

ENVIRONMENT CANADA

PROJECT REPORT 11-2

ISOLATION OF TOXIC CONSTITUENTS IN
BLEACHED KRAFT EFFLUENTS

B.C. Research

Progress to March 31, 1971.

PULP AND PAPER POLLUTION ABATEMENT

A research program sponsored by the
Department of the Environment
in cooperation with the
Canadian Pulp and Paper Industry.

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FOREWORD

This report covers work done in the fiscal year 1970/71 on a project sponsored by the Water Pollution Abatement Research Program of the federal government in cooperation with the Canadian pulp and paper industry. First announced in August, 1970 by the Minister of Fisheries and Forestry and the Minister of Energy, Mines and Resources, this program provides for the funding of research contracts aimed at reducing pollution from Canadian pulp and paper operations.

The work summarized was funded by the Department of Fisheries and Forestry and the Department of Energy, Mines and Resources. Various elements of these Departments have recently been combined with the formation of the new Department of the Environment. The program Secretariat is provided by the Canadian Forestry Service, Department of the Environment.

The program is developed and guided by a joint government-industry committee known as the Coordinating Committee on Water Pollution Abatement Research (CCWPAR). The twelve members represent the Department of the Environment, the Department of Industry, Trade and Commerce, the Canadian Pulp and Paper Association, the pulp and paper industry in eastern Canada, the industry in western Canada and the Pulp and Paper Research Institute of Canada. The Committee plans the program, assesses priorities, reviews progress and advises on the allocation of funds and awarding of contracts for research proposals from pulp and paper companies and any other recognized research institutions. The federal government enters into contract agreements with the organizations concerned for the conduct of approved projects.

In the fiscal year 1970/71 funds in an amount of up to \$500,000 were authorized to finance approved research work. From 1971/72 through 1975/76 up to \$1,000,000 will be available each year provided the pulp and paper industry's annual expenditures for this type of work are increased by a like amount over the 1970 expenditures.

Project No. 1401

May 18, 1971

PROJECT REPORT NO. 2

To: The Department of Fisheries and Forestry
Program Coordination Branch
344 Wellington Street
Room 4040
Ottawa, Canada

Attention: Dr. H. Schwartz, Chairman
Coordinating Committee on Water Pollution
Abatement Research

Subject: CONTRACT NO. 7 (CCWPAR) - ISOLATION OF TOXIC FRACTIONS
IN UNBLEACHED WHITE WATER

A. OBJECT

To summarize progress on the above research program over the period January 16 to May 11, 1971.

B. BACKGROUND

It has been demonstrated (Howard and Walden, 1965) that abnormal pH is responsible for approximately 75% of the toxicity of kraft pulping effluents. The nature of the remaining portion of toxicity, which may be ascribed to chemical toxicants, is still largely unidentified. While volatile sulphur-containing materials, such as hydrogen sulphide, mercaptans and organic sulphides, are known to contribute to the toxicity of effluents when discharged, they are rapidly removed by natural or mechanical aeration and are unlikely to be factors influencing longer-term toxicity. Early studies on the isolation of toxic fractions from kraft pulping effluents were summarised by Van Horn (1961). One of the first species of toxic organic compounds found to present in pulping liquors was the group of resin acids typified by abietic acid (Hagman, 1936). More recently, (Marvell and Wiman, 1963) 4-(p-tolyl)-1-pentanol has been shown to be a toxic component of the condensate from black liquor evaporators. In addition, an unidentified diol, also found in evaporator condensate in minuscule quantities, has been implicated as a contributor to the toxicity of pulp effluent (Banks, 1969). However, no serious attempts were made in any of these approaches to account for the total toxicity of mill effluents.

The immediate aim of the current program is to obtain a toxicity balance and to identify the active constituents of unbleached whitewater. A similar project, which was initiated some years ago in B.C. Research laboratories, was reactivated in 1970. The earlier work demonstrated that the acutely toxic portion of unbleached whitewater was confined in the precipitate produced on acidification of the effluent to pH 2.

The toxic components were further concentrated by extraction from the precipitate into petroleum ether. Chromatographic techniques were then employed in an attempt to isolate and characterise compounds responsible for the toxicity of the effluent. Significant progress had been made, demonstrating the viability of this approach, when the program was halted temporarily.

The present study has attempted to reproduce results obtained using the original fractionation scheme but employing larger effluent volumes so that sufficient quantities of discrete toxic components ultimately will be available for bioassay tests. Difficulties were encountered in achieving a toxicity balance for the initial acid precipitation and the batch of effluent was used to elaborate techniques for subsequent separation. For instance, a more efficient means of flocculating and drying the finely divided acid precipitate was developed. This involved freezing and thawing the slurry to coagulate the solid material, followed by filtration and freeze drying at temperatures less than 40°F.

