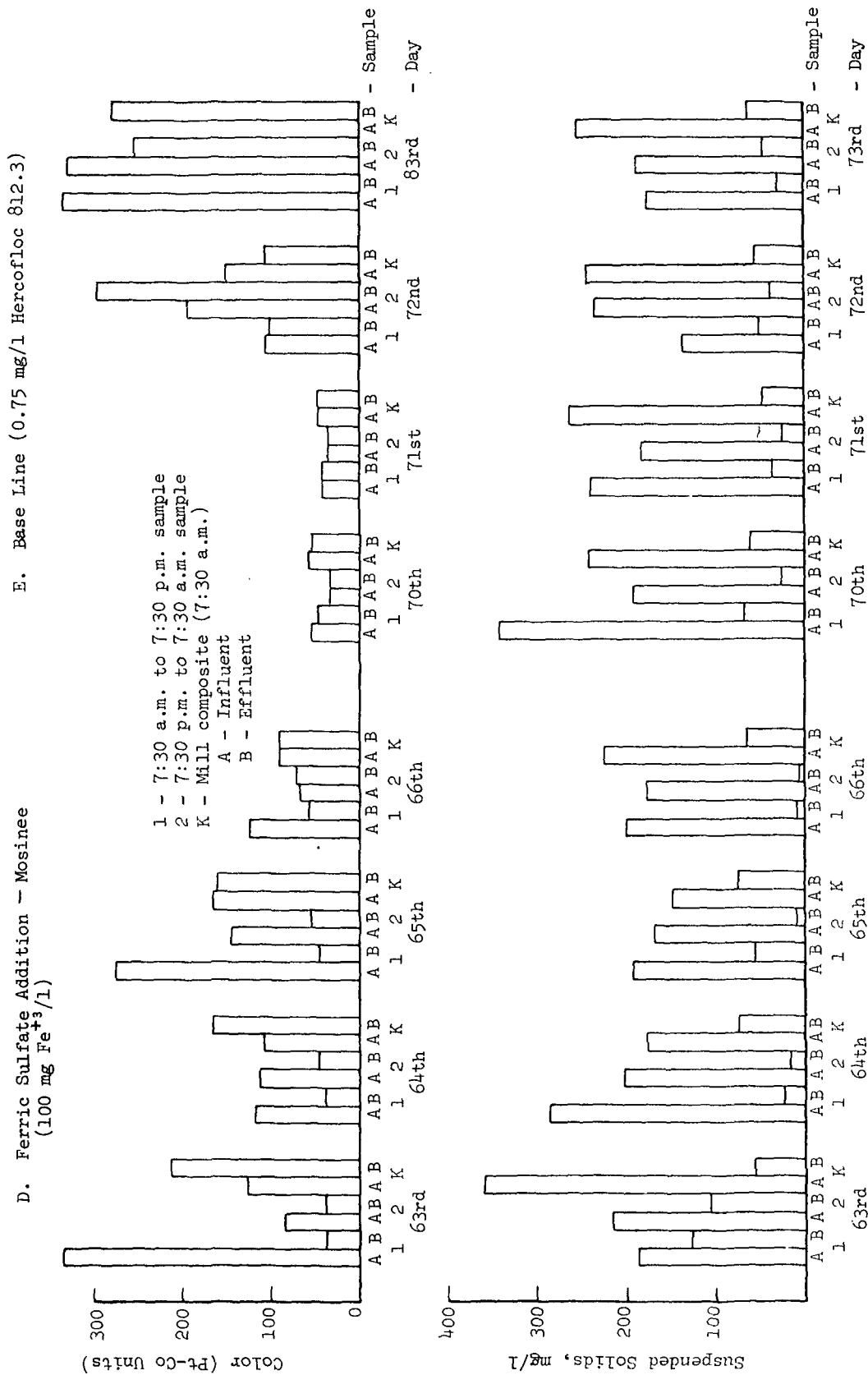


Figure 11. Color and Suspended Solids Reduction During Clarification

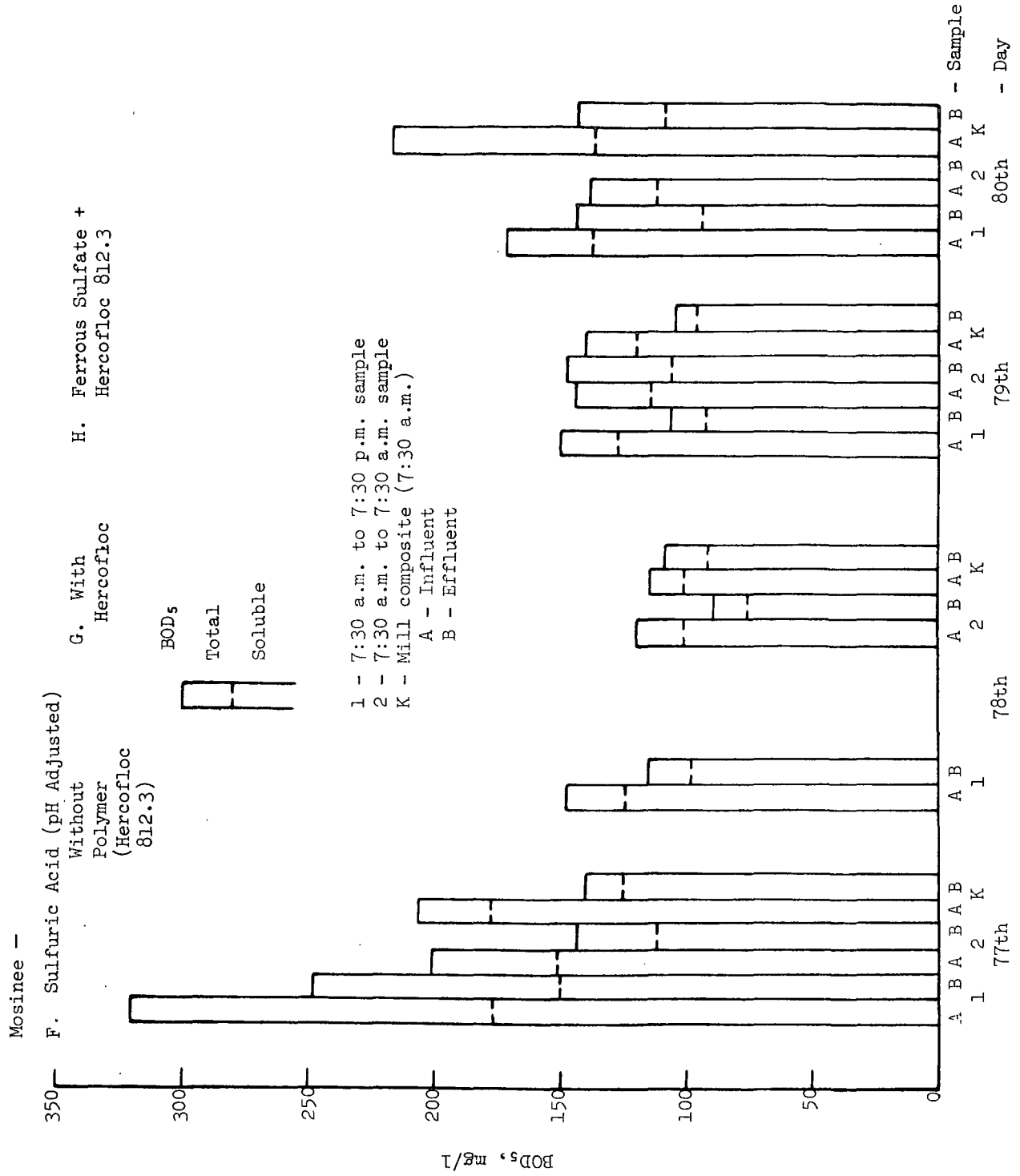


Figure 12. BOD<sub>5</sub> Reduction During Clarification

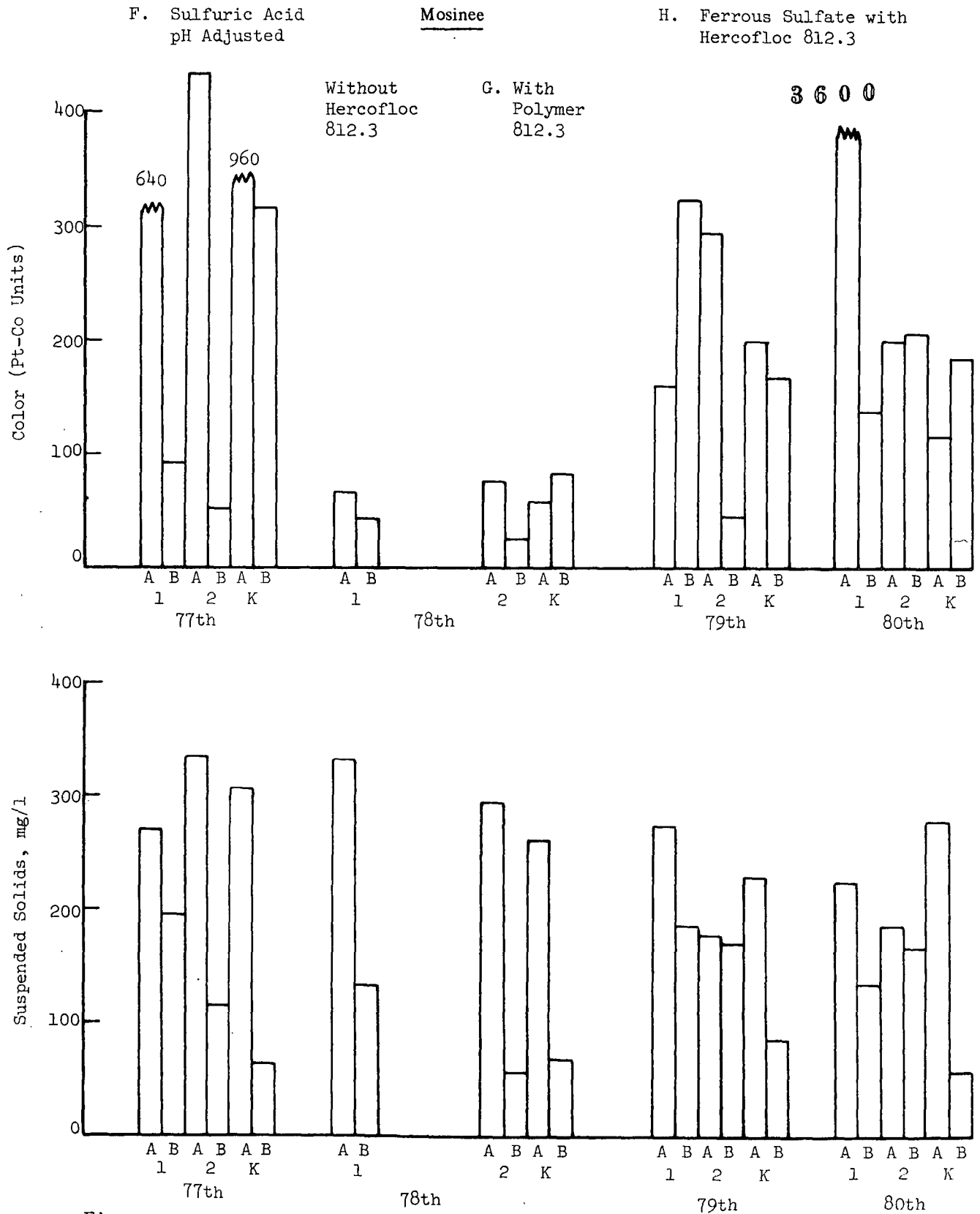


Figure 13. Color and Suspended Solids Reduction During Clarification

TABLE XIV  
CLARIFIER STUDY - MOSINEE PAPER CORPORATION

| Date  | Day | Composite | Influent (A) |                    |  | Effluent (B)   |      |                    | % Reduction                              |                |       |         |       |       |        |
|---|-----|-----------|--------------|--------------------|--|----------------|------|--------------------|--|----------------|-------|---------|-------|-------|--------|
|   |     |           | pH           | Sus. Sol.,<br>mg/l | BOD <sub>5</sub> , mg/l<br>Total Soluble | Color<br>Units | pH   | Sus. Sol.,<br>mg/l | BOD <sub>5</sub> , mg/l<br>Total Soluble | Color<br>Units | Total | Soluble | Color |       |        |
| Due to Mechanical Difficulties - No "Sets of Samples" were taken from 1/15 - 2/5/75 (1st to 22nd day) |     |           |              |                    |  |                |      |                    |  |                |       |         |       |       |        |
| 2/6   | 23  | 1         | 7.70         | 167                | 96                                       | 72             | 45   | 7.59               | 45                                       | 85             | 88    | 52      | 11.4  | -22.2 | -13.5  |
|   |     | 2         | 7.62         | 202                | 127                                      | 120            | 93   | 7.90               | 50                                       | 120            | 108   | 97      | 5.5   | 10.0  | -4.1   |
|   |     | M         | 7.82         | 196                | 116                                      | 96             | 97   | 7.61               | 41                                       | 94             | 87    | 52      | 19.0  | 9.4   | 46.4   |
|   |     | Mill*     | -            | 218                | 90                                       | -              | -    | -                  | 56                                       | 51             | -     | -       | 43.3  | -     | -      |
| 2/7   | 24  | 1         | 7.90         | 273                | 111                                      | 110            | 93   | 7.91               | 74                                       | 121            | 106   | 74      | -9.0  | 3.6   | 20.4   |
