KRAFT MILL SIMULATION

Volume I

A Thesis Submitted in Fulfillment
of the Requirements for the
Degree of
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by

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Abstract

A modular, steady-state simulation of the Kraft pulping and recovery process has been developed. The simulation has been used to model a number of operating conditions as well as different process configurations resulting from occasional addition, over a number of years, of new unit processes to a test mill in the United States.

The modules simulate the operation of equipment, and in some cases aggregates of equipment, that make up the Kraft process. The modules are based on a combination of first principles and empirical results from the literature. The simulation is based on a stream vector, common to all modules, which is composed of the minimum number of chemical components which allow an accurate representation of the chemical reactions in the process. The modular structure of the simulation facilitates its application to the variety of configurations in which this process appears. In the application discussed twenty-five modules are arranged in a flow diagram having 6 recycles. This simulation has been tuned to data gathered at the test mill to establish a base condition and ensure that it permits ready adaptation to the flow sheet constraints of a real mill.

The test mill is one of the largest and most complex Kraft mills in North America featuring a process cycle with at least four replicate process units, at each stage, operating in parallel. The spent chemical used in pulping of wood is reprocessed with approximately 95% being recovered and recycled for further use. A simulation study of the mill revealed that a change in composition of the reagent would result in economic benefits to the mill. This proposal was subsequently implemented and the data from

this implementation was used as a test of the simulation's efficacy. The simulation predicted a saving of $300,000 per year while the measurements indicate a saving of $500,000 per year.

In support of the mill trial a very simple dynamic model of the process was developed to allow calculation of a control strategy to manipulate the reagent composition. The strategy was successfully applied through a series of major process upsets. An ancilliary benefit of the dynamic model may be its application to the manipulation of storage volumes to minimize disruptions caused by process unit breakdown. This last use remains to be proven.

RESUME

Une simulation modulaire du procédé Kraft a été mise au point. La simulation a été appliquée à l'étude de différentes conditions d'opération, incluant l'addition de nouvel équipement, pendant plusieurs années dans une usine expérimentale aux Etats Unis.

Les modules simulent le fonctionnement des unités d'équipement et à l'occasion, des ensembles dont le procédé Kraft est composé. Les modules sont basés sur une combinaison de principes élémentaires et de résultats empiriques de la littérature scientifique. La simulation est fondée sur un vecteur, commun aux modules, qui est composé du plus petit nombre possible de composants chimiques qui permet une représentation précise des réactions chimiques dans la procédé. La structure des blocs facilite l'application de la simulation à une variété de configurations correspondant à ce procédé. L'application présente implique vingt-cinq modules et six recyclages. Cette simulation a été ajustée à l'aide des information recueillies dans l'usine expérimentale pour établir le point de départ et pour assurer une adaptation facile à l'organisation particulière d'une usine réelle.

L'usine en question qui est une des plus grandes et des plus compliquées en Amérique du Nord comprend au moins quatre unités identiques opérant en parallèle à chaque étape. Les produits chimiques utilisés pour produire la pâte sont récupérés à 95% pour être recyclés. Une étude en simulation dans cette usine a prédit qu'un changement dans la composition des réactifs serait économiquement avantageuse. La proposition a été

utilisées pour évaluer l'efficacité de cette simulation. La simulation prédisait une économie de l'ordre de $300,000 par an mais l'économie réelle a été de $500,000 par an.

Acknowledgments

I wish to express my gratitude to my research advisor, Professor T. J. Boyle, for his advice and direction during this project and his contributions at key stages.

Thanks are due the industrial sponsor for financial support, computing facilities and courageous exposure at an important pulp mill to large scale experimentation.

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ORIGINAL CONTRIBUTIONS

The original contributions of this work are:

1) A modular, steady-state simulation of the Kraft pulping and recovery process has been developed.
2) The simulation is based on a stream vector composed of the minimum number of chemical components which allow an accurate representation of the chemical reactions in the process.
3) The simulation has been tuned to data gathered at an operating mill to establish a base condition and ensure that it permits ready adaptation to the flow sheet constraints of a real mill.
4) The efficacy of the simulation has been tested in an operating mill by implementing a process change previously evaluated through the model and comparing the results.
5) The simulation has been documented by provision of a User's Manual.
6) A dynamic model of the Kraft process suitable to support the experiment in item 4) has been developed.