C. PRESENT WORK - EXPERIMENTAL

Another batch of unbleached whitewater effluent (530 Imp. gal.) was collected from a West Coast kraft pulp mill over a 7-hr. period. The pH was adjusted to 2 by addition of concentrated sulphuric acid (1.7 l.) and the precipitate so formed permitted to settle for 14 hr. Removal of the supernatant liquid by careful pumping left a slurry (75 l.) which was concentrated in portions (1.6 l.) by centrifugation and the combined concentrates frozen. On thawing, filtration was relatively swift and the resulting fibrous pad was lyophilised over 3 days to give a dry, dark brown humic-like material (516 g.). Nonetheless, bioassay tests using eleven juvenile coho salmon per sample did not indicate a satisfactory toxicity balance throughout the various fractions. Although the effect on mean survival time (MST) of varying concentration was not studied, bioassays of the precipitate at each stage, diluted to its equivalent concentration in the original unbleached whitewater, again pointed to a loss in toxic factors after the initial acidification. For instance, the neutralised unbleached whitewater gave, at 100% concentration, a mean survival time of 41 min., compared with 228 min. for the acid slurry diluted to an equivalent concentration. Such a discrepancy is almost certainly too large to be explicable by synergism between the precipitate and the supernatant liquid, which was shown to be non-toxic after 1500 min.

The processing of large volumes of effluent necessitates lengthy handling procedures. Opportunity exists, therefore, for deterioration of the toxic constituents through aerial oxidation or via acid or base-promoted

decompositions. Consequently, a smaller batch of effluent (45 Imp. gal.) was used to minimise the time taken to reach the stage, after petroleum ether extraction, where most manipulations can conveniently be made under a nitrogen atmosphere. As before, concentrated sulphuric acid (350 ml.) was used to precipitate material at pH 2 and the resulting slurry (40 l.) was coagulated and freeze dried, yielding a dark brown fibrous material (80.9 g.). A portion of the residue (34.0 g.) was soxhlet extracted with petroleum ether (B.P. 36-51°) for 5 hr. and gave, after removal of solvent in vacuo, a yellow, waxy, semi-solid (2.63 g.).

Bioassays were performed on the unbleached whitewater over a range of dilutions, on the acid precipitated slurry and supernatant liquid at 100% concentration, and on the freeze dried precipitate and petroleum ether extract at dilutions corresponding to their concentration in the original unbleached whitewater. The acid-precipitated sludge had an MST of 26 min. at a concentration equivalent to that in unbleached whitewater (MST 24 min.). The supernatant from the precipitation had an MST >1500 min., confirming the efficacy of the method for concentrating toxic factors in this effluent. Plots of concentration vs. mean survival time are shown in Figure 1 for unbleached whitewater, freeze dried acid precipitate and petroleum ether extract of the precipitate. Characteristic hyperbolic curves were obtained for each case. A logarithmic plot of the data gave good straight line correlations as depicted in Figure 2. For the unbleached whitewater, MST at 100% concentration differs slightly from the initial determination. It is clear that measurable deterioration occurs within relatively short time spans.

D. DISCUSSION

With reference to Figure 2 it can be seen that the acid precipitate is demonstrably more toxic at all concentrations tested than the unbleached whitewater from which it is derived. The possibility exists that components in the supernatant liquor with no measurable toxicity per se exert antagonism towards the toxic material in the precipitate, causing a lowering in net toxicity. In addition, the slope of the line obtained for freeze dried precipitate is less than that for the unbleached whitewater plot. A similar, but accentuated situation occurs in the case of the petroleum ether extract of the precipitate, where the slope of the line is appreciably less than that for unbleached whitewater. It would appear that species which have a greater than average susceptibility to dilution have been concentrated by this fractionation, firstly in the freeze dried precipitate and later, to a larger degree, in the petroleum ether extract. Anomalies arising between MST values for a particular fraction at different times are explicable on the grounds of chemical modification of certain constituents on standing.

E. FUTURE WORK

It is proposed to utilize the fractions obtained to date for laboratory purposes to optimise further stages in separation and fractionation using column, thin layer and gas chromatography. Simultaneously, another batch of effluent now being collected in the field will be processed with utmost despatch and in an inert atmosphere wherever practical. Bioassays at several dilutions will be used before and after every stage to pinpoint toxicity losses should they occur, so that remedial steps may be taken quickly. Prospective instances of synergism and antagonism will be examined.

