# **Report for 2004TX152B: Development of Optimal Water Conservation and Management Strategies for Industrial Facilities**

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Report Follows

# AN INTEGRATED APPROACH TO THE OPTIMIZATION OF WATER USAGE AND DISCHARGE IN PULP AND PAPER PLANTS

Report by

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# a] Research that has been done so far

This research has been aimed at developing a systematic methodology for the cost-effective reduction of water usage and discharge in pulp and paper plants. As the industry moves towards increased system closure, the build-up of non-process elements (NPEs) leads to serious consequences on the process equipment. In response, this research has achieved the following:

- A mathematical model to track water and primary NPEs throughout the pulping process.
- Rigorous targeting for water usage and discharge.
- A systematic framework for water reduction using mass integration strategies including no/low cost techniques as well as capital-based techniques.
- An optimization model for the optimization of allocation, recycle, and separation of aqueous streams.

These mathematical models and allocation strategies have been coded into a computer-aided tool using LINGO programming platform. The program can be readily modified to address a variety of cases. In order to demonstrate the applicability of the developed tools, a case study has been addressed. Furthermore, this research provides a generic framework that can be effectively utilized by industry to develop cost-effective water management strategies and to identify critical research needs.

# b] Any preliminary insights on what the study findings suggest

- The research has yielded the following useful insights:
- Water conception in pulp and paper mills may be reduced by more than 75% while providing value-added solutions (based on the savings in water usage, reduction in wastewater treatment, reduction in chemical usage, and debottlenecking).

- As the extent of water recycle increases, small quantities of impurities begin to accumulate. If gone un-resolved, those impurities can lead to the total failure of the process.
- There are multiple technologies to remove impurities but they have vastly different economics. Process integration provides a unique and systematic approach to screenings these alternatives and determining the optimal solutions.
- Optimum solution strategies involve a combination of in-process modifications and recycle/reuse alternatives.

# c] Papers in progress [please attach them]

Lovelady, E. M., M. M. El-Halwagi, and G. Krishnagopalan, "An Integrated Approach to the Optimization of Water Usage and Discharge in Pulp and Paper Plants", Int. J. of Environ. and Pollution (IJEP), (2005, in press). For a copy, please see **Appendix I.** 

# d] Presentations made [please attach them]

N/A

# e] Awards given to the student

Graduate Education for Minorities (GEM) Fellowship NASA/Texas Space Grant Consortium (TSGC) Fellowship

# f] How the research has led to further grants or expanded ongoing research programs

Two research grants have been secured based on Ms. Lovelady's work: one from NASA (to apply water integration techniques to conserve resources in planetary habitation missions) and one from the EPA's Gulf Coast Hazardous Substances Research Center (GCHSRC) to develop process integration tools to reduce environmental emissions of chemical, petroleum, and petrochemical plants.

# g] An overview of how much of the grant has been spent and how it was expended

The grant has provided stipend, tuition, and fees to Ms. Lovelady.

### **APPENDIX I**

# AN INTEGRATED APPROACH TO THE OPTIMIZATION OF WATER USAGE AND DISCHARGE IN PULP AND PAPER PLANTS

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### International Journal on Environment and Pollution (IJEP), in press (2005)

**Abstract-** This paper is aimed at developing a systematic methodology for the cost-effective reduction of water usage and discharge in pulp and paper plants. As the industry moves towards increased system closure, the build-up of non-process elements (NPEs) leads to serious consequences on the process equipment. In response, this paper achieves the following:

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### INTRODUCTION

Pulp and paper mills have historically been one of the major consumers of water since large amounts are needed for washing, bleaching, and processing. Slowly, mills began to close the water loop and reduce effluent discharge by looking for ways to reduce, reuse or recycle water streams in order to comply with environmental regulations. Between 1975 and 1995, water consumption in the US pulp and paper industry decreased from 27000 gal/ton of product to 16,000 gal/ton of product (Patrick, 1994). This huge consumption along with its economic burden and environmental impact underscores the need and potential for more aggressive water reduction strategies.

Indeed, recently there has been a growing demand in the pulp and paper industry to adopt waste minimization strategies in order to create a minimum impact mill. A minimum impact mill, or MIM, does not strictly mean a zero-discharge mill, but rather one which either has no discharge or whose effluent discharge has a minimum or no impact on the environment. The MIM makes optimal use of its raw materials, reduces air emissions, water usage, waste generation, and is a net producer of electricity (Elo, 1995). The need for MIM's in the pulp and paper industry can be summarized as follows (Nguyen, 1995):

- To eliminate the discharge of undesirable compounds, such as organic halides, to receiving waters
- To reduce or eliminate the cost of waste water treatment, which is currently \$1.5 \$5/ton of pulp
- To eliminate fresh water use, as there is currently a shortage of fresh water
- To reduce the cost of water use (\$5/ton pulp) and energy use
- To meet increasing demands for environmentally friendly products

In order to achieve a minimum impact mill, it is desirable to partially or completely close the water loop of the process. System closure will result in the accumulation of non-process elements (e.g. Al, Si, K, Cl, Mg, Mn), suspended solids, dissolved solids, and other pollutants in the closed water system. This buildup will result in increased equipment corrosion, detrimental plugging, problematic scaling, and deposit formation, and can adversely affect the papermaking process.

The traditional solution to waste minimization has involved simple in-plant modifications and end-of-pipe treatment systems. However, these modifications fall short of providing cost-effective solutions to the industry. What is needed is a comprehensive, generic approach to waste minimization which is applicable to a wide variety of solid, liquid and gaseous wastes and which would incorporate economics, reliability and product quality along with maximizing the use of already available process internal resources. Over the past decade, a new methodology has been developed which is capable of systematically minimizing waste and improving overall process efficiency. This approach, known as mass integration, involves the optimal allocation of species throughout the process utilizing four main strategies: stream mixing/segregation, recycle/reuse, unit manipulation, and interception.

A typical kraft pulp and paper mill with an ODEDED bleaching sequences has been the model for this case study. The overall objective is to optimize water usage, reduce discharge, reduce solid waste and debottleneck the process to improve overall production and yield. To achieve this, a global understanding of the mass flow within the process is needed to provide insight as to how to minimize waste.