I - INTRODUCTION

As in the case of other long established industrial processes, simulation has had little impact on the Kraft pulping and recovery process. A rapidly expanding market for Kraft papers in the 1960's stimulated the construction of new mills and expansion on existing sites. These expansions have resulted in mills operating parallel lines of replicate equipment and of varying age and therefore different operating efficiencies. The general result for the industry, world-wide, is the existence of Kraft mills of widely varying configurations of similar process equipment, attempting to produce a product of similar quality, often with different raw materials. More recently environmental and economic pressure on the industry are forcing process and operating changes in response. This in turn has added to the diversity of existing physical plants.

In such an environment only the most well thought out process changes will be attempted. A computer simulation of the process is one vehicle by which proposed operating and process changes can be evaluated to determine potential benefits and risks. A modular simulation has the added advantage that its building block character enables a range of process studies and plant configurations to be handled with only minor modifications to a common programme.

While there are a number of contemporaries working along similar lines (8,13,132) the dearth of past work in the area of over-all simulation is not surprising considering the immediacy of the problem and the fact that suitable computers are a recent development.

The objectives of this work are as follows:

1) To develop and place in the literature a modular, steady-state simulation of the Kraft pulping and recovery process that is composed

of sub-process models either taken from the literature where suitable or developed from experimental data or data in the literature.

2) To evaluate the simulation through an extended observational period at an operating Kraft mill so as to;

a) Gather data for tuning and validation of the simulation

b) Establish the applicability of the simulation to plant decision making by implementing a process change previously evaluated through the model and comparing the results

c) Ensure that the simulation structure permits ready adaptation to the flow sheet constraints of a real mill and

d) Demonstrate that the simulation will run on the small computers available in situ.

3) To provide full documentation of the simulation in the form of a User's Manual.

4) To develop a dynamic model of the Kraft process suitable to support the experiment above (2b).

2 - THE KRAFT PULPING AND RECOVERY PROCESS

The Kraft process is the method of separating wood fiber from lignin by the reaction of lignin with a reagent, consisting mainly of NaOH and Na_2S, at elevated temperatures and pressures.

The basic sub-processes involved can be classed as those involved in the production of pulp and those relating to the regeneration of spent reagent (Figure 2-1*).

The major elements of the pulping process are the digesters, blow tanks and washers. The digesters may be continuous or batch units. The cooking process is essentially the same in both types. A controlled amount of reagent is reacted with wood chips for a prescribed length of time and temperature. The cooking chemical reacts with and dissolves lignin resulting in a slurry of pulp and black liquor. This slurry is blown into holding tanks known as blow tanks from which it is pumped to a series of cascaded, rotating, drum washers where fresh water is used to wash black liquor from the pulp. The pulp exits the Kraft mill for further processing and the now diluted black liquor goes on to the chemical recovery section. One major difference between batch and continuous digesters (aside from the obvious one) is that the typical continuous Kamyr digester, in addition to the cooking zone, has an extraction zone following the cooking zone in which black liquor is strained from the pulp. This zone is followed by a washing zone in which pulp is washed with recycled, diluted black liquor. This extraction and washing reduces the subsequent pulp washing load with the result that continuously produced pulp requires only one or two stage drum washers while batch pulp requires three. Another difference is that in the batch process diluted black liquor is used to dilute the cooking

* Figure 2-1 includes neither a continuous digester nor black liquor oxidation.

chemical while in the continuous digester, steam and recycled condensate is the diluent. It is noteworthy that the recycled black liquor contains some active cooking chemical (particularly Na_2S) which may affect the control of pulp quality.

The major equipment of the Kraft recovery process in North America is multi-effect evaporators, strong black liquor oxidation towers (only recently gaining wide acceptance), direct contact evaporators, recovery furnaces, slakers and causticizers and rotary lime kilns (though fluid bed calciners are gaining popularity). Scandinavian mills often include weak black liquor oxidation towers and do without strong black liquor oxidation and direct contact evaporation.

