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# Dead Load Reduction in the Kraft **Pulping Process**

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Report EPS 3/PF/2 **April 1986** 



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### DEAD LOAD REDUCTION IN THE KRAFT PULPING PROCESS

by

Sandwell and Company Ltd. Vancouver, B.C.

for the

Industrial Programs Branch Environmental Protection Service Environment Canada

EPS 3/PF/2 April 1986

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#### ABSTRACT

This study was based on a review of information from available literature, experience with the white liquor evaporation process at Great Lakes Forest Products Limited, and communications with appropriate technical people in the pulp and paper industry. The results of the initial feasibility study formed a basis for assessing the technical and economic feasibility of the proposed process for dead load reduction in the kraft pulping process. The information generated from the project was intended to be used by industry and government to determine whether the proposed dead load reduction technology should be pursued, and in what way.

The study involved the preparation of various project memoranda that contained a discussion of the relevant process factors in the liquor cycle, with a strong emphasis on chemistry, and the effect of the chemistry on the operation of the equipment. Particular attention was given to the chemistry of the recovery boiler and the recausticizing system.

### RESUME

La présente étude est fondée sur l'information recueillie dans la documentation existante, sur les résultats expérimentaux du procédé d'évaporation de la liqueur blanche à la Great Lakes Forest Products Limited, et sur les communications de spécialistes de l'industrie des pâtes et papier. Les résultats de l'étude initiale de faisabilité ont servi de base pour l'évaluation de la faisabilité technique et économique du procédé proposé, qui vise la réduction de la charge inutile dans la production de pâtes kraft. L'information obtenue dans le cadre du projet devait permettre à l'industrie et au gouvernement de déterminer s'il était approprié de donner suite, et si oui de quelle façon, au projet de réduction de la charge inutile.

L'étude comprenait la préparation de divers mémoires relatifs au project, lesquels examinent les facteurs intervenant dans le cycle de régénération de la liqueur, particulièrement les facteurs chimiques, ainsi que les effets des diverses caractéristiques chimiques sur le fonctionnement de l'équipement. Les données chimiques relatives à la chaudière de récupération et au système de recaustification ont fait l'objet d'une attention toute particulière.

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#### ACKNOWLEDGEMENTS

#### Technical Advisory Committee:

- Mr. J.L. Betts, Environment Canada
- E.T. Barnes, Manager, Technology and Environment, Prince George Pulp and Paper Ltd.
- R.W. Sweeney, General Manager, Celgar Pulp Operations, Westar Timber Ltd.

#### Technical Assistance:

Mr. R. Randall of Intercontinental Pulp Company Ltd. conducted mass balances specific to the Intercontinental mill, for the existing situation and the proposed process. He also assisted with the energy balances and process design considerations.

Mr. J. Crane of Envirotech Canada Ltd. and Mr. R. Hedrick of Goslin-Birmingham, Inc. assisted with the preliminary design of the white liquor evaporator and the belt leaching system, conducted heat and mass beilances for the white liquor evaporator and multiple-effect black liquor evaporator, and provided capital cost estimates for all major new equipment.

Mr. T. King and Dr. T. Adams of Weyerhaeuser Company contributed to the understanding of the chemical, physical and thermal processes in a kraft recovery boiler.

#### Laboratory Assistance:

Westar Timber Ltd. conducted laboratory experiments to estimate the effect of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> on black liquor viscosity.

#### Technical Review:

The project memoranda and this report were reviewed by technical representatives of the following companies:

- Intercontinental Pulp Company Ltd.,
- Westar Timber Ltd.,
- Tahsis Company Ltd.,
- Irving Pulp and Paper Ltd.,
- Envirotech Canada Ltd.,
- Domtar Inc.,
- Eurocan Pulp and Paper Company Ltd.,
- St. Regis (Alberta) Ltd.,

- Proctor & Gamble Cellulose Ltd.,

- Prince George Pulp and Paper Ltd.,

- Weyerhaeuser Company, and

- Cariboo Pulp and Paper Company.

Dr. T. Grace of the Appleton Institute of Paper Chemistry reviewed project memoranda on black liquor evaporation and the recovery boiler, and the recovery boiler chemistry review.

Dr. G. Dorris of the Pulp and Paper Research Institute of Canada reviewed the project memorandum on recausticizing.

#### Mill Visit:

A project team visited the Thunder Bay mill of Great Lakes Forest Products Limited to view and discuss the existing white liquor evaporation system.

#### EXECUTIVE SUMMARY

An additional \$100 000 000 per year in extra revenue could be obtained on incremental production from the Canadian kraft pulp industry if the dead load in the liquor cycle were eliminated. At a typical recovery-limited mill, the profit margin could be increased by \$20 to \$25 per tonne of pulp.

This study was based on a review of information in the literature and industrial experience. Although the proposed process is potentially applicable at any kraft mill, the specific benefits and costs were assessed for the Intercontinental Pulp Co. Ltd. mill in B.C. This mill currently has a relatively low dead load, so the benefits would probably be greater at other mills. The benefits would also be greater with CE-type boilers, compared to Intercontinental's B&W-type boiler. For British Columbia coastal mills having a high concentration of sodium chloride in the liquor cycle, the proposed process could be extended to incorporate salt removal, further increasing the benefits.

- The main benefit of dead load reduction is the potential to increase the pulp producing capacity of an existing recovery-limited mill. One important secondary benefit is a reduction of up to 50 percent in malodorous emissions from the recovery boiler. At some mills, operating problems caused by the formation of various deposits throughout the liquor cycle would be reduced, and energy efficiency could be improved.
- For the Intercontinental mill, pulp production could increase by 8 percent, resulting in an incremental revenue of about \$5 000 000 per year. Mill operating costs for maintenance, manpower, electrical energy, and steam would increase by about \$1 000 000 per year.
- The total capital cost for the proposed process at the Intercontinental mill would be about \$16 000 000. If the mill could handle the incremental pulp production without further capital investment, the gross pay-back time would be 3.7 years.
- The main disadvantage of the proposed process is the extent of equipment modification required and changes to process conditions in almost all parts of the liquor cycle.
- While the process described is feasible, substantial benefits could be obtained at relatively low cost by process changes directed at:
- $\bullet$ improved recausticizing performance,
- $\bullet$ increased reduction efficiency, and
- decreased oxidation in recausticizing.
- Two new concepts are proposed for improving recausticizing performance:  $\overline{a}$ 
	- the lime mud recycle, and
	- partial countercurrent flow.
- For a capital cost of approximately \$200 000, recycle of lime mud could provide about 20 percent of the benefits obtainable with the white liquor evaporation dead load reduction process. The pay-back time would be 3 months. Alternatively, for a capital cost of \$1 000 000 to \$1 500 000 about 50 percent of the overall benefit could be realized by converting the causticizers to partial countercurrent flow. The pay-back period would be 6 months.

Dead load reduction has attractive benefits for recovery-limited mills and the new concepts of partial countercurrent flow and lime mud recycle appear to be the best course for immediate action.

#### INTRODUCTION

Kraft mills in Canada produce about 9 000 000 ADt\* of pulp each year (Wilson, 1984). At more than 50% of Canada's kraft mills, the pulp producing capacity is either limited, or on the verge of being limited, by the capacity of the recovery boiler(s), a capital-intensive piece of equipment. One of the factors affecting recovery boiler capacity is a dead load of unreactive inorganic chemicals in the liquor cycle. If this dead load could be eliminated, the equivalent pulp capacity of most recovery boilers could be increased by approximately 10%. The incremental profit on extra pulp production from an established mill is typically in the range of \$200 to 300/ADt, depending on mill-specific conditions. Considering the foregoing, the dead load in kraft liquor cycles prevents the Canadian kraft pulping industry from pursuing an additional \$100 000 000 per year in extra profit on incremental pulp production. If the dead load were eliminated, there would be an increase in productivity, a decrease in atmospheric emissions, and a reduction in operating problems due to process deposits, at many kraft mills. In some situations, there would also be an improvement in mill energy efficiency. At a typical recovery limited mill, the profit margin could be increased by  $$20$  to 25 per ADt.

#### 1.1 Industrial Involvement

The Intercontinental Pulp Company Ltd. mill at Prince George, B.C. was used as a specific example to assess the proposed process. The process design, heat and mass balances, capital and operating costs, savings and operational benefits are specific to that mill. The proposed process would be generally applicable to other mills, recognizing that more or less equipment may be needed, and that costs, savings and operational benefits would differ. For other mills, however, the benefits would probably be greater because currently the Intercontinental Pulp Company Ltd. mill is relatively efficient with respect to both black liquor dead load and the lime cycle dead load, in the context of existing technology. The white liquor causticity leaving the causticizers is 82%, and the reduction efficiency, measured in the green liquor leaving the smelt dissolving tank, is 92%. The Intercontinental Pulp Company Ltd. has a B&W-type recovery boiler. There would probably be a greater improvement in boiler performance, for a given reduction in black liquor dead load using a CE-type recovery boiler. The temperature increase in the bottom part of the furnace of a CE-type boiler is higher, and the decrease in the temperature of

<sup>\*</sup> ADt - air dry tonne of finished bleached pulp

the furnace exit gases is greater than temperature decreases in a B&W-type boiler. Furthermore, for B.C. coastal mills having a high concentration of NaCl in the liquor cycle, the proposed process could be extended to incorporate salt removal, thereby adding to the increase in recovery boiler capacity.

#### 1.2 Adequacy of Information

The project results are based on the best information from currently available literature and industry sources. This information was adequate to confirm that the proposed process should be technically feasible, giving a reasonable basis for establishing a process design, making the heat and mass balances, and estimating costs, savings and operational benefits. There were some areas, however, where information was limited necessitating the use of conservative assumptions, which tended to underrate the benefits of the process. In other cases, educated speculations had to be made. If the proposed process were to be pursued, the information deficiencies would have to be addressed by laboratory and mill work.

The eight most important information deficiencies are:

- 1) Impact of the dead load of sodium carbonate (Na $\gamma$ CO3) and sodium sulphate  $(Na<sub>2</sub>SO<sub>4</sub>)$  on recovery boiler operation, particularly the effect on the rate of deposit formation, reduction efficiency and TRS (total reduced sulphur) emission. No direct mill experimental data are available. For purposes of this project, the impact was estimated based on logical consideration of calculations and related scientific information. These considerations clearly indicate significant benefits, but they should be experimentally validated. One possible approach is to add the electrostatic precipitator catch from one boiler to the liquor fed to another boiler, at a mill having two or more recovery boilers. Due to the lack of direct mill data, the predictions concerning the recovery boiler must be regarded as speculative; nonetheless, they are considered to be realistic, based on logical assessment of the information available. Various aspects of recovery boiler chemistry need to be investigated, as do factors affecting heat transfer, fireside deposit formation and corrosion.
- 2) The effect of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> on the viscosity of black liquor. No direct experimental data were available. Westar Timber Ltd. did some laboratory work at their Castlegar mill as part of the project. The laboratory results indicate that viscosity would increase somewhat if the dead load were reduced, but a reliable quantification was not possible because the viscosity could not be measured

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precisely with the technique used. Considering the work by Westar Timber Ltd. and related information, however, it is doubtful that liquor viscosity would be a significant problem. Some controlled laboratory work with elaborate viscosity measuring equipment is required for confirmation.

- 3) White liquor evaporation data. Information on the solubility of  $Na<sub>2</sub>CO<sub>3</sub>$  and  $Na<sub>2</sub>SO<sub>4</sub>$ in concentrated white/liquor, and the corrosive properties of concentrated white liquor are limited. The available information was adequate for the feasibility study, but should be confirmed before designing a white liquor evaporation system.
- 4) White liquor usage. Lack of reliable data on the effect of recycling black liquor to continuous digesters, lead to the assumption that white liquor usage could not be reduced. There is potential for a reduction of about 2 to 3% compared to normal usage. This would improve the benefits of the proposed process, because the inorganic loading on the recovery boiler would be reduced accordingly. Mill-scale experience would be required to reliably evaluate this.
- 5) Belt leacher performance. The performance of the belt leacher was predicted based on one set of published equilibrium data. These data were consistent with related data from other sources but were limited, resulting in a conservative design. There is some potential that the belt filter might perform better than expected. Trials with a pilot belt filter are required.
- 6) Cyclone efficiency. It was assumed that a cyclone system could be designed to remove 95% of the crystals from concentrated white liquor. There is no direct evidence to support this. The relative sizes of burkeite and  $Na<sub>2</sub>CO<sub>3</sub>$  crystals should be investigated to see if they could be fractionated to any extent using cyclonic separators.
- 7) Deliquoring filter performance. A precoat-type lime mud filter has never been used to deliquor the underflow from a white liquor clarifier. A cake solids content of 55 wt  $\%$  is expected based on related industry experience with belt filters. This is substantially higher than the value used in the mass balances, 47 wt %. Westar Timber Ltd. use a precoat-type filter on white liquor clarifier underflow during lime mud washer outages in their mill at Castlegar, B.C.; the cake is washed on the filter with water and the discharge cake has a solids concentration of about 71%. This suggests that a precoat-type filter should function as expected, allowing for the higher viscosity of white liquor, compared to water.
- 8) Brownstock washing efficiencies for organics, inorganics and sodium. In absence of reliable data on the relative washing efficiencies of organics and inorganics, it was

assumed that the increase in the amount of organics entering the brownstock washing system expected with the proposed process could be compensated for by an increase in washwater flow (Section 3). The assumption used may have resulted in an overestimation in washwater requirements with the proposed process. Mill data on the relative washing efficiencies are required.