As a result of legislation, pulp and paper mills have taken steps to create a Minimum Impact Mill (MIM). A minimum impact mill is one that will meet the following objectives (Nguyen, 1995):

- To eliminate the discharge of harmful material to receiving waters
- To reduce or eliminate the cost of waste water treatment
- To meet increasing demands for environmentally-friendly products
- To reduce the cost of water and energy

Towards this end, mills have done work in applying simple modifications and good housekeeping approaches that can be quickly implemented without much cost (Mehta, 1996). Their impact, however, is quite limited. As mills strived to achieve high-levels of water recycle, a new problem arose; the build-up of non-process elements. Non process elements (referred to as NPE's from hereon) are those elements that do not take part in the delignification process of wood. In an open mill, the presence of NPEs is not important since they are purged naturally from the system in the product, bleach plant effluent, black liquor losses, recovery boiler flue gas, dregs, grits, lime kiln flue gas, and lime mud purges. In a closed mill, however, many of these outlets are no longer available. These NPEs will begin to build up and can have a number of adverse effects on process equipment such as corrosion of the recovery boiler, sticky deposits on the evaporator tubes, and scale formation in the digester. Non-process elements can be divided into two categories: those that accumulate in the sodium cycle and those that accumulate in the calcium cycle. Most NPE's will accumulate in either cycle to some degree but their accumulation factor and effect on process equipment will differ. In an open cycle, NPE accumulation is low due to chemical and liquor losses that acted as natural purges. As mills approach closure and these natural purges disappear, NPE's will build up in the sodium and calcium cycle in the following manner (from most to least) (Galloway, 1994):

Sodium Cycle: K > Cl > Al > Fe > Si > Mn > Mg > CaCalcium Cycle: Mg > Al > Fe > Mn > Si > Na > K > S > Cl

Though accumulation of most NPE's will have adverse effects on process equipment and chemical reactions, three NPEs stood out as major offenders: potassium, chloride, and sodium. As a result, the rest of this work will focus on these three NPEs.

Potassium and chloride have the greatest tendency to accumulate in the sodium cycle. Both NPE's can be found in higher concentrations in the recovery boiler fumes (Jordan, 1996). Chloride and potassium compounds, such as NaCl, KCl, and KOH, have high vapor pressures. In the recovery boiler, these compounds can volatilize from the smelt bed into the dust stream and be carried over to the upper furnaces. These particles will condense and form deposits on the cooler boiler tubes of the upper furnace, which results in tube plugging (Jordan 1996). This leads to a unit downtime since the recovery

boiler will need to be shut down for cleaning. NaCl also causes severe corrosion of the superheater tubes and black liquor evaporators. In addition, accumulation of all these compounds will accelerate equipment corrosion and cause ring formation in the lime kiln. Failure to account for the buildup of NPEs can have serious consequences. Indeed, the first major attempt at achieving a closed cycle mill in Thunder Bay, Ontario (Isbister, 1979; Pattyson, 1979; Galloway, 1994) was discontinued in 1985 with the primary reason attributed to the buildup of NPEs that caused severe corrosion, deposits, and scaling problems. This failure and other incidents underscore the need for a comprehensive, generic approach to water reduction that is based on integrating the various units, streams, and species within the process. This approach should also incorporate economics, reliability and product quality issues along with maximizing the use of already available process internal resources.

Over the past decade, a new methodology has been developed which is capable of systematically minimizing waste discharge and fresh-resource consumption while improving overall process efficiency. This holistic approach is known as mass integration. It provides a fundamental understanding of the global flow of mass within the process and employs this understanding in identifying performance targets and optimizing the allocation, separation, and generation of streams and species. Various process objectives such as pollution prevention, debottlenecking, and resource conservation can be systematically tackled through mass integration. For an overview of the subject and application, the reader is referred to review literature (e.g.; El-Halwagi 1997, 1998; El-Halwagi and Spriggs 1998, Bedard, 2001; Kuofos, 2001; Stuart, 2002; Paris, 2003).

### **PROCESS DESCRIPTION**

Consider the Kraft pulping process shown in Figure 1. The wood chips and the white liquor (composed primarily of NaOH and Na<sub>2</sub>S) are fed into a continuous digester. The cooked pulp undergoes brown stock washing in which the pulp is separated from the residual liquor in a series of countercurrent vacuum drum washers. Following brown stock washing, the pulp is screened and cleaned. After brown stock washing, the residual cooking liquor, also known as weak black liquor, is concentrated to strong black liquor through a series multiple effect evaporators and concentrators. This strong black liquor is burned in a recovery boiler in order to reduce oxidized sulfur compounds to sulfide, burn the organic chemicals, recover the heat of combustion as steam, and recover the inorganic chemicals (known as smelt) which will be used to regenerate the cooking liquor. The flue gas from the recovery furnace, which contains particulate matter such as Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub>, goes to an electrostatic precipitator, where these dust particles are removed from the flue gas and can be returned to the strong black liquor system.



Fig. 1 A Schematic Representation of the Kraft Pulping Process

The smelt from the recovery furnace is composed primarily of Na<sub>2</sub>S, Na<sub>2</sub>CO<sub>3</sub> and some Na<sub>2</sub>SO<sub>4</sub>. Weak wash liquor from lime mud and dregs washing is used to dissolve the smelt and form green liquor. The green liquor is clarified to remove any undissolved materials (known collectively as dregs) such as unburned carbon and inorganic impurities. The dregs are then washed to remove any sodium compounds and then discarded. The clarified green liquor and reburned lime are fed to a slaker, where the lime and water react to form slaked lime:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Any grits (unreactive lime particles and insoluble materials) are removed via a clarifier contained in the slaker. White liquor is then formed by the causticizing reaction between the slaked lime and sodium carbonate

$$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$$

Much of the causticizing takes place in the slaker before flowing to the causticizer. The white liquor is sent to a clarifier to remove lime mud,  $CaCO_3$  formed in

the causticizing reaction, unreacted  $Ca(OH)_2$ , and any inert material before it is returned to the digester. The lime mud from the white liquor clarifier is washed to remove entrained alkali and sent to the lime kiln where the lime mud is converted to reburned lime for use in the slaking reaction. The filtrate from the lime mud and dregs washing is known as weak wash liquor and used to dissolve the smelt leaving the recovery furnace.

# **PROBLEM STATEMENT**

The problem to be addressed can be stated as follows:

Given a typical Kraft pulping process, it is desired to develop cost-effective strategies for the reduction of water discharge from the mill. Any water reduction objectives will entail the use of recycle; consequently, various species will build-up, leading to operation problems. To alleviate the detrimental effect of build-up, comprehensive mass integration strategies are required to provide answers to the following questions:

- What are the rigorous targets for reduction in water usage and discharge?
- Which streams need to be recycled? To which units?
- Should these streams be mixed or should mixing be avoided?
- What load should be removed by interception devices?

# APPROACH

In order to address the abovementioned problem, the following critical tasks must be undertaken:

• A simulation model should be developed to track water and the targeted NPEs throughout the process. The model should allow simulation for the modeling case as well as the process after.

### DEVELOPMENT OF SPECIES TRACKING MODEL

In developing a model to track the various species of interest, it is necessary to strike the right balance in details. A too-detailed model cannot be readily incorporated into the process integration and optimization framework and will negatively impact the effectiveness of the optimization computations. On the other hand, a too-simplified model cannot describe the process with high fidelity and may not capture critical aspects of the process is the "path diagram equation" (El-Halwagi et al., 1996; Noureldin and El-Halwagi, 1999). It is a mass integration tool whose objective is to track targeted species (e.g., NPEs and water) as they propagate throughout the process and provides the right level of details to be incorporated into a mass integration analysis. A typical form of the path equations is to describe outlet flows and compositions from each critical unit as a function of inlet flow, inlet compositions, and appropriate design and operating parameters.

# CASE STUDY

The base-case data and assumptions for the case study are given in the Appendix. The model development and details are also shown in the Appendix. The resulting model consists of a set of nonlinear equations which may be solved simultaneously using the software LINGO.