|   |     | 2         | 7.81         | 211                | 137                                      | 131            | 103  | 7.82               | 45                                       | 113            | 92    | 74      | 17.5  | 29.8  | 28.2   |
|   |     | M         | 7.52         | 266                | 132                                      | 123            | 82   | 7.61               | 44                                       | 113            | 99    | 63      | 14.4  | 19.5  | 23.2   |
|   |     | Mill*     | -            | 260                | 84                                       | -              | -    | -                  | 56                                       | 63             | -     | -       | 25.0  | -     | -      |
| 2/11  | 28  | 1         | 7.60         | 358                | 372                                      | 179            | 374  | 9.73               | 101                                      | 365            | 246   | 5040    | -1.9  | -37.4 | -124.7 |
|   |     | 2         | 7.50         | 359                | 177                                      | 142            | 86   | 8.40               | 153                                      | 149            | 150   | 118     | 15.8  | -5.6  | -37.2  |
|   |     | M         | 9.20         | 257                | 262                                      | 254            | 1580 | 9.09               | 53                                       | 222            | 217   | 1420    | 15.3  | 14.6  | 10.1   |
|   |     | Mill*     | -            | 249                | 249                                      | -              | -    | -                  | 71                                       | 195            | -     | -       | 21.7  | -     | -      |
| 2/12  | 29  | 1         | 7.39         | 416                | 152                                      | 122            | 50   | 7.40               | 106                                      | 134            | 127   | 45      | 11.8  | -4.1  | 10.0   |
|   |     | 2         | 7.70         | 344                | 188                                      | 142            | 144  | 6.88               | 97                                       | 143            | 124   | 56      | 23.9  | 12.7  | 61.1   |