General information requirements include.

- 1) Factors affecting the formation of pirssonite need to be more completely investigated.
- 2) The chemical nature of various chemical species in green liquor dregs needs to be more reliably defined.
- 3) The dregs removal efficiency of green liquor clarifiers needs to be defined as a function of the upflow rate. Also, information is required to establish the removal efficiency of dregs components.
- 4) A reliable description of the kinetics of the recausticizing reaction is needed.
- 5) The mechanism by which the nature of the particles affects the settling rate of lime mud in white liquor should be investigated. In particular the physical and chemical factors involved in the reduction of the settling rate as a result of overliming should be identified.
- 6) Information is needed on the effect of calcining temperature on the reactivity of reburned lime and the settling properties of the lime mud produced, particularly for the low range of calcining temperatures.
- 7) The chemical state of various chemical species such as silicon and aluminum in the lime mud and reburned lime should be determined.
- 8) The impact of recausticizing flow schemes other than concurrent flow needs to be evaluated.
- 9) Conflicting evidence on the effect of residual Ca(OH)<sub>2</sub> on the filter ability of lime mud should be resolved.
- 10) The ability of a precoat-type filter to deliquor the underflow from a white liquor clarifier needs to be established by physical testing.
- 11) Many of the predicted changes in the recausticizing system, with respect to the proposed process, should be investigated and verified by laboratory testing.
- 12) Metallurgical testing is recommended for the process conditions of interest.
- 13) The predicted boiling point rises for the conditions of interest should be confirmed by laboratory analyses.
- 14) Pilot plant trials are required to demonstrate the feasibility of the leaching process. Envirotech Canada Ltd., rent a small-scale belt filter that could be used for this purpose. The existing belt filter at the Thunder Bay mill of Great Lake Forest Products Limited could also be used for such a trial, if they were willing.
- 15) Further recycle trials at Great Lakes Forest Products Limited would be of interest. In such trials, conditions should be carefully monitored.
	- 16) The effect of Na<sub>2</sub>SO<sub>4</sub> concentration on crystal size formation during white liquor evaporation should be investigated.

Parts of the proposed process, particularly white liquor evaporation, may be subject to existing patient claims; this was not investigated as part of this project.

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#### $2<sup>1</sup>$ THE CONCEPT

#### 2.1 Dead Load

The kraft liquor cycle has a number of inefficiencies which result in a recirculating dead load of inactive inorganic chemicals. The two main inefficiencies are the conversion of Na2C03 to sodium hydroxide (NaOH) in the recausticizing system (which is only about 80% complete) and the chemical reduction of  $Na<sub>2</sub>SO<sub>4</sub>$  to sodium sulphide (Na<sub>2</sub>S) in the recovery boiler (which is only about 90% complete). Some of the Na2S from the recovery boiler is oxidized in the recausticizing system. The residual Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> circulates through the liquor cycle as a dead load with no apparent benefit. The liquor cycle can also carry a dead load of sodium chloride (NaCl) if inputs of NaCl with the wood are not purged from the recovery cycle. In addition, the liquor cycle has a small dead load of inorganics containing magnesium (Mg), aluminum (Al), silicon (Si), manganese (Mn) and iron (Fe) which enter the process along with the wood, process water and make-up limestone.

Typically, at inland mills, about 20 to 25% of the inorganics circulating in the liquor cycle are present as a dead load. Sodium carbonate typically accounts for about two-thirds of this dead load, with the balance being sodium sulphate. At coastal mills, the amount of NaCl present can be more than the normal dead load of Na2CO3 and Na2SO4. The total load of miscellaneous compounds containing magnesium, aluminum, silicon, magnesium and iron in the liquor cycle is usually about 2% of the total dead load (Keitaanniemi and Virkola, 1978).

The recausticizing system carries a dead load through the lime kiln circuit, originating from three sources:

- 1) Recycle of dust. The off-gas leaving the kiln contains entrained dust equivalent to approximately 5 to 15% of the kiln feed. Traditionally, the dust is captured in a venturi scrubber and returned to the kiln via the lime mud washing system. Since the solids concentration of the cake leaving the lime mud filter is essentially fixed, the return of the captured dust via the washing system brings extra water into the kiln.
- 2) Unreacted calcium oxide (CaO) or calcium hydroxide (Ca(OH)2) in the lime mud. This can range from 0 to 10% by weight, but is typically less than 0.5 wt%.
- 3) Inert material (i.e., material other than CaO, Ca(OH)<sub>2</sub> or CaCO<sub>3</sub>). Inappropriate cations include Na, Mg, Fe and Mn, in compounds such as Na2S, Na2S04, NaOH, Na<sub>2</sub>CO<sub>3</sub>, (magnesium hydroxide) Mg(OH)<sub>2</sub>, (ferric oxide) Fe<sub>2</sub>O<sub>3</sub>, and (manganese

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oxide) Mn<sub>3</sub>O $\mu$ . Inappropriate anions include aluminum complexes, silica complexes, phosphate (PO $\bar{a}$ ) and sulphate (SO $\bar{a}$ ), in compounds such as calcium aluminum silicate (Ca2AlySiO3), calcium silicate (Ca2SiO4), calcium phosphate (Ca(PO)4) and calcium sulphate  $(CaSO_4)$ . Incomplete lime mud washing is responsible for the Na2S, Na2SO4, NaOH and Na2CO3 in lime mud; sodium compounds typically account for about 0.5 wt%, as Na<sub>2</sub>O, of lime mud fed to the kiln.  $CaSO<sub>4</sub>$  originates from the reaction of Na<sub>2</sub>SO<sub>4</sub> with CaCO<sub>3</sub>; this reaction is very limited, so the amount of CaSO<sub>4</sub> in lime mud fed to the kiln is probably less than 0.2 wt%. The total amount of inert material in lime mud fed to the kiln is typically about 5 wt%.

# 2.1.1 Disadvantages of Dead Load. The main disadvantages of recovery cycle dead load are:

- 1) restriction of the capacity of process equipment, particularly the recovery boiler;
- 2) increase of recovery boiler TRS emissions, due to indirect temperature effects;
- 3) consumption of energy to heat, evaporate and pump the associated water; and
- 4) deposit formation in transfer lines, in digester heaters and in black liquor evaporators.

The main disadvantage of the lime cycle dead load is that it carries water into the kiln, adding to the evaporation requirements. The dead load solids must also be heated to calcining temperature, along with the CaC03. Heat requirements attributable to the dead load are ultimately an integral part of the kiln's capacity to produce CaO. If the kiln dead load can be decreased, the capacity of the kiln increases and its fuel consumption decreases.

#### 2.2 Proposed Dead Load Reduction Process

The proposed process is based on white liquor evaporation. As white liquor is evaporated, a point is reached where  $Na<sub>2</sub>CO<sub>3</sub>$  precipitates in conjunction with burkeite  $(Na_2CO_3$ <sup>2</sup>Na<sub>2</sub>SO<sub>4</sub>). The solubility points for NaCl and Na<sub>2</sub>S are reached with further evaporation.

The proposed process is shown in Figure 1 and detailed in Figure 2, as it would be applied at the Intercontinental Pulp Company Ltd. mill. For comparison, the existing process situation at Intercontinental Pulp Company Ltd. is shown in Figure 3. In the proposed process, white liquor would be evaporated to precipitate most of the Na2CO3 and Na<sub>2</sub>SO<sub>4</sub>, as a mixture of Na<sub>2</sub>CO<sub>3</sub> and burkeite, but stopping short of precipitating Na<sub>2</sub>S and NaCl. The precipitated material would be separated from the concentrated



FIGURE 1 PROPOSED DEAD LOAD REDUCTION PROCESS

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# FEBRUARY 28,1985



white liquor using cyclonic separators, and the crystals would then be leached with warm water on a belt filter. The leaching operation would dissolve both  $Na<sub>2</sub>CO<sub>3</sub>$  and Na<sub>2</sub>SO<sub>4</sub>; the Na2C03 dissolving preferentially. The leachate would be recycled to the existing slaker, so the Na<sub>2</sub>CO<sub>3</sub> could be recausticized. The residual crystals would be about onethird Na<sub>2</sub>SO<sub>4</sub> and two-thirds Na<sub>2</sub>CO<sub>3</sub>. These crystals would be dissolved in weak wash and processed in a secondary recausticizing system to convert most of the  $Na<sub>2</sub>CO<sub>3</sub>$  to NaOH. The white liquor produced in the secondary causticizing system would be mixed with the concentrated white liquor from the evaporator. This combined stream would be diluted to normal strength with excess dilute black liquor from the brownstock washing system, before entering the digester.

The proposed process is a method for reducing the amount of  $Na<sub>2</sub>CO<sub>3</sub>$  in black liquor. The decrease in Na<sub>2</sub>CO<sub>3</sub> can be quantified with some precision and confidence for each mill situation. In the case of Intercontinental Pulp Company Ltd., the decrease in Na2C03 would be about 80%. White liquor evaporation and recycle of precipitated Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> to the recausticizing system would have no direct effect on the dead load of Na<sub>2</sub>SO<sub>4</sub>. As a result of the reduction in the amount of Na<sub>2</sub>CO<sub>3</sub> in black liquor; however, conditions in the recovery boiler would improve, such that the reduction efficiency for the smelt should increase. Furthermore, as part of the proposed process, precautions would be taken to minimize the oxidation of Na<sub>2</sub>S in the recausticizing system by reducing the infiltration of air into the smelt dissolving tank. Consequently, the dead load of  $Na<sub>2</sub>SO<sub>4</sub>$  in the liquor cycle would be reduced, but as an indirect result of white liquor evaporation. While there is some technical basis for predicting the increase in the reduction efficiency, the exact improvement expected is speculative. Nonetheless, it is clear that the reduction efficiency would increase, and some quantification was needed for the mass balance calculations. Considering the information available, it was predicted that the reduction efficiency in green liquor at Intercontinental Pulp Company Ltd. would increase from the current value of 92% to 96% which represents a 50% reduction in the Na<sub>2</sub>SO<sub>4</sub> dead load in green liquor.

If the material precipitated by white liquor evaporation were to be directly recycled to the existing recausticizing system, there would be a significant accumulation of Na<sub>2</sub>SO<sub>4</sub> in the existing recausticizing system. The resulting amount of Na<sub>2</sub>SO<sub>4</sub> in the recausticizing system would be about 10 times higher than the amount of Na<sub>2</sub>SO<sub>4</sub> in the smelt. The most obvious disadvantage of high  $Na<sub>2</sub>SO<sub>4</sub>$  concentrations in the recausticizing system is that  $Na<sub>2</sub>SO<sub>4</sub>$  reduces the equilibrium causticity because the total sodium ion concentration is increased. Another potential disadvantage is that  $Na<sub>2</sub>SO<sub>4</sub>$ 

may react with Na<sub>2</sub>CO<sub>3</sub> to form CaSO $\mu$  which would form a dead load on the lime kiln; the extent of this reaction appears to be limited. Elevated levels of  $Na<sub>2</sub>SO<sub>4</sub>$  in the recausticizing system would not affect the rest of the mill liquor cycle during normal operation of the white liquor evaporation system. Circumstances could arise, however, when it would be necessary to shut the white liquor evaporation system down, and use unevaporated white liquor for the pulping operation in the standard manner. In such cases, there could initially be a substantial inventory of unevaporated white liquor, having a high Na2S04 concentration, that would have to be introduced into the pulping and recovery systems.. One obvious problem with this is a high rate of  $\text{Na}_2\text{CO}_3$  -  $\text{Na}_2\text{SO}_4$ deposit formation in the black liquor evaporators; a significant disadvantage. Small concentration factors for Na<sub>2</sub>SO<sub>4</sub>, such as 2, would probably be acceptable, but high concentration factors, such as 10, would not. The proposed process, therefore, was designed to allow a controlled escape of  $Na<sub>2</sub>SO<sub>4</sub>$  from the recausticizing system, while minimizing the amount of Na<sub>2</sub>CO<sub>3</sub> that would leave with the Na<sub>2</sub>SO<sub>4</sub>. The belt leacher and the secondary recausticizing system would accomplish this.