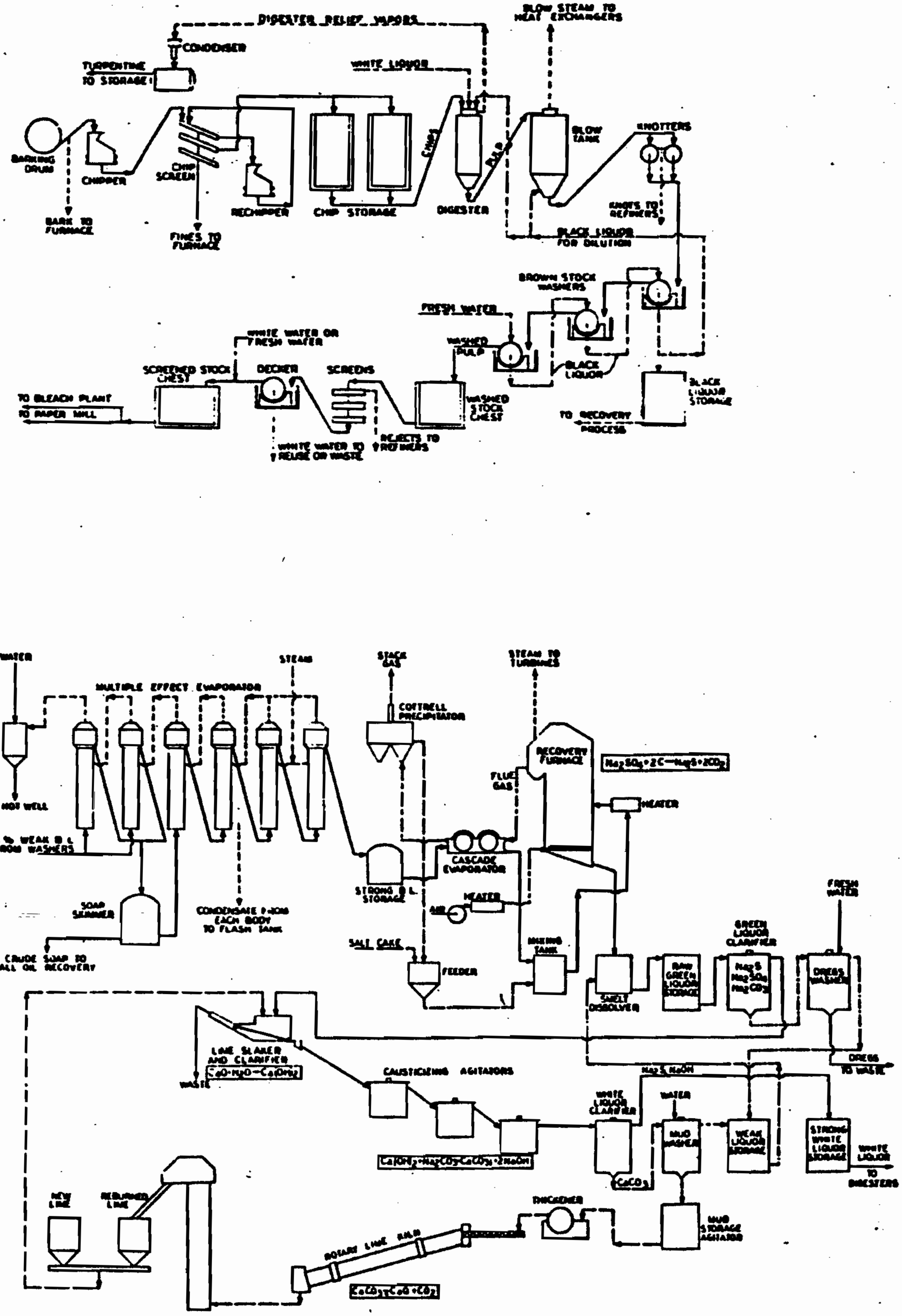
In the typical North American operation weak black liquor (14-16% solids) is concentrated in a counter-current, multiple effect evaporator (40-45% solids). The strong liquor then passes to the oxidation towers where air blown through the tanks oxidizes active Na_2S in the black liquor. Oxidation of Na_2S reduces subsequent emission of H_2S in the direct contact evaporator. The oxidized black liquor is further concentrated (55-65%) in the direct-contact evaporator by hot flue gases from the furnace. The liquor is fired into a tube lined recovery furnace where the organics in the liquor burn, boiling the water in the tubes to produce steam for the rest of the mill. The air flow to the furnace is balanced so that the flow to the lowest or primary zone is insufficient to completely burn lignin. The oxygen deficiency in the primary zone is carefully controlled so that Na_2SO_4 and other sulphates are reduced to Na_2S while the Na in lignin and free NaOH in the liquor react to form Na_2CO_3. This mixture forms a smelt which pours out of the furnace at temperatures between 1500 and 1750°F. The smelt is dissolved in water recylced from the mud washers forming green liquor. The green liquor is causticized with slaked lime (from the lime kiln). The Na_2CO_3 reacts to form NaOH thus producing white liquor which is the cooking reagent. The $CaCO_3$ based mud, produced by the causticizing reaction, is separated from the white liquor which is recycled to the digesters. The mud is washed and then dried and calcined in a rotary lime kiln. The residence time is typically 2 hours and the exit temperature about $2200^{o}F$. This regenerated lime is recycled to be slaked in green liquor and causticize it.