|   |     | M         | 8.40         | 502                | 174                                      | 166            | 38   | 7.59               | 88                                       | 141            | 144   | 81      | 82.5  | 19.0  | -53.1  |
|   |     | Mill*     | -            | 338                | 141                                      | -              | -    | -                  | 66                                       | 114            | -     | -       | 19.1  | -     | -      |
| 2/13  | 30  | 1         | 8.53         | 364                | 138                                      | 120            | 56   | 8.29               | 114                                      | 124            | 126   | 63      | 10.1  | -5.0  | -12.5  |
|   |     | 2         | 8.69         | 256                | 204                                      | 162            | 284  | 8.38               | 131                                      | 162            | 142   | 168     | 20.6  | 12.3  | 40.8   |
|   |     | M         | 8.21         | 290                | 152                                      | 129            | 104  | 7.89               | 85                                       | 130            | 120   | 115     | 70.5  | 7.0   | 10.6   |
|   |     | Mill*     | -            | 160                | 111                                      | -              | -    | -                  | 73                                       | 108            | -     | -       | 2.7   | -     | -      |
| 2/14  | 31  | 1         | 8.40         | 228                | 170                                      | 114            | 63   | 8.12               | 73                                       | 111            | 114   | 49      | 68.0  | 0     | 22.2   |
|   |     | 2         | 8.21         | 266                | 150                                      | 127            | 48   | 8.19               | 49                                       | 120            | 125   | 38      | 81.6  | 0     | 15.6   |
|   |     | M         | 8.12         | 289                | 128                                      | 97             | 86   | 7.70               | 37                                       | 124            | 110   | 59      | 87.2  | 2.9   | 31.4   |
|   |     | Mill*     | -            | 210                | 99                                       | -              | -    | -                  | 57                                       | 75             | -     | -       | 24.2  | -     | -      |