Since the leachate from the belt filter would contain some  $Na<sub>2</sub>SO<sub>4</sub>$ , there would be an accumulation of Na<sub>2</sub>SO<sub>4</sub> in the existing recausticizing system. The degree of accumulation would be limited to a factor of 2.5 (i.e., the amount of  $\text{Na}_2\text{SO}_4$  in the main recausticizing system would be 2.5 times higher than the amount of  $Na<sub>2</sub>SO<sub>4</sub>$  entering the recausticizing system in the smelt, and leaving in the combined white liquor. With the proposed process, the amount of  $Na_2SO_4$  in the smelt would be half that for the existing situation. Even with a concentration factor of 2.5, therefore,  $\text{Na}_2\text{SO}_4$  concentrations in the main recausticizing system with the proposed process would not be much more than is currently the case.

The secondary recausticizing system is a required part of the proposed process because the crystals leaving the belt leacher would contain  $Na<sub>2</sub>CO<sub>3</sub>$ . If a secondary recausticizing system is not used, the effectiveness of the proposed process for reducing the dead load of Na2C03 would be decreased by about 25%. The overall process effectiveness would then be tied to the smelt reduction efficiency, because the ratio of  $\text{Na}_2\text{CO}_3/\text{Na}_2\text{SO}_4$  in the leached crystals would be approximately fixed at 2:1.

The preliminary design of the proposed process was based on a relatively high green liquor concentration, in order to minimize white liquor evaporation requirements. However, the green liquor strength was limited to about 130 g/L as Na<sub>2</sub>O to avoid pirssonite deposit formation. Pirssonite was also a factor in the design of the belt leaching filter, dictating that hot water be used as the wash instead of weak wash and

that the leachate be added to the slaker. With the high green liquor strength, and the recycle of the leachate to the existing slaker, the white liquor in the white liquor clarifier would have a concentration of about  $142 g/L$ , as Na<sub>2</sub>O. There was concern with this high strength, that the white liquor clarifier would lose some of its ability to provide clear white liquor during process upsets. To address this concern, a polishing filter for the clarifier overflow has been included in the preliminary process design.

The solids concentration of the clarifier underflow would decrease somewhat with the high white liquor strength. This, in combination with the increased soda concentration of the white liquor, would increase the amount of sodium compounds in the white liquor clarifier underflow by about 35%. At the same time, the allowable washwater usage would be decreased by about 25% due to the increased green liquor strength. These two factors indicated a potential lime mud washing problem. To avoid such a problem, the preliminary process design included a precoat-type deliquoring filter on the clarifier underflow, to increase its solids concentration to  $47$  wt  $%$  prior to lime mud washing. The lime mud could then be adequately washed in the existing system using 25% less washwater than is currently used.

The proposed process was developed from the perspective of maximizing its effectiveness and minimizing the overall mill energy consumption, and is presented as such. The focus on these objectives resulted in extra equipment requirements and increased process complexity. By sacrificing effectiveness and/or energy efficiency, the proposed process could be simplified.

#### 2.3 Industrial Experience with White Liquor Evaporation

The application of white liquor evaporation is not new. It is presently being applied at the Thunder Bay mill of Great Lakes Forest Products Limited. There, white liquor is evaporated in two stages. The first stage of evaporation removes  $Na_2CO_3$  and burkeite (as proposed here); the second and subsequent stage removes NaCl, which accumulates in the recovery cycle at that mill as the result of the novel application of the closed cycle mill concept. Development problems have been solved and the white liquor evaporation system is now relatively trouble-free. Start-up is fairly simple and there are no serious operating or maintenance problems. The proposed process is based on use of the first stage of evaporation only, as most inland pulp mills do not have significant amounts of NaCl in the liquor cycle. At coastal mills, where accumulation of NaCl in the liquor cycle can be a concern, the proposed process could be extended to include the

second stage of evaporation, to remove NaCl, as is done by Great Lakes Forest Products Limited, but to do this the liquor sulphidity may have to be reduced.

The white liquor evaporation scheme applied at Great Lakes differs from the proposed process in four significant ways:

- 1) The concentrated white liquor is diluted by bleach plant effluent rather than dilute black liquor, due to the application of the closed cycle mill concept.
- 2) The material crystallized in the first stage of evaporation (Na<sub>2</sub>CO<sub>3</sub> plus burkeite) is added to diluted white liquor, rather than recausticized. There is no belt leaching filter for this material and no secondary recausticizing system. At the Thunder Bay mill, therefore, the dead load is not reduced at any point in the process.
- 3) Steam use at Great Lakes is higher than with the proposed process due to a lower steam economy (less evaporation stages), a lower green liquor strength (more water to be evaporated) and the need to evaporate the liquor to a higher concentration to precipitate NaCl.
- 4) With the lower green liquor strength at Great Lakes, the white liquor clarifier is adequate, so a polishing filter and a deliquoring filter are not required. These extra units are included in the design of the proposed process as conservative measures to be sure that possible problems would be avoided.

In one of their earlier technical papers on the closed cycle mill concept, Rapson and Reeve (1973) suggested that white liquor be evaporated in one stage to precipitate NaCl and Na<sub>2</sub>CO<sub>3</sub>, and that the precipitate be leached to dissolve all the Na<sub>2</sub>CO<sub>3</sub> and only part of the NaCl, leaving pure NaCl. They indicated that the leach liquor could be added to the dissolving tank or to green liquor. Therefore, in the early stages of development of the closed cycle mill, Rapson and Reeve (1973) appeared to recognize the opportunity for dead load reduction with white liquor evaporation. It was not mentioned in subsequent publications, but direct recycle of precipitated burkeite and Na2C03 was allowed for in the design of the closed cycle mill at Great Lakes Forest Products Limited. The dead load reduction aspect of white liquor evaporation, however, is not practiced as part of normal operation.

For a trial period. Great Lakes Forest Products Limited recycled 80% of the material precipitated from white liquor to the smelt dissolving tank by dissolving it in weak wash. Few specific details are available concerning this trial but some general facts are known. Two problems were experienced; formation of fine crystals in the first stage of white liquor evaporation, and excessive deposit formation in parts of the green liquor

system. During the trial, no measures were taken to bleed  $\text{Na}_2\text{SO}_4$  from the recausticizing system. As a consequence,  $\text{Na}_2\text{SO}_4$  concentrations in the recausticizing system probably increased by a factor of about  $4$ . The trial lasted for several weeks.

During the trial, the structure of the crystals formed in the white liquor evaporators apparently changed from the desired heterogenous growth (large crystals) to a homogeneous dispersed growth (small crystals). This change may have been caused by the elevated Na<sub>2</sub>SO<sub>4</sub> concentrations in the unevaporated white liquor. High Na<sub>2</sub>SO<sub>4</sub> concentrations in unevaporated white liquor would be avoided with the proposed process, as discussed earlier. Furthermore, the equipment at Thunder Bay for separating the crystals from evaporated white liquor has since been changed from a sedimentation system to a cyclone-based system. The cyclones are more capable of removing small crystals, if they form. The problems of poor crystal growth that were experienced during the recycle trial would probably not be a problem in the proposed process.

The second problem experienced while recycling burkeite and  $Na<sub>2</sub>CO<sub>3</sub>$  at Great Lakes was excessive deposit formation in the weak wash piping and the piping leading to the green liquor clarifier. The cause of the deposit formation was investigated, and found to be due to pirssonite formation. It is expected that the deposit problems experienced during the recycle test at Great Lakes could be avoided with regard for the factors affecting pirssonite formation. In particular, with the proposed process, the precipitated material would be leached with hot water, so weak wash would not be used to transport the recycled material. Also, the recycled material would not be added until the slaker, thereby avoiding the obvious problems in the smelt dissolving tank, green liquor clarifier and green liquor transfer lines.

#### 3 MASS BALANCE OVERVIEW

A summary of the mass balances for the implementation of the proposed process at the Intercontinental Pulp Company Ltd. mill is provided in Figure 4. For comparison, the mass balances for the existing situation at Intercontinental Pulp Company Ltd. are shown in Figure 5. When studying these mass balances some minor inconsistencies may be apparent, as the balances were conducted in three separate parts: recausticizing and white liquor evaporation; the digester and brownstock washing; and from brownstock washing to the recovery boiler liquor gun. The calculations also involved trial and error in many places. In conducting the calculations, there were some conceptual simplifications. For example, the loss of chemicals to the sewer as black liquor was taken to occur only at a single point. Similarly, in the recausticizing system, chemical losses were taken to occur at one point as a weak wash. These simplifications are not exactly representative of the mill situation. Nonetheless, the simplifications were applied equally to the proposed process and the existing situation. The minor inconsistencies and the conceptual simplifications should not introduce any significant error when comparing the proposed process and the existing situation.

Na<sub>2</sub>S is essentially completely dissociated in green liquor, white liquor and black liquor. Therefore, all the mass balance calculations were based on hydrolysis of Na<sub>2</sub>S to NaHS in the smelt dissolving tank and the Na<sub>2</sub>S being present as NaHS in the rest of the cycle. However, to be conventional, NaHS is expressed as Na<sub>2</sub>S in Figures 4 and 5.

In comparing the mass balances for the proposed process in Figure  $4$  with the existing situation in Figure 5, the following points merit highlighting with respect to the proposed process:

- 1) The amount of sodium carbonate in white liquor entering the digester would be reduced by 80%.
- 2) The causticity of the white liquor going to the digester would increase to 96%, from 83%.
- 3) The amounts of Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>3</sub>, sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) and polysulphides in white liquor entering the digester would be 50% less.
- 4) White liquor active alkali usage and sulphidity would remain unchanged.
- 5) Pulp yield would remain unchanged.
- 6) The amount of water going to the digester with the white liquor would be decreased by 70%. About 55% of the excess brownstock washer filtrate bypass (see stream



 $1.8$ 

 $\overline{0}$ 

 $\begin{bmatrix} 0 \\ -1 \\ 0 \\ 2 \end{bmatrix}$ 

380

 $\begin{array}{c|c} 6265 & 7200 \\ - & 0.1 & - & - \\ \hline 0.1 & - & - & - \\ \end{array}$ 

88.8

9047

 $3.7$ 

 $\frac{1}{1.7}$ 

 $1.0\,$ 

 $\left[ 9.2 \right]$ 

 $15.4$ 

 $1.05$ <br>-------

 $10.29$ <br>========

 $z = z = z$ 

78

 $12$ 

 $38$ 

====

 $:= = =$ 

78

 $262$ 

8797

 $15.4$ 

 $5911$   $13.5$  1597

49.7

3850

 $7.3$ 

 $z = z = 1$ 

 $\begin{bmatrix} 67 \\ -11 \end{bmatrix}$ 

 $\frac{1}{3.5}$ 

 $\frac{1}{318}$ 

 $\begin{bmatrix} 0 \\ 0 \end{bmatrix}$ 

 $\begin{array}{c} \overline{105} \\ -\end{array}$ 

 $\overline{0}$ 

 $25 \mid 49.2$ 

 $1.15$ 

 $85.3$ 

 $\frac{1}{1.646}$ 

 $3.7$ 

 $\overline{0}$ 

 $\begin{array}{c} - - - - \\ 221 \end{array}$ 

 $\bullet$ 

 $\begin{bmatrix} 0 \\ 0 \end{bmatrix}$ 

 $\begin{bmatrix} 1435 \end{bmatrix}$ 

 $\begin{bmatrix} 1.7 & 1.7 & 1.7 \\ 90.0 & 90.0 & 90.0 \\ 1.7 & 1.7 & 1.7 \\ 1.0 & 1.0 & 1.0 \\ 10.2 & 10.2 & 10.2 \\ \end{bmatrix}$ 

 $53.0$   $53.0$ 

 $\begin{bmatrix} 1 & 1 & 1 \\ 1 & 3 & 3 & 4 \\ 1 & 1 & 1 & 1 \end{bmatrix}$ 

 $56.0$ 

 $\frac{1}{1.25}$ 

≈≈*===*≠

NaHS (as Na2S)