The LINGO program was run on a PC Pentium II with a convergence time of 3 seconds. The results are shown in Appendix I and are illustrated in Fig. 2.



Fig. 2. Solution to Nominal Case Study (all numbers are in tons per day)

### TARGETING FOR OPTIMIZATION OF WATER USAGE AND DISCHARGE

#### **Overall Water Balance**

Before proceeding to determine the optimal strategies for water management, it is insightful to determine maximum targets for reduction in fresh water usage and discharge. We start with the nominal material balances shown in Figure 2. Based on these results, the overall water balance can be determined.

We now turn our attention to the water balance for streams that include fresh water usage of the discharge of recyclable water streams. Fig. 3 depicts the four fresh water streams currently used ( $S_2$ ,  $S_6$ ,  $S_{24}$ , and  $S_{33}$ ). By adding up the flowrates of these streams, the total usage of fresh water is 52,197 tons per day. The figure also shows the potentially recyclable wastewater streams ( $S_8$ ,  $S_{10}$ ,  $S_{12}$ , and  $S_{37}$ ). Based on these streams, the total flowrate of water that may be potentially recycled is 42,365 tons per day. If all the recyclable water is intercepted and cleaned up till their contents are acceptable to be used in lieu of fresh water and if self recycle (reuse of wastewater from a unit in the same unit after cleanup), then the target for fresh water usage can be calculated as follows:

Target for minimum water consumption = 52,197 - 42,365 = 9,832 tons per day (1)

These results are schematically illustrated in Fig. 4. Also, by adding up the flowrates of the water streams leaving the process except the recyclable streams ( $S_8$ ,  $S_{10}$ ,  $S_{12}$ , and  $S_{37}$ ) and water in the produced pulp ( $W_{35}$ ), we get a target for wastewater discharge to be 1,669 tons per day.



Fig. 3. Fresh and Recyclable Water Streams



# Fig. 4. Determination of Target for Minimum Fresh Water Consumption

# Water Targeting without Self-Recycle

A particularly important constraint is recycle without self-recycle. In some cases, it is forbidden to recycle effluent to the same unit to be used in lieu of fresh water. Several reasons can cause this limitation including the following:

- To prevent the accumulation of certain impurities that will build up in a flow loop.
- To avoid dynamic instabilities that may arise as a result of high interconnection between output (effluent) and input (recycled effluent replacing fresh water)
- To enhance process reliability by disengaging the dependence of input (recycled water) from output (effluent).

If self-recycle is not allowed, then the minimum water target may not be attained even if interception is used to clean up the recycled water. For practical reasons, we will consider the use of an interception device. For the case study, we also assume that the bleach plant can only accept water without any dissolved solids (e.g., same quality as the stripper water leaving the multiple effect evaporator or the concentrator). Let us calculate the new target without self recycle with one interceptor for two cases:

- Interception of bleach plant effluent (S<sub>37</sub>)
- Interception of screening effluent (S<sub>8</sub>)

In the case of intercepting  $S_{37}$ , the flow of  $W_{37}$  (30,990 tpd) is high enough to provide all the need for fresh water in the pulping process. Hence the target for fresh water in pulping is zero. As for the bleach plant, only the effluent from the multiple effect evaporator ( $W_{10} = 8901$ ) and the concentrator ( $W_{12} = 1024$ ) can be used to replace fresh water. Hence the target for fresh water usage in the case of no self-recycle with one interceptor applied to the bleach plant effluent is calculated through equation 2. These results are shown in Fig. 5

Water target 
$$= 30,990 - 8,901 - 1,024 = 21,065$$
 tpd (2)



# Fig. 5. Minimum Water Target without Self Target while Intercepting Bleach Plant Effluent

The same approach can be adopted for estimating the minimum-water target for the case of no self-recycle while intercepting the screening effluent. Assuming that the quality of the bleach plant effluent is acceptable for direct recycle to the pulping process, we can recycle 21,207 to replace all the fresh water used in pulping. We can also replace a portion of the fresh water needed for bleaching with the effluent from the multiple effect evaporator, the concentrator and intercepted screening effluent. Hence, in this case, the water target is calculated in equation 3. These results are shown in Fig. 6.

Water target = 30,990 - (1,450 + 8,901 + 1,024) = 19,615 tpd (3)



# Fig. 6. Minimum Water Target without Self Target while Intercepting Screening Effluent $(S_8)$

# **Need for Detailed Strategies**

The aforementioned discussion indicates that there is a significant potential for reducing fresh water usage from 53,194 tpd to 9,832 tpd. How do we determine the detailed strategies that can attain this target (Fig. 7)? Mass integration strategies should be employed to determine optimal ways of reaching this target. This will be the subject of the next section.



Fig 7 Water Impact Diagram

### DEVELOPMENT OF MASS INTEGRATION STRATEGIES

# **Overall Approach**

In order to develop solution strategies to the problem of optimizing water allocation in a pulping process, it is necessary to coordinate two important activities in tandem: process integration and process simulation. As shown in Fig. 8, process integration techniques can handle process objectives, data, and any requirements or constraints. The application of process integration provides performance targets, solution strategies, and proposed changes to the process. As a result of these changes, the process performance must be reassessed using process analysis or simulation (such as the aforementioned modeling equations, etc). The use of process simulation enables the update of flowrates and compositions throughout the process. By closing the information loop of integration and simulation, it is ensured that the developed insights and solution strategies activities are refined and validated.



### **Fig. 8.** Coordination of Process Integration and Simulation

Since water and NPEs, mass integration techniques constitute the primary focus of the needed process integration tools. The first step in creating a mass integration model is the development of a mass allocation representation of the process from a species viewpoint. For each species there are sources and sinks. Sources can be defined as any stream that has the desired species (e.g., water) in it and sinks are any stream or unit that can accept the species. For our case, the *sources* are recyclable water streams and the *sinks* are the various units that consume fresh water. Each source, I, has a flowrate denoted by  $L_I$  and  $N_{ions}$ . The composition of each ion (NPE) is referred to as  $y_{ion,I}$ . The index for ions is referred to as ion and it ranges from 1 to  $N_{ions}$  where ion is Cl, K, Na, etc.

The overall objective of mass integration is to provide maximum utilization of water while satisfying all process requirements and constraints. In other words, what is the best scheme to allocate the water and deal with NPEs? As can be seen in Fig. 9., mass integration seeks to identify optimum allocation of water streams from sources to sinks. The integration strategies include segregation and mixing of streams, assignment to units, and adjustment of NPE content using interception (e.g. separation) devices that employ mass and energy separating agents. The following analysis shows how these solution strategies can be developed.

Consider a number  $N_{sinks}$  of process units (sinks) that employ fresh water which are designated by the index j, where j ranges from 1 to  $N_{sinks}$ . For the j<sup>th</sup> sink, there are two sets of constraints on flowrates and compositions:

$$W_j^{\min} \le W_j \le W_j^{\max} \qquad j=1,2,\dots, N_{\text{sinks}}$$
(4)

where  $W_i$  is the water flowrate entering the  $j^{th}$  sink.

$$Y_{ion,j}^{\min} \le Y_{ion,j} \le Y_{ion,j}^{\max} \qquad j=1,2,\dots, N_{sinks} \text{ and } ion=1,2,\dots, N_{ions} \qquad (5)$$

where Y<sub>ion,j</sub> is the composition of a certain NPE (indexed ion) entering unit j.