The major loss of solid chemicals occurs at the brown stock washers. Minor, but still significant, solids losses occur at the recovery furnace, lime kiln and dregs washers. Particulate losses from recovery furnaces can be very significant in mills where the flue gases are not passed through electrostatic precipitators. In addition malodorous, sulphur bearing gases are emitted at the blow tank, multi-effect evaporator, and direct contact evaporator.

Major and minor differences between installations of the Kraft process have already been alluded to. It should be pointed out that mills also operate different numbers of the basic equipment described often at different operating conditions due to equipment age and slight design differences. Figure 2-2 is the flow diagram of an exceptionally complex mill operating in the southern United States.

Finally, recent environmental pressures and continually rising energy costs are causing changes in the process that often involve addition of new sub-processes. Thus the basic Kraft process is in a state of almost constant change.

Fig. 2-1: Typical Kraft Mill Flow Diagram (102)



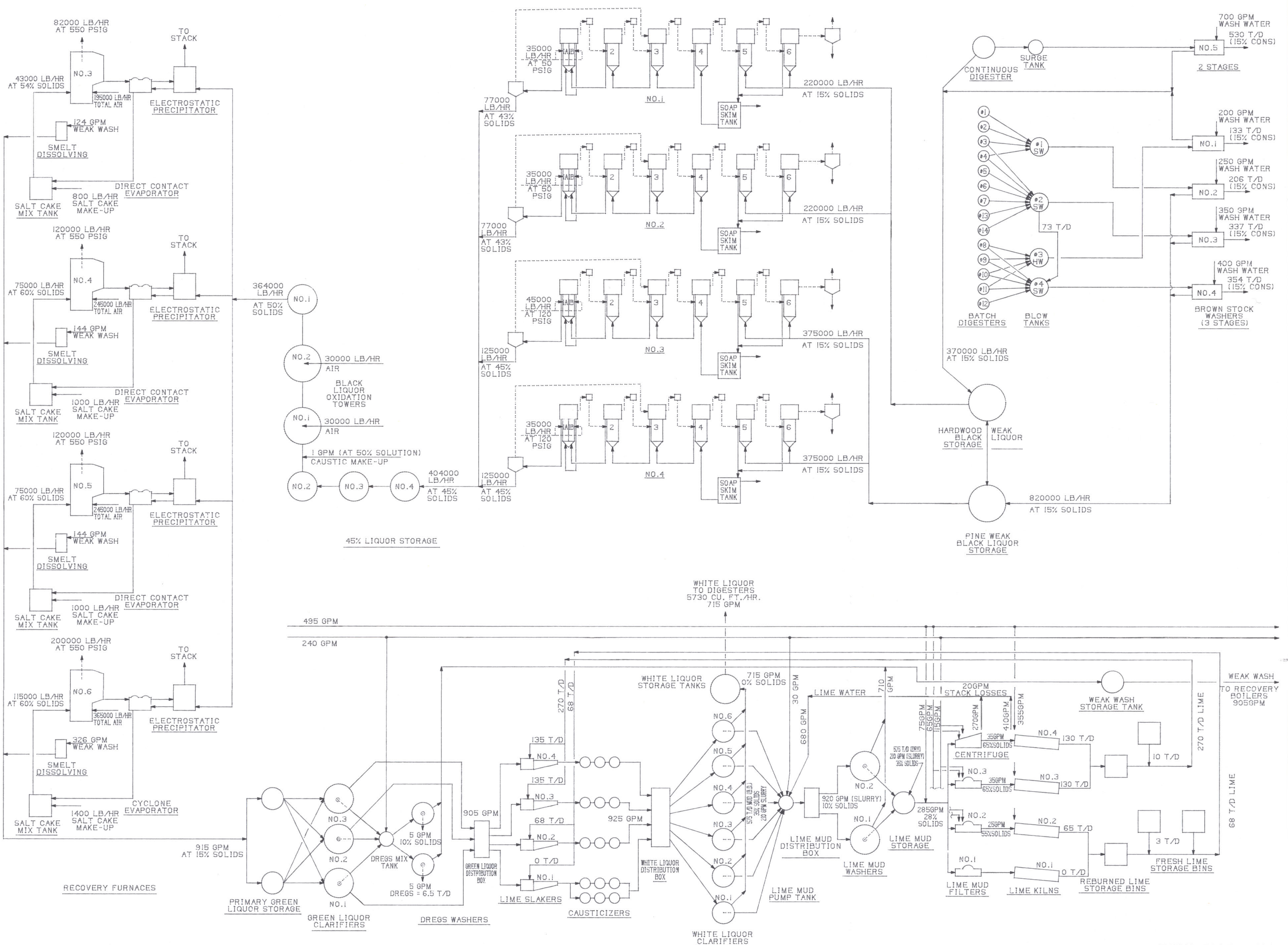


FIGURE 2-2. TEST PULP MILL FLOW DIAGRAM

COMPUDRAFT JAN. 12, 1979

3 - LITERATURE REVIEW

The most direct approach to the problem of simulating a large system is the development of an ad-hoc model which is system and problem specific. The strength and weakness of such an approach is its specificity, which while reducing the complexity of the model also increases its inflexibility to solution of different problems and different process configurations. The earliest recorded attempt at a Kraft mill model was made by Carroll (31). He applied a number of realistic economic and physical constraints to the model of a hypothetical kraft mill and used mathematical programming to optimize it. This pioneering work was limited by the lack of basic research on the system sub-processes and the unsophisticated computers of the time. Following closely along the lines of Carroll, Boyle and Tobias (25) developed a model of a single line Kraft mill which featured a more flexible cooking and energy model. Discarding the approach involving a superimposed optimization scheme they developed an easily manipulated tool for evaluating the effects of proposed process changes on operating economics. Both models are ad-hoc and their applicability is therefore limited by their specificity.