Composites

A1 - From 7:30 AM to 7:30 PM

A2 - From 7:30 PM to 7:30 AM

B1) - 2 hours after A's to

)  
B2) allow for holding time

M - 24-hour mill composite (7:30 AM)  
analyzed in Appleton labs

Mill\* - Same sample (M) analyzed by mill

TABLE XV  
CLARIFIER TRIALS - MOSINEE PAPER CORPORATION

| Date  | Day | Composite | Influent (A) |                    |                            |                                 | Effluent (B) |                    |                            |                                 | % Reduction |                        |               |       |       |
|---|-----|-----------|--------------|--------------------|----------------------------|---------------------------------|--------------|--------------------|----------------------------|---------------------------------|-------------|------------------------|---------------|-------|-------|
|   |     |           | pH           | Sus. Sol.,<br>mg/l | BOD <sub>5</sub> ,<br>mg/l | Total Soluble<br>Color<br>Units | pH           | Sus. Sol.,<br>mg/l | BOD <sub>5</sub> ,<br>mg/l | Total Soluble<br>Color<br>Units | Sus. Sol.   | Total BOD <sub>5</sub> | Soluble Color |       |       |
| B. Alum (200 mg/l) plus Hercofloc 812.3 (0.75 mg/l) |     |           |              |                    |                            |                                 |              |                    |                            |                                 |             |                        |               |       |       |
| 2/18  | 35  | 1         | 9.40         | 188                | 112                        | 108                             | 8.01         | 10                 | 78                         | 80                              | 4           | 94.7                   | 30.4          | 25.9  | 96.3  |
|   |     | 2         | 8.78         | 54                 | 130                        | 106                             | 5.80         | 8                  | 77                         | 85                              | 0           | 85.2                   | 40.8          | 19.8  | 100.0 |
|   |     | M         | 9.29         | 342                | 128                        | 632                             | 8.58         | 61                 | 74                         | 76                              | 97          | 82.2                   | 42.2          | 40.2  | 85.1  |
|   |     | Mill*     | -            | 464                | 81                         | -                               | -            | 64                 | 66                         | -                               | -           | 86.2                   | 18.5          | -     | -     |
| 2/19  | 36  | 1         | 8.51         | 213                | 146                        | 128                             | 7.32         | 4                  | 104                        | 98                              | 19          | 98.1                   | 28.8          | 23.4  | 90.6  |
|   |     | 2         | 9.11         | 222                | 190                        | 888                             | 8.65         | 0.5                | 108                        | 107                             | 41          | 99.9                   | 43.2          | 38.5  | 95.5  |
|   |     | M         | 8.80         | 218                | 150                        | 356                             | 7.72         | 63                 | 136                        | 108                             | 188         | 71.1                   | 9.3           | 3.6   | 47.2  |
|   |     | Mill*     | -            | 234                | 99                         | -                               | -            | 74                 | 69                         | -                               | -           | 68.4                   | 30.3          | -     | -     |
| 2/20  | 37  | 1         | 7.30         | 119                | 103                        | 73                              | 8.55         | 15                 | 92                         | 94                              | 22          | 87.4                   | 10.7          | -28.8 | 72.5  |
|   |     | 2         | 8.11         | 136                | 139                        | 117                             | 6.80         | 18                 | 90                         | 88                              | 15          | 86.8                   | 35.2          | 24.8  | 95.2  |
|   |     | M         | 8.41         | 153                | 116                        | 99                              | 7.78         | 40                 | 102                        | 78                              | 125         | 73.8                   | 12.1          | 21.2  | 26.5  |
|   |     | Mill*     | -            | 216                | 159                        | -                               | -            | 62                 | 135                        | -                               | -           | 71.3                   | 15.1          | -     | -     |
| 2/21  | 38  | 1         | 7.83         | 278                | 116                        | 112                             | 8.19         | 44                 | 104                        | 99                              | 52          | 84.2                   | 10.3          | 11.6  | 26.8  |
|   |     | 2         | 8.08         | 289                | 140                        | 127                             | 7.62         | 70                 | 126                        | 106                             | 74          | 75.8                   | 10.0          | 16.5  | 44.4  |
|   |     | M         | 7.59         | 206                | 112                        | 88                              | 7.39         | 55                 | 104                        | 87                              | 74          | 73.3                   | 7.1           | -1.1  | -32.1 |
|   |     | Mill*     | -            | 204                | 129                        | -                               | -            | 58                 | 108                        | -                               | -           | 71.6                   | 16.3          | -     | -     |
| 2/26  | 43  | 1         | 7.41         | 221                | 114                        | 112                             | 8.84         | 60                 | 100                        | 94                              | 4           | 72.8                   | 12.3          | 16.1  | 90.2  |
|   |     | 2         | 7.58         | 176                | 113                        | 94                              | 8.71         | 7                  | 113                        | 98                              | 0           | 96.0                   | 0             | 4.2   | 100.0 |
|   |     | M         | 7.54         | 215                | 140                        | 96                              | 7.40         | 60                 | 104                        | 84                              | 15          | 72.1                   | 25.7          | 8.3   | 51.6  |
|   |     | Mill*     | -            | 283                | 114                        | -                               | -            | 79                 | 105                        | -                               | -           | 82.2                   | 7.9           | -     | -     |
| 2/27  | 44  | 1         | 7.55         | 155                | 108                        | 108                             | 6.90         | 24                 | 96                         | 92                              | 22          | 84.5                   | 11.1          | 14.8  | 81.7  |
|   |     | 2         | 7.78         | 153                | 100                        | 104                             | 6.88         | 18                 | 87                         | 85                              | 12          | 88.2                   | 13.0          | 18.3  | 90.2  |
|   |     | M         | 7.65         | 180                | 110                        | 104                             | 7.25         | 62                 | 86                         | 93                              | 78          | 65.6                   | 21.8          | 10.6  | 37.8  |
|   |     | Mill*     | -            | 248                | 96                         | -                               | -            | 57                 | 75                         | -                               | -           | 77.0                   | 21.9          | -     | -     |
| 2/28  | 45  | 1         | 7.53         | 82                 | 96                         | 95                              | 6.55         | 9                  | 84                         | 83                              | 22          | 89.0                   | 12.5          | 12.6  | 64.5  |
|   |     | 2         | 7.70         | 130                | 94                         | 80                              | 6.20         | 15                 | 83                         | 80                              | 12          | 88.5                   | 11.7          | 13.0  | 85.0  |
|   |     | M         | 7.32         | 201                | 86                         | 68                              | 7.25         | 71                 | 78                         | 71                              | 49          | 64.7                   | 9.3           | 20.2  | 27.9  |
|   |     | Mill*     | -            | 121                | 108                        | -                               | -            | 30                 | 36                         | -                               | -           | 75.2                   | 66.7          | -     | -     |