 $\overline{H}$  20

Na2S203

Polysulfide

% sulfidity (AA)

 $EA$  (g/l as Na2O)

% Diss. solids

DENSITY (g/cm3)

-------------------<br>VOLUME (m3/ADUt)

---------<br>Na2SO3

 $NaCl$ 

GAS PHASE

 $-22$   $-5888$ 

-------<br>5907

 $\frac{1}{8}$ , 4

 $18.5$ 

1.05

 $\begin{array}{c|c} 473 & 237 \\ -333 & 237 \\ \hline 120 & 100 \\ -333 & 100 \\ \hline \end{array}$ 

 $30.7$  65.5

 $\begin{bmatrix} -51.3 \end{bmatrix}$ 

 $1.12$ 

 $\begin{bmatrix} -5.77 \\ -5.77 \end{bmatrix}$ 

------<br>| 105<br>|-----

 $\frac{1}{9.2}$ 

 $5197$  5197

⊨======<br>| 85

======<del>|</del><br>\_\_100<br>========

7200

 $\frac{1.04}{7.80}$ 

9735

 $57$ 

FIGURE 5

EXISTING SITUATION:

MASS BALANCE SUMMARY



V5350 DEAD LOAD REDUCTION IN THE KRAFT PULPING PROCESS

# **FEBRUARY 28, 1985**

All units in kg/ADUt,

unless otherwise specified





ENVISIER<br>TEMP (Deg. C)<br>Passessessesses<br>C Tholuded -----------------------

## All units kg/ADUt, unless otherwise specified



**FEBRUARY 28, 1985** 



 $\sim$
numbers 92 and 93 in Figure 2) would be used to dilute the concentrated white liquor to normal strength before it entered the digester. Where some of the washer filtrate is bypassed around the digester, this stream would be the best source of material for diluting the concentrated white liquor, because the resulting changes in digester conditions would be minimal. At mills where none of the washer filtrate is bypassed around the digester, weak black liquor from the digester extraction flow would have to be used to dilute the white liquor; the higher solids concentration of the extraction liquor would result in more significant changes in digester conditions, particularly in the solids concentrations.

- 7) If the dissolved solids concentration of the liquor in the digester increased, for example, the solids concentration of the extraction liquor would increase to 19.3%, from 18.5%.
- 8) Because of the higher solids concentration, the residual effective alkali concentration at the bottom of the cooking zone would increase by about 0.8 g/L, as Na<sub>2</sub>O (indicated by the effective alkali concentration in the extraction flow).
- 9) To compensate for the 0.8 g/L increase in the effective alkali concentration at the bottom of the cooking zone, enough dilute black liquor would be recycled to reduce the effective alkali concentration at the top of the cooking zone by 0.8 g/L. The use of the recycle stream of dilute black liquor gives the flexibility to adjust the effective alkali concentration at the top of the digester; however, it would not influence the effective alkali concentration at the bottom of the cooking zone.
- 10) Due to the recycle of the dilute liquor, the sulphidity at the top of the digester would increase from 30.7% to 31.9%, but would remain unchanged at the bottom of the cooking zone at 65.5%.
- 11) The net downward flow rate of liquor in the continuous digester would increase by about 4% at the top and about 2% just above the extraction point in the cooking zone; however, there would be no change below the extraction point.
- 12) The ratio of organics to free inorganics in the liquor at the bottom of the cooking zone would increase from 4.98 to 6.94.
- 13) The total amount of black liquor solids entering the brownstock washing system would decrease by 0.5%. However, with the increase in the ratio of organics to inorganics, the amount of organic solids entering brownstock washing would increase by about 4.4%; to compensate for this, the washwater flow rate would be increased by essentially the same amount, 4.5%. The dilution factor would increase by 12.7%. This increase in washwater should be more than adequate to ensure that the loss of

black liquor solids in the pulp, as total solids, would not increase. For the mass balances, it was assumed that there would be no change in the liquor solids lost in the pulp. The organics include bound inorganics incorporated into the organics by the pulping reactions.

- 14) The dissolved solids concentration of the excess washer filtrate would decrease from 7.3% to 6.9% and the amount of excess filtrate bypass added to the weak black liquor from the digester extraction would be decreased by about 11%. However, with the proposed process, about 55% of the excess filtrate would be used to dilute the concentrated white liquor. As a result, the amount of excess filtrate bypass added to the weak black liquor from the digester extraction would be decreased by about 49%, with the proposed process.
- 15) Due to the use of half the excess washer filtrate to dilute the concentrated white liquor, the dissolved solids concentration of the weak black liquor entering the multiple-effect evaporator would increase from 15.4% to 17.9%. Evaporation requirements in the black liquor multiple-effect evaporator would be reduced by 25.5%. Considering this, and the slightly increased efficiency due to the small increase in the temperature of the feed liquor, steam requirements would be reduced by a total of 26.0%. The reduced evaporation requirements, and the increased concentration of dissolved solids in the feed liquor would be accomodated in the existing multiple-effect evaporator by a combination of lowering the inlet steam pressure and allowing the condensate to accumulate somewhat in most of the shells (i.e., partially flooding the shells) to reduce the effective heat transfer areas; this would not influence the steam economy.
- 16) Although the amount of NaOH in black liquor would remain essentially unchanged, the NaOH concentration, as a portion of the total black liquor solids, would increase by about 5% due to the decrease in total solids; this may reduce the viscosity of the liquor. The effect was not included in assessing the impact of the proposed process on liquor viscosity, as available information was not adequate to reliably quantify the effect.
- 17) The ratio of organics to free inorganics in the liquor in the multiple-effect evaporator would increase from 4.88 to 6.78.
- 18) The multiple-effect evaporator would concentrate black liquor to 49.7%, the same as the existing situation.
- 19) The amount of water evaporated in the black liquor oxidizer, the electrostatic precipitator and the cyclone evaporators would remain unchanged, in kg/ADUt\*.
- 20) The solids concentration of the black liquor leaving the cyclone evaporators would remain unchanged at 63.0%.
- 21) Considering the lower solids content of the liquor, in terms of kg/ADUt, in conjunction with items 19 and 20 previously mentioned, the solids concentration of liquor in the black liquor oxidizer could be lowered slightly from 53.0% to 52.4%. The lower solids concentration would be helpful in moderating the expected viscosity increase due to the increased organic to inorganic ratio. The solids concentration at the black liquor oxidation system would be lowered by bypassing more weak black liquor around the multiple-effect evaporator.
- 22) The ratio of organics to free inorganics in the black liquor in the cyclone evaporators would increase from 3.23 to 3.78.
- 23) The amount of free inorganic solids in the liquor fired to the recovery boiler would be decreased by 16%, and the amount of organic solids would remain the same. The ash content of the solids would decrease from 49.7% to 47.7%.
- 24) The total amount of black liquor solids fired to the recovery boiler would decrease by 4.0%. The amount of water in the liquor fired to the boiler would decrease by 3.8%.
- 25) A 20% increase in chemical fume production in the recovery boiler was allowed for (the actual increase would probably be less than this).
- 26) There would be 12.5% less smelt from the recovery boiler.
- 27) The reduction efficiency, measured in green liquor, would be expected to increase from 92% to 96%.
- 28) Water input to the recausticizing system would be reduced by 17%, such that the green liquor TTA (total titratable alkali) concentration would increase to 130 g/L, as Na<sub>2</sub>O, from the current  $108.5 g/L$ .
- 29) The volume of green liquor would decrease by 24%.
- 30) Recycle of leachate from the belt filter would increase the liquor TTA concentration in the slaker to  $142$  g/L, as Na<sub>2</sub>O.
- 31) For the current situation, the causticity of the white liquor leaving the white liquor clarifier is 82.2%, which is 8.3 percentage points below the estimated equilibrium causticity of 90.5%. For the proposed process, a causticity of 73% was used for the

ADUt - air dry tonne of unbleached pulp, at the digester.

white liquor leaving the white liquor clarifier, which is 12.5 percentage points below the estimated equilibrium causticity of 85.5%. This provides a conservative estimate of the attainable causticity with the proposed process. The decreased causticity is not a concern, because unreacted Na<sub>2</sub>CO<sub>3</sub> would be precipitated in the white liquor evaporator.

- 32) The lime mud feed going to lime mud washing (i.e., the product from the deliquoring filter) would have a suspended solids concentration of 47.3%, versus 33.7% for the existing situation (i.e., the white liquor clarifier underflow). Pumping the slurry would not be a problem because the cake from the deliquoring filter would fall into a repulper where it would be diluted with kiln scrubber underflow to a suspended solids concentration of 11.8%, before going to the lime mud washer.
- 33) The amount of dissolved sodium compounds in the lime mud going to lime mud washing would be reduced by 25%. The allowable water use in lime mud washing would be reduced by 20%.
- 34) The amount of lime mud fed to the kiln, and its moisture content would remain unchanged.

With the proposed process, the amount of water fed to the recovery boiler with the black liquor would be reduced by 40 kg/ADUt. It is interesting that the amount of water added to the liquor via the direct liquor heaters is about 60 kg/ADUt. If the direct heaters could be replaced with indirect heaters, essentially all of the recovery boiler temperature benefits of the proposed process would be obtained.

In examining the new equipment associated with the proposed process in Figure 2, the following points merit emphasis:

- 1) The white liquor concentration, as NaOH + Na<sub>2</sub>S, would be increased in the white liquor evaporator from 13.2 wt% to 34.0 wt%, removing 69% of the water.
- 2) The steam economy in the four-effect white liquor evaporator would be  $3.72$  kg H<sub>2</sub>O evaporated per kg of steam applied. For comparison, the steam economy of the quintuple-effect black liquor evaporator would be 4.75.
- 3) Make-up NaOH would be added to the white liquor before evaporation to minimize the possibility of Na<sub>2</sub>S precipitation.
- 4) A value of 94% was used for the efficiency for separating the crystals of Na<sub>2</sub>CO<sub>3</sub> and burkeite from the concentrated white liquor in the three-stage cyclone separation system.
- 5) The ratio of Na<sub>2</sub>CO<sub>3</sub> to Na<sub>2</sub>SO<sub>4</sub> in the solid phase at the end of the belt leaching filter could not be reduced below 2.0 kg/kg, because of equilibrium considerations.
- 6) Lime use in the secondary recausticizing system would be 4.2% of the kiln product.
- 7) The secondary causticizing system would operate at a low TTA concentration, 70.5 g/L as Na<sub>2</sub>O, to enhance the recausticizing efficiency. White liquor leaving the secondary causticizing system would be expected to have a causticity of 90%.
- 8) The lime mud underflow from the pressure filter in the secondary causticizing system would be expected to have a suspended solids concentration of about wt. 40%.
- 9) There are heat effects associated with the dissolution of  $Na_2CO_3$  and  $Na_2SO_4$  on the belt leaching filter and in the cake dissolving tank. As a result, the temperatures of the leachate and the solution leaving the cake dissolving tank are somewhat higher than otherwise expected.

#### 4 OVERVIEW OF ENERGY BALANCE

Hot water balances for the Intercontinental Pulp Company Ltd. mill are summarized in Figures 6 and 7. Currently, energy requirements for preparing hot water for the bleach plant at Intercontinental Pulp Company Ltd. are quite high. However, a capital project is being initiated to address this situation. Figure 6 is the modified hot water balance that will apply after the project is implemented. The changes to the modified hot water balance that would result with the proposed process are shown in Figure 7. A comparison of Figures 6 and 7 shows that the proposed process would result in a small increase in energy usage to prepare hot water.



FIGURE 6 EXISTING SITUATION: MODIFIED HOT WATER BALANCE, Normal Winter, L/s-°C (Peak Summer, L/s-°C)

The overall results of the energy balances for the proposed process and the existing situation are summarized on a relative basis in Table 1. The proposed process would result in steam savings in some areas of the mill, particularly in the black liquor



FIGURE 7 DEAD LOAD REDUCTION PROCESS HOT WATER BALANCE, Normal Winter, L/s«°C (Peak Summer, L/s-°C)

multiple-effect evaporator and in the recovery boiler. However, there would be some added steam requirements in other areas of the mill, particularly for white liquor evaporation. The net result is a slight increase in mill steam usage, about 0.337 GJ/ADUt in the winter and 0.186 GJ/ADUt in the summer.