# Fig. 9. Mass Integration Framework for Water Allocation (El-Halwagi, et.al. 1996)

We now move to the source side. Each source, i, is split into  $N_{sink}$  fractions that can be assigned to the various sinks (Fig. 10). The flowrate of each split is denoted by  $l_{i,j}$ .



Fig. 10. Splitting of Sources

Next, we examine the opportunities for mixing these splits and assigning them to sinks. Figure 11. shows the mixing of the split fractions into a feed to the  $j_{th}$  sink.



Fig. 11. Mixing of Split Fractions and Assignment to Sinks

### **Direct Recycle/Reuse**

It is instructive to first consider direct recycle/reuse of wastewater streams. This refers to the allocation of wastewater streams to process units without the use of new equipment to intercept and remove NPEs. This situation is important when no capital investment is to be spent on new equipment. The structural representation of this no/low cost strategy is shown in Fig. 12. Each split flowrate  $l_{i,j}$  does not have to perfectly match the sink requirement. It can be mixed with other split flows or water to match the sink requirements. This mixing (represented in Fig. 12) must satisfy the sink constraints given by Eqs. (4) and (5).



# Fig. 12. Direct Recycle/Reuse Source-Sink Assignment Problem (No/Low Cost Solution)

The following constraints represent the material balances associated with the splitting and mixing operations:

Splitting of the <sup>th</sup> source:

$$L_i = \sum_{j=1}^{N_{\text{sinks}}} l_{i,j}$$
 where n = 1,2, ..., N<sub>sources</sub> (6)

Mixing for the j<sup>th</sup> sink:

$$W_{j} = FreshW_{j} + \sum_{i=1}^{N_{sources}} l_{i,j}$$
 where j = 1,2, ..., N<sub>sinks</sub> (7)

where  $FreshW_j$  is the amount of fresh water fed to the  $j^{th}$  sink.

$$W_{j} * Y_{ion, j} = \sum_{i=1}^{N_{sources}} l_{i, j} * y_{ion, i}$$
  
where j = 1,2, ..., N<sub>sinks</sub> and ion = 1,2, ..., N<sub>ions</sub> (8)

### **Optimization Formulation for Direct Recycle**

In order to solve the above-mentioned assignment problem systematically, it is useful to formulate the task as an optimization problem. A theoretical model is formulated based on the structural representation of the problem to account for mass balances and assignment of sources to sinks. The objective function is to be fresh water used in the process. The objective function can be mathematically represented as:

Minimize flowrate of fresh water via direct recycle =  $\sum_{j=1}^{N_{sinks}} FreshW_j$ 

This objective function can be readily modified to accommodate other objective functions.

Subject to the following constraints: Flowrate to each sink

$$W_i^{\min} \le W_i \le W_i^{\max}$$
 j=1,2,..., N<sub>sinks</sub>

NPE content in feed to each sink:

$$Y_{ion,j}^{\min} \le Y_{ion,j} \le Y_{ion,j}^{\max}$$
  $j=1,2,\ldots, N_{sinks}$  and ion =1,2,..., N<sub>ions</sub>

$$L_i = \sum_{j=1}^{N_{\text{sinks}}} l_{i,j}$$
 where n = 1,2, ..., N<sub>sources</sub>

Mixing for the j<sup>th</sup> sink:

$$W_j = FreshW_j + \sum_{i=1}^{N_{sources}} l_{i,j}$$
 where j = 1,2, ..., N<sub>sinks</sub>

Component material balances for the NPEs

$$W_j * Y_{ion, j} = \sum_{i=1}^{N_{sources}} l_{i, j} * y_{ion, i}$$
, where j = 1,2, ..., N<sub>sinks</sub> and ion = 1,2, ..., N<sub>ions</sub>

Non-negativity of each fraction of split sources:

$$l_{n,j} \ge 0$$
 where n = 1,2, ..., N<sub>sources</sub> and j = 1,2, ..., N<sub>sinks</sub>

Finally, since the various sources are interconnected and will be affected when fresh water is replaced with recycled water, it is necessary to include a simulation model to track the changes for the NPEs throughout the process. This is consistent with the philosophy summarized by Fig. 8. Hence, we include the path equations developed in Chapter Five in the mathematical formulation.

This optimization program can be solved using software LINGO to identify the minimum consumption of fresh water, the optimal allocation from each source to each sink, and the new steady state after these changes are implemented. Appendix II shows the detailed formulation for the case study along with the solution obtained from LINGO software. Again, this is a general purpose formulation that can be readily modified to address other case studies or specific mills.

In the case study, we have four recyclable sources: wastewater from screening, multiple effect evaporator, concentrator, and, bleach plant effluent. Also, fresh water can be used at minimum consumption. There are four sinks that employ fresh water: screening, brown stock washer, washers/filters and the bleach plant. Figure 13. shows the assignment representation for the case study. In our case study, no self-recycle is allowed (i.e., effluent from a unit cannot be used in the same unit to replace fresh water). This constraint (done by assigning a zero flow from sink to unit) is placed to ensure practical operation and to reduce control problems. It is further assumed that the bleach plant can only accept demineralized water.

Sources

Sinks



Fig. 13. Assignment Representation for the Case Study

Our objective is to minimize the usage of fresh water in the four sinks subject to the process constraints. The primary constraint on the buildup of NPEs is associated with the "stick temperature" for the recovery furnace. It can be related to the Cl, K, and Na through the following constraints:

$$\frac{K_{11} + K_{16} + K_{18}}{39.1} \le 0.1 \frac{N_{11} + N_{16} + N_{18}}{23}$$
(7.8)

$$\frac{C_{11} + C_{16} + C_{18}}{35} \le 0.02(\frac{N_{11} + N_{16} + N_{18}}{23} + \frac{K_{11} + K_{16} + K_{18}}{39})$$
(7.9)

where C<sub>i</sub>, N<sub>i</sub>, and K<sub>i</sub> are the ionic loads of Cl, Na, and K (respectively) in the i<sup>th</sup> source.

The results are illustrated in Fig. 14.



Fig. 14. Optimum Solution for Direct Recycle/Reuse (all flows are in tons per day)

As can be seen from Fig. 14, the fresh water consumption is now reduced to 40,123 tons per day. This is a 23% reduction from the nominal fresh water usage of 52,197 tons per day. The solution is a direct recycle/reuse which requires piping and

pumping but involves no capital investment for new processing units. Another advantage of the developed mathematical program is its ability to generate alternative solutions.