Composites

- A1 - From 7:30 AM to 7:30 PM
- A2 - From 7:30 PM to 7:30 AM
- B1) - Two hours after A's to )
- B2) allow for system holding time
- M - 24-hour mill composite analyzed at Appleton labs
- Mill\* - Same as (M) analyzed at mill



TABLE XVI  
CLARIFIER STUDY - MOSINEE PAPER CORPORATION

| Date  | Day | Composite | Influent (A) |                 |                         | Effluent (B)  |             |     | % Reduction     |                         |               |             |           |       |         |
|---|-----|-----------|--------------|-----------------|-------------------------|---------------|-------------|-----|-----------------|-------------------------|---------------|-------------|-----------|-------|---------|
|   |     |           | pH           | Sus. Sol., mg/l | BOD <sub>5</sub> , mg/l | Total Soluble | Color Units | pH  | Sus. Sol., mg/l | BOD <sub>5</sub> , mg/l | Total Soluble | Color Units | Sus. Sol. | Total | Soluble |
| C. Ferric Chloride (100 mg/l Fe <sup>3+</sup> ) plus Hecofloc 812.3 (0.75 mg/l) |     |           |              |                 |                         |               |             |     |                 |                         |               |             |           |       |         |
| 3/4   | 49  | 1         | 7.85         | 189             | 190                     | 93            | 78          | 70  | 72              | 45                      | 90.5          | 63.2        | 22.5      | 42.3  |         |
|   |     | 2         | 8.75         | 136             | 244                     | 130           | 130         | 124 | 106             | 30                      | 77.9          | 49.2        | 23.2      | 76.9  |         |
|   |     | M         | 8.00         | 204             | 226                     | 102           | 162         | 110 | 84              | 140                     | 63.7          | 51.3        | 17.6      | 13.6  |         |
|   |     | Mill*     | -            | 230             | 135                     | -             | -           | 72  | -               | -                       | 71.3          | 46.7        | -         | -     |         |
| 3/5   | 50  | 1         | 7.73         | 126             | 128                     | 88            | 133         | 86  | 78              | 34                      | 77.8          | 32.8        | 11.4      | 74.4  |         |
|   |     | 2         | 8.51         | 199             | 158                     | 117           | 204         | 83  | 78              | 27                      | 58.3          | 47.5        | 33.3      | 86.8  |         |
|   |     | M         | 7.62         | 207             | 148                     | 108           | 204         | 37  | 92              | 156                     | 82.1          | 17.6        | 14.8      | 23.5  |         |
|   |     | Mill*     | -            | 190             | 135                     | -             | -           | 42  | 105             | -                       | 77.9          | 22.2        | -         | -     |         |
| 3/6   | 51  | 1         | 8.40         | 240             | 140                     | 95            | 168         | 86  | 75              | 27                      | 90.8          | 38.6        | 21.0      | 83.9  |         |
|   |     | 2         | 7.61         | 169             | 142                     | 88            | 74          | 6   | 88              | 12                      | 96.4          | 38.0        | 13.6      | 83.8  |         |
|   |     | M         | 7.80         | 276             | 122                     | 91            | 98          | 63  | 82              | 74                      | 76.9          | 13.1        | 9.9       | 24.5  |         |
|   |     | Mill*     | -            | 264             | 107                     | -             | -           | 49  | 77              | -                       | 81.4          | 28.0        | -         | -     |         |
| 3/7   | 52  | 1         | 7.11         | 198             | 88                      | 86            | 82          | 80  | 78              | 27                      | 98.0          | 9.1         | 9.3       | 67.1  |         |
|   |     | 2         | 7.31         | 213             | 94                      | 76            | 56          | 2   | 79              | 19                      | 99.1          | 2.1         | -3.9      | 66.1  |         |