There would be added energy usage in six areas with the proposed process, the main area being the additional steam use for the white liquor evaporator. The increased steam usage in the digester heaters would result from a combination of the need to heat the relatively cool excess filtrate bypass liquor used to dilute the concentrated white liquor, and the cooler white liquor, with the proposed process. In comparing the liquor stream going to the digester, stream number 71 in Figure 5 for the existing situation has a temperature of 90°C, while stream number 79 in Figure 4 for the proposed process has a temperature of 73°C. Due to this temperature difference, steam requirements in the



# TABLE 1 CHANGE IN ENERGY USAGE (G3/ADUt)

digester heaters would increase by 18% with the proposed process. The need to use steam in the green liquor heater and slaker would be eliminated, because at the higher liquor concentration relative to the existing situation, the liquor would be hot enough. Steam savings of 26% in the black liquor multiple-effect evaporator would be provided, because of the increased weak black liquor solids concentration, resulting from the use of excess filtrate bypass to dilute the concentrated white liquor. In effect, with the proposed process, part of the evaporation currently done in the black liquor multiple-effect evaporator would be transferred to the white liquor evaporator. Every effort was made to maximize the steam economy of the white liquor evaporator. It is doubtful that it would be technically feasible to obtain an economy much higher than 3.72 kg H<sub>2</sub>O evaporated per kg of steam. Since this is lower than the steam economy for the black liquor evaporator, 4.73 at the Intercontinental Pulp Company Ltd. mill, a partial shift in evaporation from black liquor to white liquor inherently means an increase in total steam consumption for liquor evaporation. This increase was moderated with the proposed process by decreasing the water input to the recausticizing system such that the unevaporated white liquor would have a higher TTA concentration.

The proposed process would provide some energy savings in the recovery boiler operation due to a decreased need for sootblowing with reduced deposit formation and a small reduction in steam needs for smelt shattering due to the reduced quantity of smelt. There would also be extra steam generated in the recovery boiler due to the reduced quantity of water in the black liquor feed and the reduced sensible heat loss with the smelt; this extra steam would reduced fuel requirements in the power boiler.

The decrease in sootblowing steam was predicted on the basis that there would be a reduction in the rate of deposit formation in problem areas such as the screen tubes, superheater, and the first part of the boiler bank, where deposits tend to be tenacious and difficult to remove via sootblowing. There would also be less tendency to have sticky deposits in the latter part of the economizer because the potential for bisulphate formation would be reduced. With the expected increased fume production (up to 20% more), there might be an increase in the rate of deposit formation in the latter part of the boiler bank and the economizer, but deposits in these regions are normally easy to remove by sootblowing; therefore, steam usage for sootblowing in these areas would not necessarily increase. Because of improvements in the most difficult areas, there would be a reduction in sootblowing steam requirements.

Consideration was given to possibly reducing the net energy requirements for the proposed process by integrating the white liquor evaporator with the multiple-effect black liquor evaporator or with flash steam from the digester. It was found that it would not be technically possible to integrate the white liquor and black liquor evaporator, for several critical reasons. It would be technically feasible to use digester flash steam as a partial steam source for the white liquor evaporator but it would have to be added to the second effect, rather than the first, due to its pressure. As shown in Figures 6 and 7, the digester flash steam condenser is an important part in the hot water supply system at the Intercontinental Pulp Company Ltd. mill, because it is a high-grade heat source. If digester flash steam were used in the white liquor evaporator, there would be essentially an identical increment in the amount of fresh steam needed to heat washwater for the bleach plant. Considering the inefficient use of the digester flash steam in the white liquor evaporator, there would actually be a net increase in mill steam consumption at the Intercontinental Pulp Company Ltd. mill. Due to the distance between the digester and the white liquor evaporator, some new equipment would also be involved in using digester flash steam as a partial steam source for the white liquor evaporator. Considering the added process complexity, the cost for the extra equipment and the lack of savings incentive, there was no justification for integrating digester flash steam with white liquor evaporation at the Intercontinental Pulp Company Ltd. mill. The conclusion that there is no incentive to integrate digester flash steam with the white liquor evaporator would apply generally to mills where the digester flash steam condenser is an important component of the mill hot water balance. However, the integration may be attractive for mills producing unbleached kraft pulp or for bleached kraft mills that prepare hot water from recovery boiler flue gas in a scrubber.

The energy balance for the proposed process would be extremely mill specific, due to varying hot water usage in the bleach plant. At mills with a high water usage in the bleach plant, the proposed process could provide a slight decrease in mill steam usage. On the other hand, at mills producing unbleached pulp or a bleached kraft mill having a recovery boiler flue gas scrubber that prepares hot water, the proposed process may increase mill steam usage to a greater extent that indicated for Intercontinental Pulp Company Ltd.

## 5 BENEFITS AND DISADVANTAGES OF THE PROPOSED PROCESS

# 5.1 Advantages

The main benefit of the proposed process is the potential to increase the pulp producing capacity of a recovery-limited mill. This could be accomplished without a lengthy mill shutdown, as with major recovery boiler modifications. The secondary benefits are reduced atmospheric emissions, reduced operational problems due to deposit formations at various points in the process, and slightly improved digester conditions. The benefits are discussed with specific reference to the kraft mill of Intercontinental Pulp Company Ltd. at Prince George, B.C.

5.1.1 Increased Pulp Producing Capacity. The proposed process would increase the capacity (in equivalent pulp production) of the recovery boiler and the multiple-effect black liquor evaporator. It would also contribute to a capacity increase for the liquor cycle in an indirect way by increasing the equivalent hours of storage for various process liquors.

The increase in recovery boiler capacity is the key benefit of the proposed process. This benefit would apply to recovery boilers limited by the rate of deposit formation on the pendent heat transfer surfaces of the boiler. Deposit formation in the problem areas such as the screen tubes, superheater, first part of the boiler bank and the later part of the economizer would be reduced. Factors contributing to the reduction in deposit formation are a decrease in the amount of inorganic ash particles entrained in the furnace exit gas, the reduction in the potential for formation of melting-point-depressant bisulphates in the economizer, and a lower furnace exit gas temperature.

The expected increase in the allowable organics firing rate in the recovery boiler cannot be accurately defined, but there is a reasonable technical basis for predicting a 7% increase for the B&W-type boiler at the Intercontinental Pulp Company Ltd. mill. Prince George, B.C. This prediction is supported by the amount of inorganic ash entrained in the furnace exit gas which should be reduced by about 10%, mainly due to the 7.5% reduction in the inorganic ash content (in kg/ADUt) of the liquor. It is expected that the organic load could be increased by about 7% before the amount of entrained inorganic ash returned to the current situation. The dead load reduction process is expected to reduce the furnace exit gas temperature by  $17^{\circ}$ C. This would permit a 8.5% increase in the furnace heat load before the furnace exit gas temperature returned to the current situation. With the proposed process, there would be a 1.1% increase in the furnace heat

load due to reduced heat requirements for evaporation of water from the liquor and reduced sensible heat loss in the smelt. Considering the foregoing, it should be possible to increase the organics load by  $7.4%$  before the furnace exit gas temperature returned to its current level. Therefore, a 7% increase in organic loading per ADUt appears to be well supported.

The capacity of the existing multiple-effect black liquor evaporator would increase by about 25% with the process, due to reduced evaporation requirements resulting from the use of recycled black liquor to dilute the concentrated white liquor to normal strength.

If black liquor viscosity problems could be circumvented, the proposed process would also provide for a capacity increase of up to 10% in the direct contact evaporators. Adequate information is not available concerning liquor viscosity, so the mass balances for the process were not based on taking advantage of this capacity increase to save some energy.

The proposed process would increase the equivalent storage time for various process liquors due to increased liquor strengths and two new storage tanks. The increases are shown in Table 2.



# TABLE 2 INCREMENTAL LIQUOR STORAGE WITH PROPOSED PROCESS

The increased storage time available would provide more flexibility for both unscheduled and scheduled maintenance. This should translate into a small increase in production due to more annual operating hours on production limiting equipment.

The proposed process would not reduce the dead load on the lime kiln, so the capacity of the kiln would not be affected. Similarly, the digester capacity would not be affected.

5.1.2 Reduced Atmospheric Emissions. The proposed process would increase the temperature in the lower region of the recovery furnace by about  $20^{\circ}$ C to  $25^{\circ}$ C. Higher temperatures reduce the formation of TRS,  $SO<sub>2</sub>$  and  $SO<sub>3</sub>$ . The decrease cannot be reliably predicted, but could be as much as 50%. Also, with a tendency for a 10% reduction in the amount of entrained inorganic ash particles in the furnace exit gas, the total amount of combustion air could be increased, mainly as tertiary air, to convert TRS to SO2; however, this could not be done if the organics firing rate were to be increased to increase pulp production.

The volume of off-gas from the smelt dissolving tank would be reduced due to changes in the dissolving tank heat balance and reduced air infiltration. The decrease cannot be reliably predicted but is expected to be about 50%, based on some tentative calculations. This should reduce particulate emissions from the smelt dissolving tank.

There would be no change in atmospheric emissions from the lime kiln.

5.1.3 Reduced Deposit Formation. Scale deposits in digester heaters normally consist of CaC03. The chips provide the main source of calcium for these deposits, but some calcium comes with the white liquor. The proposed process, with a white liquor polisher, would reduce the amount of particulate CaCO3 and particulate Ca(OH)2/CaO in white liquor. Mill experience with white liquor filters and polishers indicates that a reduction in the amount of particulate calcium reduces the frequency of digester heater cleaning; however, the boil-out frequency for evaporators is not affected. Based on this experience, the proposed process would probably reduce the cleaning frequency for the digester heaters, although not significantly. Digester heater deposits are not presently a significant problem for the Intercontinental Pulp Company Ltd. mill.

Deposits formed on extraction screens of continuous digesters are mainly organic in nature. They originate from lignin, probably by initial precipitation due to a low residual alkali concentration or a high calcium concentration, followed by slow insolubilization by lignin condensation reactions. The cleaner white liquor with the proposed process may reduce the rate of formation of these deposits, but probably not significantly. Digester screen deposits are not presently a significant problem for the Intercontinental Pulp Company Ltd. mill, although they may create problems at other mills.

Due to the complexity of scale formation in black liquor evaporators, it is not possible to predict the expected reduction in evaporator boil-out frequency. In most cases, where  $Na_2CO_3-Na_2SO_4$  deposition is typical, the boil-out frequency would be reduced. In situations where CaCO3 is the predominant component of the deposit, the required boil-out frequency would probably not decrease, and may even increase. Deposit formation in the black liquor multiple-effect evaporator is not a significant problem at Intercontinental Pulp Company Ltd.

It appears that pitch deposits are formed by the chemical adsorption of fatty acid soaps on calcium carbonate particles that have been predeposited on a surface. The proposed process would reduce the amount of CaC03 entering the digester and brown stock washing system via the white liquor. However, CaCO3 formed in the digester is from the calcium in the wood. For a continuous digester, about 90% of the CaCO<sub>3</sub> entering the brown stock system would come from the wood; the corresponding figure for a batch digester system would be about 65%. This suggests that reduced input of CaC03 via white liquor would have little impact on pitch formation. However, mill experience seems to indicate that mills practicing white liquor polishing have less problems with pitch formation. Based on mill experience, the proposed process may reduce pitch formation in brownstock washing and screening systems.

5.1.4 Improved Digester Conditions. The slightly higher sulphidity in the first part of the cooking zone of the continuous digester, resulting from the recycle of some dilute black liquor, would be a beneficial factor, tending to improve pulp yield and pulp strength. Corrosion, however, may increase at higher sulphidities. Generally, the impact of the slightly higher sulphidity would not be significant.

The recycle of dilute black liquor would increase volumetric flow rates in the digester slightly. This would help to avoid chip hangups.

# 5.2 Disadvantages of the Proposed Process

The main disadvantage of the proposed process is its scope. A substantial amount of new equipment would be required and some minor modifications would have to be made to existing equipment. The process conditions would be altered in almost every part of the liquor cycle. Also, the process engineering considerations are relatively complicated by today's mill standards.

Increased temperatures in the lower furnace of the recovery boiler would result in an increase of fume formation. The increase cannot be reliably predicted, but would probably be in the range 5 to 20%. Consequently, the load on the electrostatic

precipitator would increase and atmospheric particulate emission would probably increase if the precipitator efficiency was marginal. It may be possible to moderate the increase in fume production by making conditions in the reducing zone of the furnace slightly more oxidizing, but available information is not adequate to make a reliable assessment. Moreoxidizing conditions would not necessarily jeopardize the reduction efficiency, considering the increased temperatures in the lower furnace.