### **Interception Problem**

The minimum fresh water targets when interception is employed have been determined earlier. It is important to identify the interception tasks that can lead to such targets. Typically, the cost of an interceptor of a specific stream is monotonically increasing with the load to be removed. Hence, our objective will be to minimize the NPE load to be removed from the intercepted stream so as to reach the minimum water target. Since we are considering three NPEs, we will solve the program three times (one per ion). Therefore, we formulate an optimization program whose objective is to minimize the load of the NPE to be removed from the intercepted stream. The formulation can be described as follows:

Minimize Load of NPEs to be removed from targeted species

Subject to:

- Desired water target
- Path equations for tracking water and NPEs
- Recycle model
- Interception equations
- Constraints on units

For instance, in order to reach the water usage target of 21,065 (shown in Fig. 15), 8.997 tpd of Cl must be removed from the bleach plant effluent. The same procedure can be repeated for removing NPEs from any source. After all single-interception solutions are exhausted, the rest of water reduction strategies will have to include new technologies that enable self recycle and may involve the use of hybrid interception devices. For each intercepted stream, the same optimization model can be used to determine the task of the new technology. The specific nature of this new technology is not known yet. However, its task has been determined. This is a valuable finding that defines needed research to be carried out. Figure 16 shows the water impact diagram for the case study.



Fig. 15 Schematic Representation for Revised Flowsheet with Interception of Bleach Plant Effluent



Fig. 16. Water Impact Diagram for the Case Study

### CONCLUSIONS

This work has developed a comprehensive framework for the systematic management of water and non-process elements pulp and paper plants. Specifically, this research has achieved the following:

- Process simulation: In order to track water and the NPEs throughout the process, a mathematical model has been developed to simulate the performance of a typical kraft bleached process under nominal conditions. Algebraic equations have been developed based on conservation laws, literature values, and judicious assumptions. The model has the capability of simulating the process under nominal conditions as well as after changes recommended by mass integration.
- Targets: Based on mass-integration strategies, rigorous targets have been developed for minimum feasible water usage and discharge.

Solution strategies: Based on mass integration techniques, various strategies have been recommended to attain the targets. These strategies include no/low cost techniques as well as capital-based techniques. To extend the applicability of this work, a mathematical programming code has been developed and implemented for the optimization of allocation, recycle, and separation of aqueous streams. This program has been coded into LINGO platform. The program can be readily modified to address a variety of cases. In order to illustrate the usefulness and applicability of the developed framework, a case study has been solved. The results demonstrate that for a typical kraft mill, significant reduction in water usage can be achieved. For the selected case study, 23% reduction in water usage can be achieved using simple recycle/reuse strategies. When interception is added to recycle/reuse, 62% reduction in water usage can be achieved. Finally, when new technologies are developed for removal of NPEs, 81% reduction in water usage can be accomplished. Although the work here does not specify the exact nature of these new technologies, it defines what tasks must be undertaken by these technologies and points out the research needed to reach this target.

In addition to developing specific solution strategies systematically, this work shed insightful light on the integrated nature of the task of managing water and NPEs. It also provides an easy-to-modify platform, which can be effectively utilized to address a wide variety of water-conservation objectives in pulp and paper plants.

# REFERENCES

Ahlers, P., Norrstrom, H. and B. Warnqvist. 1978. "Chlorides in Kraft Recovery: Effects on Process Equipment" *Pulp & Paper Canada* 79(5): 63 – 66.

Bedard S, Sorin M, and C. Leroy. 2001. "Application of process integration in water reuse projects - It gives process engineers another tool to reduce water use." *Pulp & Paper Canada* 102 (3): 53-56.

Biermann, C.J. 1996. Handbook of Pulping and Papermaking. 2<sup>nd</sup> Ed. Academic Press.

Brown, D., Maréchal, F., and J. Paris. 2005. "A Dual Representation for Targeting Process Retrofit, Application to a Pulp and Paper Process." Applied *Thermal Engineering* (25): 1067 – 1082.

Bryant, P.S., L.L. Edwards and K. Robarge. 1993. "Transition-Metal Profiles in Open and Closed Kraft Fiber Lines." *Tappi Journal*. 76 (10): 148 – 159.

Dogan, I and A. Güniz Gürüz., 2004. "Waste Minimization in a Bleach Plant." *Advances in Environmental Research* (8): 359 – 369.

El-Halwagi, M.M. and H.D. Spriggs. 1996. "An Integrated Approach to Cost and Energy Efficient Polllution Prevention" *Proceedings of Fifth World Congr. Of Chem. Eng.* 3:344-349. San Diego.

El-Halwagi, M.M. and H.D. Spriggs. 1998 Solve Design Puzzles with Mass Integration." *Chem. Eng. Prog.* 94(8): 25-44.

El-Halwagi, M.M. 1997 *Pollution Prevention Through Process Integration: Systematic Design Tools.* 1<sup>st</sup> Ed. Academic Press. San Diego.

El-Halwagi, M. M., A. A. Hamad and G. W. Garrison, 1996, "Synthesis of Waste Interception and Allocation Networks", *AIChE J*. 42(11), 3087-3101

Elo, A.N., "MIM – The Minimum Impact Mill", Paper Technology (5) 1995: 20 – 25.

Galloway, L. 1994. "Closed-Cycle Technologies for Bleached Kraft Pulp Mills." *National Pulp Mills Research Program Technical Report No.* 7. Canberra.

Gleadow, P. and C. Hastings. "Use of Computer Modeling in Closed-Cycle Assessment and Design" *1996 International Pulp Bleaching Conference*: 595 – 600.

Hough, G., 1985 *Chemical Recovery in the Alkaline Pulping Processes*, TAPPI, Atlanta, GA.

Isbister, J.A., Rae, R.G., Reeve, D.W. and D.C. Pryke. 1979. "The Closed Cycle Concept Kraft Mill at Great Lakes – An Advanced Status Report." *Pulp & Paper Canada* 80(6): 121 – 130.

Jordan, J.M. and P. S. Bryant. 1996. "Cluster Rule Impact on Recovery Boiler Operations: Chloride and Potassium Concentrations in the Kraft Liquor Cycle." *Tappi Journal* 79 (12) 108 – 116.

Keitaaniemi, O. and N.E. Virkola. "Amounts and Behavior of Certain Chemical Elements in Kraft Pulp Manufacture: Results of a Mill Scale Study", *Paperi ja Puu* 60 (9): 507 – 517 (1978).

Koufos D. and T. Retsina. 2001. "Practical Energy and Water Management Through Pinch Analysis for the Pulp and Paper Industry." *Water Science and Technology* 43 (2): 327-332.

Lama, I., Perrier, M., and P.R. Stuart. 2003. "Applying Controllability Techniques To Analyze a White Water Network for Improved Productivity in Integrated Newsprint Mills." *Resources, Conservation and Recycling* (37): 181-192.

Mehta, Y.M. 1996, "Reduced Water Use Critical to Minimum-Impact Manufacturing." *Pulp & Paper* 70(6): 93 – 96.

Nguyen, K.L. and R. Johnston. 1995. "Research Findings and Emerging Technologies for the Development of Closed Bleached Kraft Pulp Mill" *49th Appita Annual General Conference*.

Paris, J. and P. R. Stuart. 2003. "Process Integration and the Pulp & Paper Industry" Proceedings, International Conference on Chemical Technology of Wood, Pulp & Paper, Bratislava, Slovakia.