|   |     | M         | 7.22         | 204             | 91                      | 74            | 100         | 75  | 70              | 60                      | 63.2          | -7.0        | 5.7       | 40.0  |         |
|   |     | Mill*     | -            | 224             | 105                     | -             | -           | 65  | 81              | -                       | 71.0          | 22.8        | -         | -     |         |
| 3/11  | 56  | 1         | 8.89         | 182             | 102                     | 82            | 170         | 8   | 66              | 15                      | 95.6          | 28.4        | 19.5      | 91.2  |         |
|   |     | 2         | 7.81         | 209             | 114                     | 98            | 60          | 5   | 77              | 19                      | 97.6          | 31.6        | 21.4      | 68.3  |         |
|   |     | M         | 7.70         | 197             | 102                     | 81            | 111         | 65  | 87              | 118                     | 67.0          | -6.8        | -7.4      | -6.0  |         |
|   |     | Mill*     | -            | 264             | 111                     | -             | -           | 51  | 93              | -                       | 80.7          | 16.2        | -         | -     |         |
| 3/12  | 57  | 1         | 7.69         | 228             | 170                     | 144           | 126         | 9   | 79              | 30                      | 96.0          | 29.4        | 45.1      | 76.2  |         |
|   |     | 2         | 7.19         | 22              | 109                     | 102           | 38          | 4   | 71              | 27                      | 81.8          | 35.8        | 30.4      | 28.9  |         |
|   |     | M         | 7.70         | 258             | 130                     | 100           | 71          | 45  | 94              | 38                      | 82.6          | 27.7        | 6.0       | 46.5  |         |
|   |     | Mill*     | -            | 236             | 132                     | -             | -           | 39  | 81              | -                       | 83.5          | 38.6        | -         | -     |         |
| 3/13  | 58  | 1         | 8.26         | 220             | 160                     | 136           | 192         | 12  | 90              | 52                      | 94.5          | 43.8        | 33.8      | 72.9  |         |
|   |     | 2         | 7.99         | 199             | 161                     | 127           | 174         | 13  | 99              | 52                      | 94.0          | 37.9        | 22.0      | 70.1  |         |
|   |     | M         | 7.82         | 206             | 140                     | 114           | 222         | 81  | 112             | 122                     | 60.7          | 13.6        | 1.8       | 45.0  |         |
|   |     | Mill*     | -            | 294             | 141                     | -             | -           | 57  | 126             | -                       | 80.1          | 10.6        | -         | -     |         |
| 3/14  | 59  | 1         | 7.10         | 192             | 122                     | 101           | 115         | 15  | 83              | 38                      | 92.2          | 24.6        | 17.8      | 67.0  |         |
|   |     | 2         | 7.29         | 128             | 128                     | 102           | 159         | 4   | 86              | 34                      | 96.9          | 32.8        | 20.6      | 78.6  |         |
|   |     | M         | 7.41         | 245             | 142                     | 110           | 126         | 59  | 110             | 108                     | 75.9          | 9.2         | 0         | 14.3  |         |
|   |     | Mill*     | -            | 176             | 144                     | -             | -           | 59  | 108             | -                       | 66.5          | 25.0        | -         | -     |         |

Composites

- A1 - From 7:30 AM to 7:30 PM )
- A2 - From 7:30 PM to 7:30 AM )
- B1) - Two hours after A's to ) on 60-minute
- B2) allow for system holding time ) cycle
- M - 24-hour mill composite )
- analyzed at Appleton Labs )
- Mill\* - Same as (M) analyzed by mill