The viscosity of the black liquor would increase due to the increased organic/inorganic ratio. Reliable data are not available to quantify the viscosity effect. Consideration of related information, however, indicated that the increased viscosity should not be a significant constraint.

Cooling of the white liquor in conjunction with the deliquoring filter on the white liquor clarifier underflow may result in pirssonite deposits in the heat exchanger. This would have to be investigated in the laboratory, and addressed at the detailed design stage, if necessary.

While there is related technology to support the concept of a deliquoring filter on the white liquor clarifier underflow, such filters have never been used in this service in the pulp and paper industry.

While the added equipment and the scope of the proposed process would complicate a start-up, there are no obvious factors that would cause prohibitive problems. Complications could be reduced to some extent by bringing most of the aspects of the proposed process on line after the rest of the mill was operating satisfactorily. Although the added equipment of the proposed process would add to operations concerns, there are no obvious factors that would lead to prohibitive operating problems.

## 6 IMPACT ON WHITE LIQUOR USAGE AND KILN DEAD LOAD

### 6.1 White Liquor Usage

With the proposed process, there is the potential to reduce white liquor application by up to 2 to 3%, based on kg of active alkali per ADUt, due to the higher effective alkali concentrations in the lower part of the cooking zone and the increased sulphidity in the top of the digester. This is of interest from the perspective of lime kiln capacity, and a further increment to recovery boiler capacity. The higher concentrations of organics in the cooking liquor, however, may have adverse effects on pulping performance that would preclude a reduction in white liquor application. Furthermore, if white liquor usage were reduced by more than 1%, the NaOH concentration of black liquor would fall below the current situation and there may be an unacceptable increase in liquor viscosity. Available information was not adequate to make a reliable decision. To be conservative, it was assumed for the feasibility study that there would not be a reduction in white liquor usage.

# 6.2 Kiln Dead Load

Generally, the proposed process offers the potential to reduce the dead load on the lime kiln because overliming to achieve a high causticity would no longer be required, so the lime mud feed to the kiln would contain little unreacted Ca(OH)<sub>2</sub>. However, continuous overliming is not practised at the Intercontinental Pulp Company Ltd. mill, and the lime mud normally contains little  $Ca(OH)_2$ , so there is little potential to reduce the dead load on the lime kiln in this way.

With the proposed process, the removal efficiency for dregs in the green liquor clarifier should improve, thereby reducing the concentrations of magnesium, manganese, aluminum and iron in the lime mud. The required information is not available to quantify this effect, but it is doubtful that CaO content of the kiln product would increase by more than 0.5%. The cyclonic separator on the effluent neutralization bleed from the lime kiln scrubber underflow would tend to selectively bleed inerts from the lime cycle, but again the impact would not be dramatic. The slightly increased  $\text{Na}_2\text{SO}_4$  concentrations in the recausticizing system would slightly increase the  $CaSO<sub>4</sub>$  content of the lime mud fed to the kiln, but this factor is not considered to be of much consequence. Generally, it is doubtful that there would be much change in the dead load on the lime kiln with the proposed process, except at mills where overliming is typical.

## 7 ECONOMICS OF PROPOSED PROCESS

## 7.1 Benefits

7.1.1 Increased Pulp Production. The average production of finished pulp at the Intercontinental Pulp Company Ltd. mill is 645 ADt per day. The proposed process should increase the capacity of the recovery boiler for burning organics by about 7%. If there were no other significant equipment constraints in the mill, this would permit an increase in daily production of 45 ADt per day. Equipment constraints are presently not well defined, so the economics of the proposed process cannot properly reflect such possible constraints. Nonetheless, an appreciation is provided here for the economic viability of the proposed process for two cases: the most optimistic situation and a less optimistic situation.

At most mills in the interior of British Columbia, the incremental profit on pulp in recent years has been about \$300/ADt. Mills on the B.C. coast and in eastern Canada have typically experienced incremental profits in the range of \$200 to \$250 per ADt. While this describes the situation in general, it must be recognized that the incremental profit is sensitive to economic conditions and is mill specific. An incremental profit of \$300/ADt was used for the most optimistic situation, and a value of \$250/ADt was used for a less optimistic situation.

7.1.2 Increased Operating Time. The annual operating target at the Intercontinental Pulp Company Ltd. mill is 8160 hours, or 340 days. However, considering all the factors influencing whether or not the mill is in operation, experience in British Columbia in the pulp and paper industry for the past ten years has been closer to 300 days operation per year. An annual operating time of 340 days was used for the most optimistic situation, while 300 days was used for a less optimistic situation. With the increased storage time available, it is expected that the annual operating hours would increase. Also, with the proposed process, there would be less problems with process deposits (i.e., scale in digester heaters and the black liquor evaporators, and pitch in the brownstock system) which would help to further increase the annual operating time of the associated equipment.

The increase in annual operating time, due to the increased storage time and reduced deposit formation problems, is difficult to predict. For the most optimistic situation, it was assumed that the increase would be about 1%, equivalent to approximately three days per year. For the less optimistic situation, it was assumed that there would be no increase.

# 7.2 Operating Costs

Absolute maintenance costs are difficult to estimate with any degree of reliability, but there are no obvious significant maintenance problems with the proposed process. For the most optimistic situation, an allowance of \$500 000 per year was used, representing about 3% of the total capital cost of \$16 000 000. For the less optimistic situation, an allowance of \$1 000 000 was used.

One new shift position, consisting of a total of five extra operators, would be needed, four regular operators, and one for relief for annual vacation, sickness and training. An annual salary cost of \$50 000 per operator was used; this includes an allowance for fringe benefits and administration overhead.

There would be a total connected electrical capacity of about 710 kW of installed with the proposed process. On average, motors draw about 65% of the installed capacity, so the actual electrical consumption would be about 460 kW. Typically in a normal mill, about 900 kW of electrical energy is required to pump white, black and recausticizing liquors. With the proposed process, the volumes of liquors in black liquor evaporation and recausticizing would be reduced. The associated impact on electrical consumption has not been estimated precisely, but a reasonable assumption would be a 10% reduction in electrical requirements (i.e., 90 kW). The net impact of the proposed process on mill electrical consumption would be an increase of about 370 kW. For the current cost of electrical energy at the Intercontinental Pulp Company Ltd., 3.2  $\zeta$ /kWh, the annual increment in cost for electrical energy would be \$98 000.

The value of incremental steam costs and savings at the Intercontinental Pulp Company Ltd. mill is based on power boiler operation. Normally, the boiler is fired with a mixture of hog fuel and natural gas. However, for approximately 20% of the time, only natural gas is fired, to burn the bed on the grate down. The late-1984 incremental steam cost when firing natural gas alone was \$10.10/t steam, based on 2.67 MJ added per kg. For combined firing of hog fuel and natural gas, the incremental steam cost is estimated to be \$5.05/t. Considering this, the average incremental steam cost is \$6.10/t. During the summer, the power boiler steam generation requirements are less than the minimum load requirements; in this situation, energy savings or small increases in steam use do not translate into a change in fuel costs. Therefore, at the Intercontinental Pulp Company

Ltd. mill, process energy savings or small increases in steam usage have value for the winter only, approximately 6 months of the year.

Based on information in Table 1, and a winter incremental steam energy cost of \$6.10/t of steam, or \$1.90/GJ, the proposed process would result in an increase in winter steam energy cost of \$0.63 per ADUt. During the summer, the small increase in steam requirements with the proposed process would have no cost.

# 7.3 Capital Cost

The capital cost for implementing the proposed process at the Intercontinental Pulp Company Ltd. mill would be about \$16 000 000, as summarized in Table 3.

# TABLE 3 CAPITAL COST SUMMARY



The proposed process would increase the capacity of the existing recovery boiler by about 7%, and would also provide a capacity increase of about 25% in the black liquor multiple-effect evaporator. For the most optimistic situation, it was assumed that no other capital would be required for other parts of the mill, to enjoy 7% more production. However, at the Intercontinental Pulp Company Ltd. mill and at other mills as well, additional capital would be required to accommodate a 7% production increase throughout the mill. Depending on the circumstances at a specific mill, the additional capital cost might be in the range of \$2 000 000 to \$15 000 000. The economic assessment for the less optimistic situation at the Intercontinental Pulp Company Ltd. mill includes a capital allowance of \$11 000 000 for the rest of the mill; this allowance is appproximate and not based on a detailed consideration. Any detailed economic assessment would have to include an allowance for lost production associated with the downtime to make the

modifications to address the capacity limitations in other parts of the mill; this factor, which can be substantial, was not included here.

The economics are summarized in Tables 4 and 5, indicating a gross pay-back time of 3.7 years for the most optimistic situation, and 13.8 years for the less optimistic situation.

# TABLE 4 ECONOMIC SUMMARY FOR THE MOST OPTIMISTIC SITUATION



\* does not reflect possible capacity limitations in other mill equipment besides the recovery boiler and black liquor multiple-effect evaporator

\*\* does not include income tax considerations



does not include tax considerations ₩

# TABLE 5 ECONOMIC SUMMARY FOR A LESS OPTIMISTIC SITUATION

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## 8 DISCUSSION OF PROPOSED PROCESS

## 8.1 Feasibility

Based on the findings of this feasibility study and reported experience with white liquor evaporation at the Thunder Bay mill of Great Lakes Forest Products Limited, the proposed process appears to be technically feasible. The process design seems to be realistic and there are no obvious factors that would result in prohibitive operating problems. While the mass and energy balances received considerable time and attention, the results should not be viewed as the last refinement; there is still probably scope for some small improvements in process effectiveness. Similarly, further consideration and the development of missing information may point to necessary changes that could reduce the effectiveness of the proposed process.

The main economic benefit of the proposed process stems from increased recovery boiler capacity. Since little experimental mill data were available, the impact of the proposed process on recovery boiler capacity had to be estimated, based on logical consideration of calculations and related scientific information. The predictions are considered to be realistic, but it must be recognized that they are speculative. Some appreciation for the impact of dead load reduction on the recovery boiler could be gained by mill experiments involving addition of the electrostatic precipitator catch from one recovery boiler to the liquor feed on another boiler, at a mill having two or more boilers. Also, the benefits could be partially investigated by monitoring the impact of improvements in causticizing efficiency, obtained by such means as overliming, lime mud recycle, and partial countercurrent flow. However, the only clear method of establishing the recovery boiler benefits of the proposed process is to evaluate the proposed process on full scale. Until this is done, there will be some uncertainty in the quantification of the recovery boiler benefits. In this regard, modifications to the manner in which white liquor evaporation is practiced at the Great Lakes Forest Products Limited Thunder Bay mill, would be most illuminating.

The apparent economics, while not outstanding, are reasonably attractive. It must be recognized, however, that the pay-back time is almost entirely dependent on the incremental profit on extra pulp production and the installed capital cost. The pay-back time would be very mill-specific. The feasibility study capital cost estimate is considered to be realistic. During subsequent detailed design, opportunities may be identified for capital cost reduction; similarly, unforeseen factors may result in an increase in the

capital cost. Granted, the scope and complexity of the proposed process are significant disadvantages, but they are not considered to be prohibitive, in view of the significant potential benefits.

## 8.2 Process Simplification

One obvious simplification of the proposed process would be to operate with a normal green liquor strength of 110 g/L, instead of the proposed 130 g/L TTA, as Na2O, and eliminate the belt filter leacher. All the material precipitated during white liquor evaporation would go directly to the secondary recausticizing system. The advantage of the simplification is that there would be no need for a polishing filter on the white liquor clarifier overflow, or a deliquoring filter on the white liquor clarifier underflow.

However, the white liquor evaporator would have to evaporate about 25% more water; its steam consumption would increase by 25% and its capital cost would increase by about 15%. The load on the secondary recausticizing system would increase by a factor of about 4; this would be of little consequence because the present design of the secondary recausticizing system provides for considerable excess capacity from minimum standard equipment sizes which are larger than actually required for the proposed process.

The net change in the total installed capital cost with the simplification would probably be a reduction of about \$1 000 000. There would be little change in the amount of Na<sub>2</sub>CO<sub>3</sub> in the white liquor entering the digester, so the benefits to the recovery boiler would remain unchanged. The only significant disadvantage of the simplification would be increased steam usage in the white liquor and black liquor evaporators, equivalent to about 0.500 GJ/ADUt in total. For an incremental steam cost equivalent to \$1.90/GJ, this translates to about \$230 000 per year. If the incremental energy cost applied only during the winter, the cost would be about \$120 000 per year.