Patrick, K.L et. al. 1994. "Closing the Loop: The Effluent-Free Pulp and Paper Mill" *Pulp & Paper*: S1 - S24.

Pattyson, G.W., Rae, R.G., Reeve, D.W. and W.H. Rapson. 1979. "Bleaching in the Closed Cycle Mill at Great Lakes Forest Products." *1979 International Pulp Bleaching Conference*: 1 – 13.

Pokhrel, D. and T. Viraraghavan. 2004. "Treatment of Pulp and Paper Mill Wastewater – A Review." *Science of the Total Environment* (333): 37 – 58.

Shafiei, S., Domenech, S., Koteles, R. and J. Paris. 2004. "System Closure in Pulp and Paper Mills: Network Analysis by Genetic Algorithm." *Journal of Cleaner Production* (12): 131 – 135.

Smook, G.A. 1992. *Handbook For Pulp and Paper Technologists*. Angus Wilde Publications, Vancouver.

Stuart, P.R. and J. Paris. 2002. "Water Management in Pulp & Paper Process." Proceedings, International Conference on Fiber Industry and Environmental Biocomplexity – State of the Art Reviews and Developing Future Roadmaps, Auburn, Alabama – USA.

Thompson, G., Swain, J., Kay, M. and C.F. Forster. "The Treatment of Pulp and Paper Mill Effluent: A Review." *Bioresource Technology* 77 (2001): 275 – 286.

Wising, U., Berntsson, T., and P. Stuart. 2005. "The Potential for Energy Savings When Reducing the Water Consumption in a Kraft Pulp Mill." *Applied Thermal Engineering* (25): 1057 – 1066.

# NOMENCLATURE

Ci	Mass Fraction of chloride ion in stream
CHIPS	Total flowrate of woodchips on a wet basis
CY	Mass Fraction of pulp in slurry leaving washing system
DF	Dilution Factor of excess wash water in brown stock washing
FreshW <sub>j</sub>	Flowrate of fresh water to jth sink
Ki	Mass Fraction of potassium ion in stream
Li	Total flowrate of component i to jth sink
l <sub>i,j</sub>	Split flowrate in stream ij
Moisture	Moisture content of chips
Ni	Mass Fraction of chloride ion in stream
Pulp	Pulp produced = Dry Chips * Yield
Si	Total stream entering or leaving unit
SSBL	Solids in Strong Black Liquor
$W_j$	Water flowrate entering the j <sup>th</sup> sink
Y <sub>ion,j</sub>	Composition of a certain NPE (indexed ion) entering unit j
Yield	Pulp yield from dry chips

# APPENDIX

#### DEVELOPMENT OF THE NOMINAL BALANCE MODEL

The first step in the analysis is to develop a mathematical model that provides the appropriate level of details for mass integration. In this appendix, a model for the nominal case of the process is developed to track pulp, water, and three main ions (chloride, potassium, and sodium). These ions are selected because they are among the most important species that cause buildup problems and limit the extent of mass integration. The mass flowrate of water, chloride, potassium, and sodium in stream i are referred to as W<sub>i</sub>, C<sub>i</sub>, K<sub>i</sub>, and N<sub>i</sub>, respectively. We now proceed to model development unit by unit.

# **Digester:**

The flowrate of the wood chips (wet basis) is referred to as *Chips*, the moisture content (mass fraction) of the wood chips is referred to as *Moisture*, and pulp yield

 $(\frac{\text{Mass of pulp produced}}{\text{Mass of bone - dry chips fed to digester}})$  is designated by *Yield*.

The following equations can be written:

$$W1 = Moisture^* Chips \tag{A.1}$$

Thus, the flowrate of the bone-dry chips can be calculated as follows:

$$Dry Chips = Chips^*(1-Moisture)$$
(A.2)

The flowrate of pulp (bone-dry basis) can be related to the flowrate of dry chips through yield:

$$Pulp = Dry Chips*Yield$$
(A.3)

The ion content of the chips varies depending on the type of wood. The load of the targeted ions in the chips can be expressed as follows:

$C_1$ = Mass fraction of chloride ion in incoming wood chips * <i>Chips</i>	(A.4a)
$K_1$ = Mass fraction of potassium ion in incoming wood chips * <i>Chips</i>	(A.5a)
$N_1$ = Mass fraction of sodium ion in incoming wood chips * <i>Chips</i>	(A.6a)

To track the ions in the chips, we will use the data provided by Keitaanniemi and Virkola (1978)

$C_1 = 1.0$ *CHIPS/6000	(A.4b)
$K_1 = 2.50 * CHIPS/6000$	(A.5b)
N <sub>1</sub> =0.973*CHIPS/6000	(A.6b)

### Brown-Stock Washer

The dilution factor (DF) in the washers is expressed as pound of water per pound of dry pulp and typically ranges from 1.5 to 3.0 (Smook, 1994, p. 102, 104). Hence,

$$DF = \frac{W_2 - W_4}{Pulp}$$
(A.7)

The mass fraction of pulp in the slurry leaving the washing system is commonly referred to as the consistency (CY). Hence,

$$CY = \frac{Mass of pulp}{Mass of pulp + Mass of Water}$$
(A.8)

i.e., the water content in the slurry can be expressed as

$$W_4 = \left(\frac{1-CY}{CY}\right) * Pulp \tag{A.9}$$

The consistency typically ranges from 0.10 to 0.16 (Smook, 1994, p. 119). Equation (A.7) can be used to calculate the wash water,  $W_2$ , after  $W_4$  has been determined from Eq. (A.8).

The ionic content (ppm) of Cl, K and Na in the wash water can be specified based on typical values of 3.7, 1.1, and 3.6, respectively. Thus,

$$\begin{array}{ll} C_2 &= (3.7^*10^{-6})^*W_2 & (A.10) \\ K_2 &= (1.1^*10^{-6})^*W_2 & (A.11) \\ N_2 &= (3.6^*10^{-6})^*W_2 & (A.12) \end{array}$$

To calculate the flowrate of the targeted ions in the slurry stream  $(S_4)$ , we will assume ratios to the flowrate of the ions in the black liquor stream  $(S_5)$ .

$C_4 = 0.05 * C_5$	(A.13)
$K_4 = 0.02 * K_5$	(A.14)
$N_4 = 0.009 * N_5$	(A.15)

Figure A.1 illustrates the digester-washer system. Recall that it has been stated that all inlet streams values are known. Through the above ratios and equations, stream 4 is also known. Stream 5 will need to be determined. As can be seen, the number of unknowns is four (flowrates of water and the three ions in  $S_5$ ). These can be obtained via the four material balances for the four species:

$W_5 = W_1 + W_2 + W_3 - W_4$	(A.16)
$C_5 = C_1 + C_2 + C_3 - C_4$	(A.17)
	( 10)

$$K_5 = K_1 + K_2 + K_3 - K_4$$
(A.18)  

$$N_5 = N_1 + N_2 + N_3 - N_4$$
(A.19)



Fig. A.1 A Loop around the Digester-Washer System

# Multiple Effect Evaporators

The water in the evaporator condensate can be calculated using the water recovery ratio (equation 5.20). For the case study, we will assume that 80 % of the water in the weak black liquor is evaporated (i.e., water recovery ratio is 0.8). In addition, it is assumed that there are no ions in the condensate of the multiple effect evaporator.