TABLE XVII  
CLARIFIER STUDY - MOSINEE PAPER CORPORATION

| Date  | Day | Composite | Influent (A) |                    |  |                | Effluent (B)       |  |                |       | % Reduction |         |      |       |
|---|-----|-----------|--------------|--------------------|--|----------------|--------------------|--|----------------|-------|-------------|---------|------|-------|
|   |     |           | pH           | Sus. Sol.,<br>mg/l | BOD <sub>5</sub> , mg/l<br>Total Soluble | Color<br>Units | Sus. Sol.,<br>mg/l | BOD <sub>5</sub> , mg/l<br>Total Soluble | Color<br>Units | Total | Soluble     | Color   |      |       |
| D. Ferric Sulfate (50-100 mg/l Fe <sup>3+</sup> ) |     |           |              |                    |  |                |                    |  |                |       |             |         |      |       |
| 3/18  | 63  | 1         | 8.01         | 187                | 192                                      | 138            | 332                | 124                                      | 101            | 38    | 32.6        | 35.4    | 26.8 | 88.6  |
|   |     | 2         | 7.28         | 214                | 147                                      | 110            | 82                 | 120                                      | 98             | 38    | 51.4        | 18.4    | 10.9 | 53.6  |
|   |     | M         | 7.41         | 359                | 221                                      | 131            | 126                | 144                                      | 132            | 211   | 84.1        | 34.8    | -0.8 | -67.5 |
|   |     | Mill*     | -            | 246                | 195                                      | -              | -                  | 93                                       | -              | -     | 75.2        | 52.3    | -    | -     |
| 3/19  | 64  | 1         | 7.62         | 286                | 158                                      | 130            | 118                | 100                                      | 95             | 38    | 92.3        | 36.7    | 26.9 | 67.8  |
|   |     | 2         | 7.22         | 202                | 136                                      | 116            | 111                | 93                                       | 88             | 45    | 91.1        | 31.6    | 24.1 | 59.4  |
|   |     | M         | 7.40         | 178                | 146                                      | 113            | 108                | 121                                      | 106            | 163   | 59.0        | 17.1    | 6.2  | -50.9 |
|   |     | Mill*     | -            | 226                | 122                                      | -              | -                  | 110                                      | -              | -     | 73.4        | 9.8     | -    | -     |
| 3/20  | 65  | 1         | 8.09         | 191                | 180                                      | 148            | 273                | 122                                      | 107            | 45    | 71.2        | 32.2    | 27.7 | 83.5  |
|   |     | 2         | 7.22         | 168                | 173                                      | 124            | 145                | 86                                       | 83             | 52    | 94.0        | 50.3    | 33.1 | 64.1  |
|   |     | M         | 7.07         | 149                | 186                                      | 144            | 163                | 140                                      | 122            | 160   | 50.3        | 24.7    | 15.3 | 1.8   |
|   |     | Mill*     | -            | 175                | 140                                      | -              | -                  | 86                                       | -              | -     | 66.3        | 38.6    | -    | -     |
| 3/21  | 66  | 1         | 7.40         | 200                | 165                                      | 135            | 122                | 106                                      | 98             | 55    | 96.0        | 35.8    | 27.4 | 54.9  |
|   |     | 2         | 7.20         | 178                | 139                                      | 104            | 68                 | 89                                       | 86             | 70    | 96.1        | 36.0    | 17.3 | -2.9  |
|   |     | M         | 7.33         | 224                | 170                                      | 116            | 90                 | 126                                      | 106            | 90    | 72.3        | 25.9    | 8.6  | 0     |
|   |     | Mill*     | -            | 218                | 120                                      | -              | -                  | 60(?)                                    | -              | -     | 75.2        | 50.0(?) | -    | -     |
| E. Base Line (Hercofloc 812.3 at 0.75 mg/l)       |     |           |              |                    |  |                |                    |  |                |       |             |         |      |       |
| 3/25  | 70  | 1         | 11.01        | 341                | 119                                      | 91             | 52                 | 102                                      | 90             | 45    | 80.0        | 14.3    | 1.1  | 13.5  |
|   |     | 2         | 7.91         | 190                | 134                                      | 104            | 31                 | 112                                      | 112            | 31    | 88.0        | 16.4    | -7.7 | 0     |
|   |     | M         | 8.95         | 241                | 132                                      | 100            | 56                 | 88                                       | 86             | 52    | 74.7        | 33.3    | 14.0 | 7.1   |
|   |     | Mill*     | -            | 278                | 93                                       | -              | -                  | 63                                       | -              | -     | 77.3        | 32.2    | -    | -     |
| 3/26  | 71  | 1         | 7.99         | 239                | 170                                      | 146            | 41                 | 170                                      | 114            | 41    | 84.9        | 0       | 21.9 | 0     |
|   |     | 2         | 8.06         | 182                | 138                                      | 127            | 34                 | 112                                      | 112            | 34    | 86.8        | 18.8    | 11.8 | 0     |
|   |     | M         | 7.81         | 262                | 114                                      | 114            | 38                 | 125                                      | 112            | 38    | 84.0        | -       | 1.8  | 0     |
|   |     | Mill*     | -            | 300                | 92                                       | -              | -                  | 47                                       | -              | -     | 83.3        | 48.9    | -    | -     |
| 3/27  | 72  | 1         | 8.32         | 137                | 172                                      | 130            | 103                | 182                                      | 128            | 100   | 62.8        | -5.8    | 1.5  | 2.9   |
|   |     | 2         | 8.13         | 235                | 146                                      | 130            | 192                | 125                                      | 124            | 296   | 83.4        | 14.4    | 4.6  | -54.2 |
|   |     | M         | 8.19         | 245                | 192                                      | 122            | 150                | 132                                      | 104            | 103   | 76.7        | 31.2    | 14.8 | 31.3  |
|   |     | Mill*     | -            | 192                | 108                                      | -              | -                  | 57                                       | -              | -     | 73.4        | 47.2    | -    | -     |
| 3/28  | 73  | 1         | 8.28         | 177                | 184                                      | 127            | 332                | 166                                      | 139            | 460   | 82.5        | 9.8     | -9.4 | -38.6 |
|   |     | 2         | 8.51         | 189                | 150                                      | 134            | 328                | 125                                      | 124            | 251   | 74.6        | 16.7    | 7.5  | 23.5  |
|   |     | M         | 9.21         | 253                | 158                                      | 120            | 318                | 120                                      | 110            | 278   | 75.5        | 24.0    | 8.3  | 12.6  |
|   |     | Mill*     | -            | 260                | 117                                      | -              | -                  | 43                                       | -              | -     | 83.5        | -2.6    | -    | -     |

Composites

- A1 - From 7:30 AM to 7:30 PM )
- A2 - From 7:30 PM to 7:30 AM )
- B1) - 90 minutes allowed )
- ) on 30-minute )
- B2) - for system holding time )
- M - 24-hour mill composite )
- ) analyzed at Appleton labs )
- Mill\* - Same as (M) analyzed by mill