Without a polishing filter, there may be problems with pirssonite deposits in the white liquor evaporator. Also, the minor reduction in the formation of pitch deposits, plus the reduction in deposit formation in the digester heater, could not be expected, as these benefits would result directly from the polishing filter. Considering the incremental economics, process simplification would merit detailed assessment if white liquor evaporation were being considered as a means of dead load reduction.

# 8.3 Most Attractive Mill Situations For Application

The proposed process should be of most interest at kraft mills that are clearly limited by the capacity of the recovery boiler to incinerate black liquor. Furthermore, the recovery boiler would be limited by fireside deposit formation, and not by the recirculation rate. Under this condition, the proposed process offers a potential increase in the capacity to incinerate black liquor. For the Intercontinental Pulp Company Ltd. mill, the increase was estimated to be about 7%. However, at the other mills, the increase could be higher, because of two factors. The first factor is that the Intercontinental Pulp Company Ltd. mill is currently quite efficient with respect to the black liquor dead load, in the context of existing technology. The second factor is that for CE-type boilers, there would probably be a larger increase in the allowable organics firing rate for a given decrease in dead load, than would be the case for B&W-type boilers such as those operated by the Intercontinental Pulp Company Ltd. With a CE-type boiler, the temperature improvements would be somewhat greater than for a B&W type boiler. For coastal mills having a high concentration of NaCl in the liquor cycle, the proposed process could be extended to incorporate NaCl removal, thereby adding to the increase in recovery boiler capacity.

The proposed process also has the significant advantage that the capacity of the multiple-effect black liquor evaporator would be increased by 25%, and the boil-out frequency reduced. Where consideration is being given to additional black liquor evaporation capacity, it may be more appropriate to install white liquor evaporation.

In the past, limitations in recovery boiler capacity were rectified by installing new recovery boilers. In the future this remedy will probably be less common due to the almost prohibitive capital cost of new recovery boilers. The capital cost for the proposed process per incremental ton per day of capacity created is about 2.5 times higher than for a new recovery boiler and new black liquor evaporation system, but the minimum amount of capital needed for a new recovery boiler system is at least \$30 000 000, substantially more than for the proposed process. A smaller quantity of capital may be easier to obtain.

Incremental capacity increases of  $5$  to 20% can sometimes be obtained for existing recovery boilers by changes to the air delivery system, particularly for CE-type recovery boilers. The capital cost to rebuild the recovery boiler air systems is significant and there is a considerable loss of production while the modifications are made. In this regard, the proposed process has the advantage that it could be installed with little or no extraordinary production outage. The proposed process could also be taken off line to solve development and design problems while the mill continued to produce pulp in the normal manner.

## 8.4 Application at Great Lakes Forest Products Limited

The Great Lakes Forest Products Limited mill in Thunder Bay already has a white liquor evaporation system, which is responsible for most of the capital cost for the proposed process. Elements of the proposed process could be implemented at that mill with relatively little capital. For example, by installing a belt leaching filter and/or a secondary recausticizing system, the dead load of Na<sub>2</sub>CO<sub>3</sub> in black liquor could be reduced, thereby increasing recovery boiler capacity at that mill. Also, it would be appropriate to consider increasing the green liquor strength to reduce energy requirements for white liquor evaporation. Increasing the green liquor TTA concentration from 110 to 135  $g/L$  as Na<sub>2</sub>O would reduce the steam requirements for white liquor evaporation by about 20%.

# 9 OTHER OPPORTUNITIES FOR DEAD LOAD REDUCTION

Irrespective of the proposed process, which would reduce the dead load of Na<sub>2</sub>CO<sub>3</sub>, there are other opportunities for reducing the dead load of both Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>u</sub>.

# 9.1 Na<sub>2</sub>CO<sub>3</sub> Dead Load

For liquor strengths typical in North American mills, about 110 g/L TTA as Na<sub>2</sub>O, the equilibrium causticity is about 91%. However, causticities of about 78-82% are achieved in practice. Therefore, if the equilibrium causticity could be achieved, the dead load could be reduced by about 50%, achieving 60% of the benefits of the proposed process.

9.1.1 Overliming. Higher causticities can be obtained by increasing the lime dosage, which invariably results in settling problems in the white liquor clarifier. At many mills, the lime kiln is operated at or near its capacity, and the extra dead load of residual  $Ca(OH)$ <sub>2</sub> resulting from overliming can not be accommodated.

The settling problem could possibly be solved by adding a polishing filter on the clarifier overflow and a deliquoring filter on the clarifier underflow. The total installed capital cost for these two pieces of equipment would be approximately \$1 000 000.

The settling problems associated with increased lime dosages have traditionally been associated with the free  $Ca(OH)_2$  in the lime mud. This may not be the case. Tests at Intercontinental Pulp Company Ltd. indicate that the settling rate after the first causticizer, where there is free  $Ca(OH)_2$ , is only slightly slower than the settling rate after the fourth causticizer, where there is less free  $Ca(OH)_2$ . Also recent laboratory experimental work by Dorris (1984) on bypassing some of the green liquor around the slaker indicates that as the ratio of lime to liquor in the slaker increases, the surface area of the lime increases due to localized phenomena in the slaker; increased surface area leads to higher reactivity and reduced settling rates for the lime mud. Considering this information, the reduced settling rate observed when lime dosage is increased may actually be due to the increased ratio of lime to liquor during slaking and not the increased free Ca(OH) $<sub>2</sub>$  content of the lime mud. If this is the case, it may be possible to</sub> circumvent the settling rate restraint by recycling white liquor to the slaker when applying extra lime, to control the lime to liquor ratio at a point where the settling rate of the lime mud was adequate.

9.1.2 Recycling Lime Mud in Recausticizing. Except for the early stages, the rate of the recausticizing reaction appears to be controlled by the rate that carbonate diffuses into, and hydroxide diffuses out of the  $Ca(OH)<sub>2</sub>/CaCO<sub>3</sub>$  particles. From this perspective the residence time of the particles in the causticizers is much more important than the residence time of the liquid. Considering this, it would be appropriate to recycle the particles to increase their residence time in the causticizers. This could possibly be accomplished using a cyclonic separator on the overflow from a given causticizer, to separate a portion of the solids for recycle. A high separation efficiency would not be needed. Cyclonic separators would have the inherent advantage in that they would tend to remove larger particles for recycle, while smaller particles, that present less of a diffusion limitation, would pass on with the liquor. Cyclonic separators have been applied in isolated situations in recausticizing systems in the past, but not to facilitate lime mud recycle.

Under typical mill conditions, the solids concentration in the causticizers is about 10 wt%. It is doubtful that the solids concentration could be increased to more than 20 wt% without causing flow problems. The residence time of the particles, therefore, could at best be doubled.

In addition to increased residence for the particles, lime mud recycle has the benefit that the recycled particles would re-experience high driving forces for diffusion. Considering this and the increased residence time, lime mud recycle might add 2 to 5 percentage points to the achievable white liquor causticity, for a given lime mud settling rate.

A causticity increase of 2 to 3% might be expected with lime mud recycle, providing about 20% of the benefits of the proposed process. The capital cost for lime mud recycle would probably be about to \$200 000; compared to the proposed process, 20% of the benefits might be obtained for about 1% of the capital cost. The pay-back time for lime mud recycle would probably be about 3 months, based on the optimistic economic conditions.

9.1.3 Countercurrent Flow of Liquor and Solids in Recausticizing. Since the recausticizing reaction is mainly diffusion limited, it would be theoretically preferable to have the solids flow countercurrent to the liquor through the causticizers. With the conventional concurrent flow, when lime is readily available in the slaker, the driving force for diffusion of carbonate and hydroxide is high; however, in the last causticizers, where lime availability is restricted, the diffusion driving forces are low. With

countercurrent flow, the situation would be more favourable; where the diffusion driving forces were low, lime accessibility in the particles would be high, and where lime accessibility in the particles was low, the driving forces for diffusion would be high. Full countercurrent flow would not be necessary; it is expected that partial countercurrent flow would be adequate.

With partial countercurrent flow, it would not be surprising if something approaching equilibrium causticity (e.g., 88 to 90%) could be achieved in an existing causticizing system. This expectation is supported by the experience with two-stage recausticizing, used by some mills in the 1950's (Gillespie, 1953). By achieving equilibrium causticity, 50% of the benefits of the proposed process could be obtained. The capital cost for implementing partial countercurrent flow would probably be about \$1 000 000 to \$1 500 000, compared to the proposed process, half the benefits could be obtained for less than one-tenth the capital cost. The probable pay-back time for partial countercurrent flow would be about 6 months, based on the optimistic economic conditions.

Once equilibrium causticity is obtained via partial countercurrent flow, other measures directed at improving the recausticizing efficiency, like overliming and lime mud recycle, would have no potential and would become redundant.

9.1.4 Dilution of Green Liquor. Ahlstrom-Rosenblad Heat Engineering hold a patent on a dead load reduction process that involves causticizing at a lower than normal liquor strength (85 g/L TTA, as Na<sub>2</sub>O), to take advantage of increased equilibrium causticity at lower liquor strength (Ryham, 1982). After separating the lime mud from the liquor, the dilute liquor would be evaporated to a normal strength of about 115 g/L TTA. At 85 g/L TTA, the equilibrium causticity would be about 96%. In the Rhyham patent (1982), it is claimed that equilibrium causticity could be achieved. If this were the case, this patented process would be as effective as the proposed process involving white liquor evaporation to precipitate Na<sub>2</sub>CO<sub>3</sub> and burkeite. However, it is not clear how equilibrium causticity could be achieved, because the mere dilution of green liquor does make the attainment of equilibrium causticity any easier than is the case at normal liquor strengths.

Rieder and Ryham (1981) report the results of a laboratory investigation of the causticization of green liquor at a TTA concentration of 82 g/L, as Na<sub>2</sub>O. The laboratory conditions were intended to simulate implementation of the dilute green liquor causticization process at the Castlegar mill of Westar Timber Ltd., where the normal liquor TTA concentration is about 125 g/L, as Na<sub>2</sub>O. A causticization time of 56 minutes was used, 35% less than than normal 90 minute residence time at the normal TTA concentration. A causticity of about 82% was achieved with 82 g/L TTA and a 56 minute causticizing time, compared to about 78% for 125 g/L TTA liquor and a 90 minute causticizing time. The experimental results confirmed that higher causticities can be achieved with dilute green liquor, but equilibrium causticity was not achieved. In fact, the gap between equilibrium causticity and that obtained was about the same with the dilute green liquor, as was the case with the normal liquor strength. In the experiments, an increase in the lime mud settling rate was observed with the dilute liquor, more than enough to compensate for the 35% increase in upflow velocity in the clarifier. Therefore, the dilute green liquor process could probably be implemented without any additional equipment to complement the white liquor clarifier.

Lundberg (1982) conducted an economic analysis of the Ahlstrom-Rosenblad Heat Engineering process. He considered dilution of green liquor to a TTA concentration of 80 g/L as Na<sub>2</sub>O prior to causticizing and indicated that a white liquor causticity of 92% could be achieved. No justification was given for the 92% causticity, which is unrealistically high considering the laboratory experience of Rieder and Ryham (1981). Lundberg (1982) indicated that the dilute white liquor would be evaporated to a normal TTA concentration of  $125$  g/L as Na<sub>2</sub>O using a single-effect thermocompression evaporator. He estimated the cost of the evaporator not including instedlation costs to be about \$1 300 000. The total installed cost would probably be at least two or three times this amount, particularly considering the additional 900 kW electrical power requirements for 700 ADt/d.

The dilute green liquor process would be less complicated than the proposed process, and white liquor evaporation requirements about half. The capital cost would be less than for the proposed process because additional equipment needs appear to be limited to a single-effect thermocompression evaporator. The evaporator could be constructed from 304L ss, since the white liquor would not be evaporated past normal concentrations. However, the reduction in the dead load with the dilute green liquor process would probably be only about one-quarter of that which could be obtained with the proposed process that is the subject of this report. Furthermore, the dilute green liquor process suffers from the energy disadvantage that extra water is added to the liquor cycle, adding to the total evaporation requirements. With the proposed process, less water would be added to the liquor cycle, resulting in a reduction in the overall evaporation requirements.

# 9.2 Na<sub>2</sub>SO<sub>4</sub> Dead Load

The Na<sub>2</sub>SO $\mu$  dead load can be reduced by increasing the reduction efficiency in the recovery boiler and by minimizing the oxidation of Na2S in the recausticizing system.