$W_{10}$ = water recovery in evaporator* $W_5$	(A.20)
$C_{10} = 0$	(A.21)
$K_{10} = 0$	(A.22)
$N_{10} = 0$	(A.23)

Then, material balances can be used to calculate the concentrated stream leaving the evaporators:

$W_9 = W_5 - W_{10}$	(A.24)
$C_9 = C_5 - C_{10}$	(A.25)
$K_9 = K_5 - K_{10}$	(A.26)
$\mathbf{N}_9 = \mathbf{N}_5 - \mathbf{N}_{10}$	(A.27)



Fig. A.2 Multiple Effect Evaporators

# **Concentrator**

As with the multiple effect evaporator, the water in the concentrator condensate can be calculated using the water recovery ratio (eqn A.28). For the case study, we will assume that 46 % of the water in the black liquor entering the concentrator is evaporated in the (i.e., water recovery ratio is 0.46). Again, it is assumed that there are no ions in the condensate of the concentrator.

(A.28)
(A.29)
(A.30)
(A.31)

Then, material balances can be used to calculate the concentrated stream leaving the evaporators:

$W_{11} = W_9 - W_{12}$	(A.32)
$C_{11} = C_9 - C_{12}$	(A.33)
$K_{11} = K_9 - K_{12}$	(A.34)
$N_{11} = N_9 - N_{12}$	(A.35)





# **Recovery Furnace and Electrostatic Precipitator (ESP)**

The strong black liquor leaving the concentrators is combusted in the furnace to recover the inorganic chemicals, or smelt, which are primarily Na<sub>2</sub>S and Na<sub>2</sub>CO<sub>3</sub>. Smelt contains no water. Assuming that all the water in the strong black liquor leaves with the ESP off-gas, we get

$$W_{14} = 0.0$$
 (A.36)  
 $W_{16} = 0.0$  (A.37)

To track the ions in the furnace exhaust  $(S_{13})$ , we will use the data provided by Gleadow (1996):

$K_{13} = 0.278 * K_{11}$	(A.38)
$C_{13} = 0.498 * C_{11}$	(A.39)
$N_{13} = 0.154 * N_{11}$	(A.40)

We also use the data from Gleadow (1996) to relate the ions in stream 14 (ESP dust) to those in stream  $S_{11}$  (SBL):

$C_{14} = 0.048 * C_{11}$	(A.41)
$K_{14} = 0.028 * K_{11}$	(A.42)
$N_{14} = 0.002 * N_{11}$	(A.43)

Assuming that all the water in the strong black liquor leaves with the ESP off-gas and relating the entrained ions in the off-gas to the SBL stream, we get

$W_{15} = W11$	(A.44)
$C_{15} = 0.02 * C_{11}$	(A.45)
$K_{15} = 0.008 * K_{11}$	(A.46)
$N_{15} = 0.0008 * N_{11}$	(A.47)

Next, we use component material balances around the ESP,

$W_{13} - W_{14} - W_{15} - W_{16} = 0.0$	(A.48)
$C_{13} - C_{14} - C_{15} - C_{16} = 0.0$	(A.49)
$K_{13} - K_{14} - K_{15} - K_{16} = 0.0$	(A.50)
$N_{13} - N_{14} - N_{15} - N_{16} = 0.0$	(A.51)

Assuming that the salt cake has a makeup flow of 0.0375 \* Pulp, we get

$$Saltcake = 0.0375*PULP \tag{A.52}$$

Using the molecular formula for salt cake (molecular weight of  $Na_2SO_4$  is 142 with two Na atoms whose atomic weight is 23), then

$$N_{18} = 2*23/142 * Saltcake$$
 (A.53)

The content of Cl and K in Saltcake is obtained by assuming ratios to Na in the Saltcake:

$$\begin{array}{ll} C_{18} = 0.01^* N_{18} & (A.54) \\ K_{18} = 0.0014^* N_{18} & (A.55) \end{array}$$

Since there is virtually no water contained in Saltcake, then

$$W_{18} = 0.0$$
 (A.56)  
 $W_{17} = 0.0$  (A.57)

For the ions in the smelt, we can use component material balances around Fig. A.4:

$C_{11} + C_{18} - C_{15} - C_{14} - C_{17} = 0.0$	(A.58)
$K_{11} + K_{18} - K_{15} - K_{14} - K_{17} = 0.0$	(A.59)
$N_{11} + N_{18} - N_{15} - N_{14} - N_{17} = 0.0$	(A.60)

### Smelt Flowrate

Since the solids in the strong black liquor make up are taken as 65 % of that stream, then Solids in SBL (referred to as SSBL) =  $65/35*W_{11}$ i.e., SSBL =  $1.86*W_{11}$  (A.61) The solids in the electrostatic precipitator flue gas and purge stream are small. Assuming 5% of the solids in the strong black liquor leave the ESP in the flue gas and the purge stream (streams  $S_{14}$  and  $S_{15}$ ) and 47% of the strong black liquor solids are volatilized in the furnace, we can use the following solids balance around Fig. A.4 to estimate the flowrate of the smelt:

Saltcake + Solids in SBL (SSBL) = Smelt + Solids lost with flue gas and the purge stream (streams  $S_{14}$  and  $S_{15}$ ) + Solids volatilized in the furnace (A.61a)

Hence, Saltcake + SSBL = Smelt + 0.05\*SSBL + 0.47\*SSBL (A.61b)

Rearranging and simplifying, then

Smelt = Saltcake + 0.48\*SSBL



Fig. A.4. Furnace-ESP System

#### **Dissolving Tank**

Next, we move to the dissolving tank (Fig. A.5). The dissolving water is typically used in a ratio of 85 to 15 to the smelt. Hence,

$$W_{19} = (85/15) * Smelt = 5.67 * Smelt$$
 (A.62)

34

(A.61c)

 $\begin{array}{ll} \mbox{The ionic content in $S_{19}$ is obtained by assuming ratios to the ionic content of $Cl$ and $K$ in the smelt and $N$a in the white liquor (Hough, p. 243): $$C_{19} = 0.136*C_{17}$$ (A.63) $$K_{19} = 0.136*K_{17}$$ (A.64) $$N_{19} = 0.196*N_3$$ (A.65) $$ (A.65$ 



Fig. A.5. Dissolving Tank

Now, we can use component material balances around the dissolving tank to evaluate the ionic content in the feed to the green liquor clarifier:

$W_{20} - W_{17} - W_{19} = 0.0$	(A.66)
$C_{20} - C_{17} - C_{19} = 0.0$	(A.67)
$K_{20} - K_{17} - K_{19} = 0.0$	(A.68)
$N_{20} - N_{17} - N_{19} = 0.0$	(A.69)

# **Green-Liquor Clarifier**

Fig. A.6. is a schematic representation of the green-liquor clarifier. In order to get the flows and ionic contents of the overflow and underflow streams, we assume the following typical ratios of overflow to feed:

$W_{21} = 0.992 * W_{20}$	(A.70)
$C_{21} = 0.863 * C_{20}$	(A.71)
$K_{21} = 0.880 * K_{20}$	(A.72)
$N_{21} = 0.968 * N_{20}$	(A.73)

Then, material balance equations can be written around the clarifier:

$W_{22} + W_{21} - W_{20} = 0.0$	(A.74)
$C_{22} + C_{21} - C_{20} = 0.0$	(A.75)
$K_{22} + K_{21} - K_{20} = 0.0$	(A.76)
$N_{22} + N_{21} - N_{20} = 0.0$	(A.77)



Fig. A.6. Green-Liquor Clarifier

# Washer/Filter System

The system is shown in Fig. A.7. The dregs leaving the washer/filter system contain little water which can be estimated by relating it to the water content in the underflow from the green-liquor clarifier based on the data of Hough:

$$W_{23} = 0.075 * W_{22}$$

(A.78)

We also assume ratios of Na, Cl, and K (based on Keitaanniemi and Virkola, 1978) to water in the dregs:

N <sub>23</sub> - 0.250*W <sub>23</sub>	(A.79)
C <sub>23</sub> - 0.010*W <sub>23</sub>	(A.80)
K <sub>23</sub> - 0.001*W <sub>23</sub>	(A.81)

Using the data of Hough, we can relate streams  $S_{32}$  and  $S_{21}$ :

$$W_{32} = 0.160^* W_{21} \tag{A.82}$$

$$C_{32} = 0.237 * C_{21}$$
(A.83)  

$$K_{32} = 0.016 * K_{21}$$
(A.84)  

$$N_{32} = 0.156 * N_{21}$$
(A.85)

The wash water (W24) is assumed to be 90% of smelt dissolution water, i.e.

$$W_{24} = 0.9^* W_{19} \tag{A.86}$$

We also specify the ionic content of Cl, K, and Na in the wash water based on typical values to be 3.7, 1.1, and 3.6 ppm, respectively. Hence,

$C_{24} = (3.7*10^{-6})*W_{24}$	(A.87)
$\mathbf{K}_{24} = (1.1^{*}10^{-6})^{*}\mathbf{W}_{24}$	(A.88)
$N_{24} = (3.6*10^{-6})*W_{24}$	(A.89)

Component material balances around washer/filter system:

$W_{22} + W_{24} + W_{32} - W_{19} - W_{23} - W_{25} = 0.0$	(A.90)
$C_{22} + C_{24} + C_{32} - C_{19} - C_{23} - C_{25} = 0.0$	(A.91)
$K_{22} + K_{24} + K_{32}$ - $K_{19}$ - $K_{23}$ - $K_{25} = 0.0$	(A.92)
$N_{22} + N_{24} + N_{32} - N_{19} - N_{23} - N_{25} = 0.0$	(A.93)



Fig. A.7. Washer-Filter System

# Lime Kiln

The lime leaving the kiln (Fig. A.8) is assumed to be free of water. Hence,

$$W_{27} = 0.0$$
 (A.94)  
 $W_{25} = W_{26}$  (A.95)

We also assume that the ratio of Cl and K in  $S_{26}$  is 0.0001 and that 95% of sodium entering the kiln is lost in  $S_{26}$  (i.e., 5% of Na leaves in  $S_{27}$ ). Hence,

$K_{26} = 0.0001 * W_{26}$	(A.96)
$C_{26} = 0.0001 * W_{26}$	(A.97)
$N_{27} = 0.05 * N_{25}$	(A.98)

Component material balances around the kiln:

$C_{25} - C_{26} - C_{27} = 0.0$	(A.99)
$K_{25} - K_{26} - K_{27} = 0.0$	(A.100)
$N_{25} - N_{26} - N_{27} = 0.0$	(A.101)





### <u>Slaker</u>

Figure A.9 represents the slaker. The slaking reaction is given by:

 $CaO + H_2O = Ca(OH)_2$ 

(A.102)

Since the molecular weights of water and lime are 18 and 56, respectively, then the amount of water consumed is 18/56 or 0.32 of the consumed lime, i.e.

### WATERSLK = 0.32\*LIME

(A.103)

(A.104)

where WATERSLK is the amount of water consumed by the slaking reaction. According to Biermann (p. 117, 1996), the amount of lime fed to the slaker is 35% of the pulp, so:

### LIME = 0.35\*PULP

We also assume that the slaker vapor is 0.5% of the water in the green-liquor overflow  $(S_{21})$  and is ion free. Hence,



### Fig. A.9. Slaker

For the grits, we can get assumptions relating it to the green-liquor overflow by adopting data from Hough for water and Cl and from Keitaanniemi and Virkola (1978) for K and Na:

$W_{28} = 0.0013 * W_{21}$	(A.109)
C <sub>28</sub> - 0.0015*C <sub>21</sub>	(A.110)
$K_{28} = 0.0053 * K_{21}$	(A.111)
$N_{28} = 0.001 * N_{21}$	(A.112)

Component material balances around the slaker:

$K_{21} + K_{27} - K_{28} - K_{29} - K_{30} = 0.0$	(A.115)
$N_{21} + N_{27} - N_{28} - N_{29} - N_{30} = 0.0$	(A.116)

### **Causticizer/White Liquor Clarifier**

Figure A.10 shows the causticizer/white liquor clarifier system. Since the causticizing system provides an additional residence time for the causticizing reactions to take place, we can assume that the water and ionic content of the entering and leaving streams are the same (although their chemical forms may change). Hence,

$W_{31} = W_{30}$	(A.117)
$C_{31} = C_{30}$	(A.118)
$K_{31} = K_{30}$	(A.119)
$N_{31} = N_{30}$	(A.120)

Then, we carry out material balances around the white liquor clarifier:

$W_{31} - W_{32} - W_3 = 0.0$	(A.121)
$C_{31} - C_{32} - C_3 = 0.0$	(A.122)
$K_{31} - K_{32} - K_3 = 0.0$	(A.123)
$N_{31} - N_{32} - N_3 = 0.0$	(A.124)



Fig. A.10. Causticizer/White Liquor Clarifier

# Bleaching

Figure A.11. illustrates an overall view of the bleach plant. As shown in the figure, it is assumed that the ratio of used water to bone-dry pulp is 10.33. Also, it is

assumed that the bleach plant effluent has a fixed outlet composition of Cl, K, and Na (500, 5, and 500 ppm, respectively). Furthermore, it is assumed that used water is equal to discharged water. Hence,

$W_{33} = 10.33 * PULP$	(A.125)
$\mathbf{W}_{35} = \mathbf{W}_7$	(A.126)
$W_{37} = W_{33}$	(A.127)
$C_{37} = 0.0005 * W_{37}$	(A.128)
$K_{37} = 0.000005 * W_{37}$	(A.129)
$N_{37} = 0.0005 * W_{37}$	(A.130)



# Fig. A.11. Overall Bleach Plant

The foregoing equations constitute the necessary model to track the flow of water and targeted NPEs throughout the process. It is a general purpose simulation model that can be easily modified to relax or modify any assumptions.

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