Adler and Goodson (2) developed a very complex ad-hoc model thereby negating the advantage of the approach and further compounded the problem by superimposing an optimization scheme.

Rogers et. al. (132) have developed a model containing elements of the work of both Carroll and Boyle and Tobias. There is a much stronger emphasis on modelling the pulp line from digesters to bleach plant and a linear programming scheme is used for optimization. More recently the same group (133) has expanded the model's capability to handle multiple pulp lines thus increasing its power but the basic approach is still ad-hoc and the causality in the recovery cycle is very basic.

Arhippainen and Venho (8) developed a modular sub-process simulation of the pulp line and some of the recovery units in order to study the effects of integrating a new bleaching process in an existing system. Theirs is the first modular simulation of the Kraft process to appear in the literature and demonstrates that a modular scheme allows easy combination of a complex sub-process model with other very simple ones when only one part of the process is of great interest while some limited information is required about the interactions between that process and the remainder of the system.

Currently Baldus and Edwards (13) are developing a modular simulation with an emphasis, similar to Rogers and Arhippainen, on the pulp lines. Of the twenty five modelling blocks that comprise the simulation twenty one are devoted to the pulp line and only four to the recovery cycle. The particular process which they modelled involves cross recovery of spent chemical from another completely separate mill. This is a highly unusual situation in North America and strongly affects the direction their work is taking. In addition the simulation is proprietary and they have not provided sufficient information to determine the validity of the model.

This short review is a fairly complete compendium of published works in the area of simulation of the entire process. There are some other simulations available of large portions of the process (16,90) but these are limited in their applicability since they are unable to handle important process interactions. Most of the work is very recent and does not cast doubt on the independence of this work since that has been established by previous publications by Boyle, Treiber and Vadnais (26) and Boyle and Treiber (27). Independence and relative merit aside the number of works in existence hardly consitute a plethora of information, leaving room for additional significant contributions.