TABLE XVIII  
CLARIFIER STUDY - MOSINEE PAPER CORPORATION

| Date   | Day | Composite | Influent (A) |                         |                         | Effluent (B)  |             |                 | % Reduction             |               |       |     |      |      |      |        |  |
|--|-----|-----------|--------------|-------------------------|-------------------------|---------------|-------------|-----------------|-------------------------|---------------|-------|-----|------|------|------|--------|--|
|  |     |           | pH           | Sus. Sol., mg/l         | BOD <sub>5</sub> , mg/l | Total Soluble | Color Units | Sus. Sol., mg/l | BOD <sub>5</sub> , mg/l | Total Soluble | Color |     |      |      |      |        |  |
| <b>F. Sulfuric Acid (pH adjustment only)</b>                   |     |           |              |                         |                         |               |             |                 |                         |               |       |     |      |      |      |        |  |
| 4/1  | 77  | 1         | 8.61         | 270                     | 320                     | 176           | 640         | 6.51            | 193                     | 248           | 150   | 92  | 28.5 | 22.5 | 14.8 | 85.6   |  |
|  |     | 2         | 8.53         | 332                     | 201                     | 151           | 432         | 6.19            | 113                     | 143           | 112   | 52  | 66.0 | 28.8 | 25.8 | 88.0   |  |
|  |     | M         | 9.72         | 307                     | 211                     | 177           | 960         | 9.51            | 50                      | 140           | 125   | 318 | 83.7 | 33.6 | 29.4 | 66.9   |  |
|  |     | Mill*     | -            | 302                     | -                       | -             | -           | -               | 62                      | -             | -     | -   | 79.5 | -    | -    | -      |  |
| 4/2  | 78  | 1         | 7.61         | 331                     | 148                     | 124           | 67          | 6.18            | 131                     | 114           | 98    | 41  | 60.4 | 23.0 | 21.0 | 38.8   |  |
| <b>G. Sulfuric Acid + Polymer</b>                              |     |           |              |                         |                         |               |             |                 |                         |               |       |     |      |      |      |        |  |
| 78   |     | 2         | 7.91         | 294                     | 120                     | 102           | 74          | 5.65            | 57                      | 88            | 76    | 23  | 80.6 | 26.7 | 25.5 | 68.9   |  |
|  |     | M         | 7.79         | 260                     | 114                     | 102           | 59          | 7.40            | 68                      | 109           | 92    | 81  | 73.8 | 4.4  | 9.8  | -37.3  |  |
|  |     | Mill*     | -            | 266                     | -                       | -             | -           | -               | 36                      | -             | -     | -   | 86.5 | -    | -    | -      |  |
| <b>H. Ferrous Sulfate (100 mg Fe<sup>2+</sup>/l) + Polymer</b> |     |           |              |                         |                         |               |             |                 |                         |               |       |     |      |      |      |        |  |
| 4/3  | 79  | 1         | 7.70         | 271                     | 150                     | 126           | 160         | 5.19            | 183                     | 106           | 92    | 322 | 32.5 | 29.3 | 27.0 | -101.2 |  |
|  |     | 2         | 8.72         | 177                     | 144                     | 114           | 296         | 7.61            | 169                     | 148           | 106   | 45  | 4.5  | -2.8 | 7.0  | 84.8   |  |
|  |     | M         | 8.19         | 227                     | 140                     | 120           | 200         | 7.30            | 83                      | 104           | 96    | 168 | 63.4 | 25.7 | 20.0 | 16.0   |  |
|  |     | Mill*     | -            | 224                     | -                       | -             | -           | -               | 52                      | -             | -     | -   | 76.8 | -    | -    | -      |  |
| 4/4  | 80  | 1         | 8.61         | 222                     | 172                     | 137           | 3600        | 5.34            | 117                     | 144           | 94    | 136 | 47.3 | 16.3 | 31.4 | 96.2   |  |
|  |     | 2         | 7.62         | 184                     | 138                     | 112           | 200         | 5.59            | 164                     | 90            | 78    | 207 | 10.9 | 34.8 | 30.4 | -3.5   |  |
|  |     | M         | 7.40         | 275                     | 216                     | 136           | 118         | 7.19            | 57                      | 143           | 108   | 185 | 79.3 | 33.8 | 19.1 | -56.8  |  |
|  |     | Mill*     | -            | 356                     | -                       | -             | -           | -               | 45                      | -             | -     | -   | 87.4 | -    | -    | -      |  |
| <b>Composites</b>  |     |           |              |                         |                         |               |             |                 |                         |               |       |     |      |      |      |        |  |
|  |     | A1        | -            | From 7:30 AM to 7:30 PM | )                       |               |             |                 |                         |               |       |     |      |      |      |        |  |
|  |     | A2        | -            | From 7:30 PM to 7:30 AM | )                       |               |             |                 |                         |               |       |     |      |      |      |        |  |
|  |     | B1)       | -            | 90 minutes allowed      | )                       |               |             |                 |                         |               |       |     |      |      |      |        |  |
|  |     | B2)       | -            | for system holding time | )                       |               |             |                 |                         |               |       |     |      |      |      |        |  |

M - 24-hour mill composite analyzed at Appleton labs  
Mill\* - Same as (M) analyzed by mill

on 30-minute cycle

APPENDIX II

SUPPORTING MILLS OF GROUP PROJECT 3216

Appleton Papers Division of NCR

Bergstrom Paper Company

Hammermill Paper Company

Hoerner Waldorf Corporation

Kimberly-Clark Corporation

The Mead Corporation

Nekoosa Edwards Paper Company, Inc.

Potlatch Corporation

The Proctor & Gamble Company

Scott Paper Company

Wausau Paper Mills Company

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