The key points for maximizing reduction efficiency are as follows:

- Maximize the temperatures in the lower region of the recovery furnace.
- Minimize reoxidation of smelt on the char bed via the primary air.

After the smelt leaves the recovery boiler, most of the oxidation of Na2S that occurs in the recausticizing system normally takes place on the smelt spout and in the dissolving tank. Oxidation at this point could be minimized by restricting the infiltration of air into the smelt dissolving tank. Obvious measures include the use of a water seal on the overflow line from the smelt dissolving tank, and an effort to minimize the size of openings in the smelt spout hoods.

Methods for reducing the  $Na<sub>2</sub>SO<sub>4</sub>$  dead load are independent of those for reducing the Na<sub>2</sub>CO<sub>3</sub> dead load. Therefore, potential improvements in the Na<sub>2</sub>SO<sub>4</sub> dead load would be additive to any improvement in the  $Na<sub>2</sub>CO<sub>3</sub>$  dead load.

## 10 SUGGESTED DIRECTION FOR DEAD LOAD REDUCTION

The study of the proposed process has provided evidence and quantified benefits of dead load reduction. To obtain the benefits of the proposed process, however, a lot of equipment would have to be installed and process changes would be necessary in almost every part of the liquor cycle. Furthermore, with the current information deficiencies, some technical risk would be involved.

From an overall-industry perspective, the most logical approach for further development of the proposed process would be alteration of the process at the Thunder Bay mill of Great Lakes Forest Products Limited to incorporate the dead load reduction aspects of white liquor evaporation. This would permit evaluation of the impact of the process on the recovery boiler in a full-scale, continuous situation, and would provide a more reliable basis for quantification of the main benefits of the proposed process.

In the long-term, the complexity and the high capital cost of the proposed process may be justified by the benefits. In the short-term, while waiting for further development of the proposed process, a simpler approach is suggested involving the following:

- improving the reduction efficiency;
- minimizing the oxidation of Na<sub>2</sub>S in the recausticizing system; and
- increasing the efficiency of the recausticizing reaction to obtain white liquor causticities closer to equilibrium.

Lime mud recycle and countercurrent flow should be investigated as means of obtaining white liquor causticities closer to equilibrium; there is considerable scope for improvement, and the ideas are promising. By increasing the white liquor causticity, improving the reduction efficiency and minimizing the oxidation of Na $2S$  in the recausticizing system, part of the benefits of the proposed process could be obtained, at a small fraction of the capital cost and without process complexity. Full-scale, long-term observations could be made on the impact of partial dead load reduction on recovery boiler operation and capacity, thereby providing critical information to more accurately assess the potential of the proposed process in the long-term.

The proposed process would generally not be of interest for a new kraft mill because the most cost-effective method of creating recovery boiler capacity would be to install a larger boiler, based on conventional technology. However, if a closed cycle mill was being considered, involving white liquor evaporation for NaCl removal, it would be logical to use the proposed process to take advantage of the dead load reduction benefits.

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## RECOMMENDATIONS AND CONCLUSIONS

- 1. The proposed dead load reduction process appears to be tecdinically feasible.
- 2. The main benefit of the proposed process is the potential to increase the pulp producing capacity of a recovery-limited mill. The secondary benefits are reduced atmospheric emissions from the recovery boiler and smelt dissolving tank, reduced operational problems due to deposit formation in digester heaters and black-liquor evaporators, reduced operational problems due to pitch deposits in brownstock washing and screening systems, and slightly improved digester conditions. There may also be a reduction in the rate of deposit formation on digester extraction screens.
- 3. The proposed process would increase the maximum organics firing rate of most recovery boilers (i.e., those not limited by the steam-side recirculation rate). The extent of the increase in the organics firing rate cannot be accurately defined because no direct experimental mill data are available. However, logical consideration of calculations and related scientific information indicated a 7% increase in the maximum organics firing rate for the B&W-type recovery boiler at the Intercontinental Pulp Company Ltd. mill. Prince George, B.C.
- 4. The capacity of an existing multiple-effect black liquor evaporator would increase by about 25% with the proposed process, due to reduced evaporation requirements resulting from the use of dilute black liquor to reduce the concentrated white liquor to normed strength. Conceptually, some of the evaporation previously done in the black liquor multiple-effect evaporator would be done in the white liquor evaporator.
- 5. The proposed process would increase the equivalent storage capacity for various process liquors due to increased liquor strengths emd two new storage temks. The increased storage should translate into a small increase in the number of operating hours per year.
- 6. TRS emission from the recovery boiler would be reduced. The reduction cannot be reliably predicted due to lack of appropriate data from operating boilers, but could be as much as 50%.
- 7. Although considerable attention was given to the energy efficiency of the proposed process, its implementation at the Prince George, B.C. mill of Intercontinental Pulp Company Ltd. would result in a small increase in mill steam demand and em increase in electrical energy consumption. The mill steam demand would increase by about

0.337 GJ/ADUt in the winter and 0.106 GJ/ADUt in the summer. Electrical power consumption would increase by about 370 kW. These increases are not significant.

- 8. With a 7% increase in recovery boiler capacity, and allowing for a 1% increase in yearly operating time, there is the potential to increase yearly pulp production by 8%. For the situation at Intercontinental Pulp Company Ltd., this would result in an incremental revenue, before tax, of about \$5 200 000 per year.
- 9. Operating costs for the proposed process at Intercontinental Pulp Company Ltd., for maintenance, manpower, electrical energy, and steam would total about \$930 000 per year.
- 10. A substantial amount of new equipment would be required, as well as minor modifications to existing equipment. The total capital cost for implementation of the proposed process at the Intercontinental Pulp Company Ltd. mill would be about \$16 000 000. Depending on the mill situation, further capital investment would be required in other parts of the mill, beyond the recovery boiler and black liquor multiple-effect evaporator, to realize the production increase; this has not been reliably defined for Intercontinental Pulp Company Ltd., but is expected to be approximately \$11 000 000.
- 11. Without considering the limiting factors in the mill beyond the recovery boiler and the multiple-effect black liquor evaporator, the proposed process would have a gross pay-back time of about 3.7 years, without tax considerations.
- 12. There may be some potential to reduce white liquor consumption slightly, but it is not clear that this benefit could be realized. The heat and mass balances for the proposed process were based on no reduction in white liquor usage.
- 13. While there are some factors that would tend to reduce the dead load on the lime kiln, it is doubtful that there would be much change in the kiln dead load, except at mills where overliming is typical.
- 14. Besides the capital cost, the main disadvantage of the proposed process is the extent of the equipment modifications, plus changes to process conditions in almost all parts of the liquor cycle. Mill operation, particularly start-up would be more complicated, but not prohibitively.
- 15. Additional minor disadvantages of the proposed process would include:
	- 5 to 20% increase in the load on the recovery boiler electrostatic precipitator;
	- increased black liquor viscosity; and
- potential deposit formation in the white liquor clarifier underflow deliquoring filter cooler.
- 16. The proposed process could be simplified by accepting a reduction in energy efficiency. The most obvious simplification would reduce the total installed capital cost by about \$1 000 000, and increase mill steam costs by \$100 000 to \$200 000 per year.
- 17. Since Great Lakes Forest Products Limited already has a white liquor evaporation system in operation, the most logical approach for further development of the proposed process, from an overall-industry perspective, would be alteration of the process at the Thunder Bay mill to incorporate the dead load reduction aspocts of white liquor evaporation.
- 18. There are other opportunities for dead load reduction besides the proposed process. The option that appears to be most attractive is the implementation of simple measures to reduce the dead load of both  $Na<sub>2</sub>SO<sub>u</sub>$  and Na<sub>2</sub>CO<sub>3</sub>. The Na<sub>2</sub>SO<sub>u</sub> dead load can be reduced by improving the reduction efficiency in the recovery boiler, and reducing the oxidation of Na<sub>2</sub>S after it leaves the furnace. The Na<sub>2</sub>CO<sub>3</sub> dead load can be reduced by improving the recausticizing reaction conditions such that white liquor causticities closer to the equilibrium value are obtained.
- 19. Two new concepts for achieving higher white liquor causticities are the recycle of lime mud to increase the solids residence time in the recausticizers, and partial countercurrent flow in recausticizing.
- 20. With lime mud recycle a causticity increase of 2 to 3% might be expected, providing about 20% of the benefits of the proposed process. The capital cost would probably be about \$200 000, and the pay-back time would be about 3 months.
- 21. With partial countercurrent flow, it would not be surprising if something approaching equilibrium causticity (e.g., 88 to 90%) could be achieved in an existing causticizing system. By achieving equilibrium causticity, 50% of the benefits of the proposed process could be obtained. The capital cost for implementing partial countercurrent flow would probably be about \$1 000 000 to \$1 500 000. The payback period would be about 6 months.
- 22. The study of the proposed process has demonstrated that dead load reduction has attractive benefits. In the long-term, the complexity and the high capital cost of the proposed process may be justified by the benefits. However, in the short-term, the simple approach of improving white liquor causticity, improving the reduction

efficiency and minimizing the oxidation of Na<sub>2</sub>S in the recausticizing system is suggested; part of the benefits of the proposed process could be obtained, at a small fraction of the capital cost, and without process complexity. In particular, the new concepts of lime mud recycle and partial countercurrent flow in recausticizing should be pursued.  $\hat{\mathcal{E}}$ 

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APPENDIX PROJECT MEMORANDA

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#### APPENDIX - PROJECT MEMORANDA

Twelve Memoranda were prepared on various aspects of the project. Eight of the Memoranda addressed some part of the kraft liquor cycle (e.g., recausticizing). These memoranda review the important chemical and physical process factors related to the part of the liquor cycle under consideration, and the impact of the proposed process on that part of the liquor cycle (e.g., on recausticizing). The Project Memoranda are as follows:

### IP-29a - Recausticizing

- review of recausticizing chemistry
- 93 pages, 118 reference citations (V5350/1)

# IP-29b - Secondary Recausticizing

- discussion of factors related to the leaching process emd the secondary recausticizing system
- 18 pages, 12 reference citations (V5350/2)

# IP-29c - White Liquor Evaporation Crystallization Technology

- description of the experience at the Thunder Bay mill of Great Lakes Forest Products Limited with white liquor evaporation
- discussion of related scientific information emd related new developments
- discussion of possible integration of white liquor evaporation with black liquor evaporation and with flash steam from the digester to save steam
- 38 pages, 33 reference citations (V5350/3)

# IP-29d - Pulping

- brief summary of digester chemistry relevant to the proposed process
- calculations for different methods for quantifying the organic to inorganic ratio in liquor
- review of information related to recycling black liquor to the digester
- 25 pages, 38 reference citations (V5350/4)

### IP-29e - Brownstock Washing

- brief discussion of washing fundamentals
- discussion of available information on the relative washing efficiency for organics and inorganics
- review of factors affecting pitch formation
- 22 pages, 36 reference citations (V5350/5)

# IP-29f - Scaling of Digester Heaters and Black Liquor Evaporators

- review of factors affecting deposit formation
- 30 pages, 49 reference citations (V5350/6)

# IP-29g - Black Liquor Evaporation

- review of factors affecting boiling point elevation and viscosity of black liquor
- heat balances for existing situation and proposed process
- 42 pages, 49 reference citations (V5350/7)

# IP-29h - Recovery Boiler

- review of factors affecting fireside deposit formation
- discussion of factors affecting heat transfer in the furnace
- the importance of high temperatures in the lower portion of the furnace
- 83 pages, 85 reference citations (V5350/8)

# IP-29i - Mass and Energy Balances

- details of mass and energy balances for the existing situation and the proposed process
- E-sized sheets, one for the proposed process and one for the existing situation, with the flow sheet at the top (e.g., Figure 2) and the matrix of data at the bottom (e.g., Figure 4), providing all the information on one sheet
- 10 pages (V5350/9)

# IP-29j - Preliminary Design

- detailed description of the proposed process
- 11 pages (V5350/10)

### IP-29k - Capital Cost Estimate

- details emd basis for the capital cost estimate
- 9pages (V5350/11)

### IP-291 - Process Economics

- integration of capital cost, operating costs and savings, to quantify economic feasibility
- 6 pages (V5350/12)

These project memoranda are available in limited quantity as unpublished documents from the Environmental Protection Service, Environment Canada, Ottawa, Ontario, KIA 1C8.

A review of recovery boiler chemistry, intended as a companion document to Project Memorandum V5350/8, is available from:

> Sandwell and Company Limited Librarian 1550 Alberni Street Vancouver, B.C. V6G 1A4