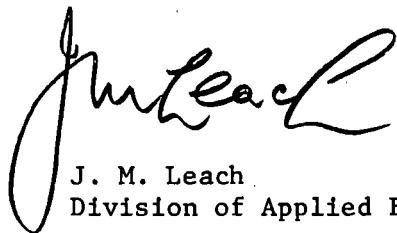
It is standard mill practice to utilize the evaporator condensate stream on the brownstock washers. Thus, the resulting effluent will be likely to contain toxic characteristics derived from both residual black liquor in the pulp and steam volatile material from the evaporators. Consideration will be given to the possibility of examining separately the streams which comprise unbleached whitewater. Fractionation of each of these streams separately should be a chemically more straightforward process since, in the case of combined condensate particularly, prior fractionation has already taken place during distillation in the evaporators. Provided the ratio is known in which the two streams are mixed on the brownstock washers it should be feasible to correlate toxic factors in unbleached whitewater with those in its contributing streams.

F. REFERENCES


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Figure 2

MST AS A FUNCTION OF CONCENTRATION

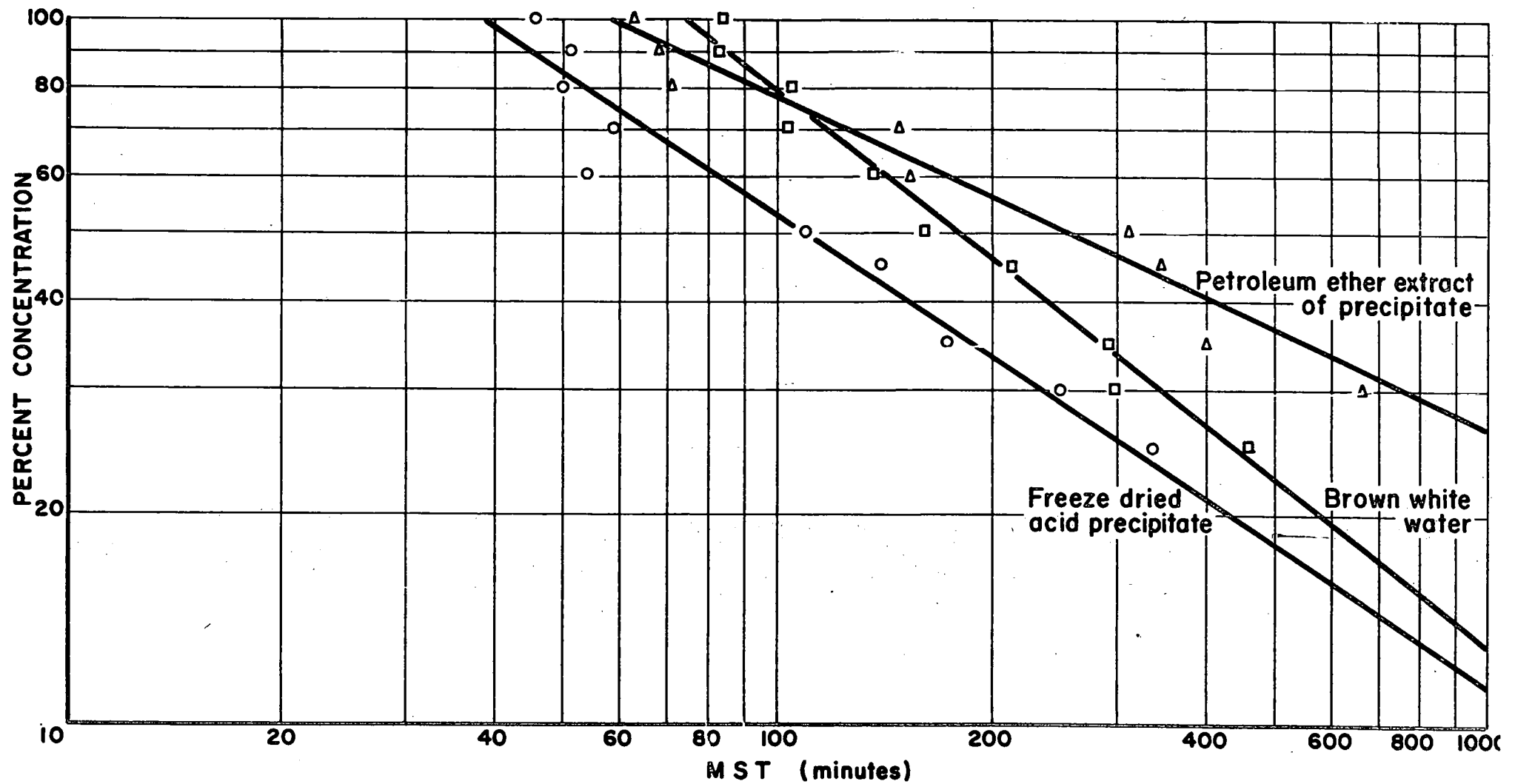


Figure 1

MST Vs CONCENTRATION FOR BWW, PRECIPITATE, AND PETROLEUM ETHER EXTRACT