A modular simulation is a construction of sub-process models linked together. Table 3-1 provides a brief review of the literature on models of the subsystems of the Kraft process and data from which such models can be constructed. While the distribution of interest is clearly uneven among the subsystems the mass of information provides an obvious opportunity for development of an overall model of the process. This work is an attempt to take advantage of that opportunity.

Table 3-1

Distribution of Kraft Mill Research*

General Simulation	2,8,13,16,25,26,27,31,46,51,56,124,132,133,164,169
Digesters	3,4,9,10,21,34,47,48,52,53,63,64,79,80,81,86,93,97,104,105,123,143,149,150,155,156,170,174,175,180,181,182
Pulp Washing	4,11,12,17,36,49,50,70,71,72,76,77,87,107,118,119,122,134,138,145,153,163,167,171
Multi-Effect Evaporation	1,7,14,73,74,95,121,178
Direct Contact Evaporation	114,146,154,176
Recovery Furnaces	5,15,19,32,33,37,41,57,69,94,148,157,158,159
Slaking & Causticization	54,66,67,68,89,90,98,100,101,108,135,139,151,152
Clarification	65,90,92,179
Mud Washing	90,162
Lime Kilns	20,24,35,38,42,45,59,60,61,62,78,88,90,109,120,141,142,165,168,172,173
Pollution	6,18,22,23,29,30,39,40,43,44,55,83,84,85,99,103,110,111,113,115,116,117,125,126,140,147,161,166,183

* Numbers denote references in the Bibliography

4 - THE MODULAR APPROACH TO SIMULATION*

The modular approach to process simulation was developed in the 1960's in response to the then growing interest in process simulation in the chemical industry. The particular modular system used here is known as GEMCS - General Engineering Management & Computation System and was developed by A. I. Johnson and his co-worker (92). Its main advantage over other existing systems is that it is in the public domain. Specific details of the technique have been discussed by Boyle et. al. (26) and in the User's Manual (Appendix A) so it would be inappropriate to supply more than utilitarian information here.

The modular approach to process simulation is best suited to systems which contain recycle, duplication of basic processing units and appear in alternate configurations at different installations. That the Kraft process is a prime candidate for this approach should be clear from previous chapters and has been demonstrated by Boyle et. al. (26) and Boyle and Treiber (27). The term modularity refers to the building block structure of the simulation which consists of a set of modules (subroutines) each of which models one or more of the sub-processes that make up the Kraft process. Each module accepts input through information streams (viz. process streams), modifies that information according to its model of the sub-process and passes the modified information on through a set of output streams. The modules exist within a framework of programmes known as the executive, which handles the flow of information from module to module, the reading of data, the storage of intermediate values of the computations and the calling of modules in the proper sequence.

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* The engineering system of units has been used throughout this work for consistency with the units used by the pulp and paper industry.

The great strength of the GEMCS approach is that it is data oriented. The sequencing of module execution and the stream interconnections are ordered in the data set. Associated with each module is an equipment vector containing the parameters of the sub-process model which conveniently allows the causality to appeal to empiricism where that proves to be more suitable than models based directly on principles of physics and chemistry. It then becomes possible, using this approach, to simulate replicate sub-process units operating at different conditions by executing the same subroutine again and again but using a different set of data each time which calls for different input and output streams and possibly different physical parameters. The result is a very significant saving of computer space and given the basic set of modules any combination may be constructed (viz. any configuration of the process may be simulated) by only creating a new data set and without modifying the programme (with the exception of possibly adding more space to the COMMON areas if needed) (26,27). Iterative computation about recycle loops is controlled by a convergence testing module which like the simulation modules may be replicated many times with different data sets. The number of computational loops controlled by a convergence testing module is entirely at the discretion of the user. Though a convergence promoting module is available (92) the method of successive substitution is satisfactory for many systems.

The output from a computer simulation of a system such as that described in Figure 2-2 is cumbersome and difficult to analyse due to its size. Because the GEMCS executive acts as a central processor for information transmission special purpose report modules can be written for the purpose of outputting key operating data in a concise format convenient for analysis. These report modules along with the facility of manipulating the simulation through the data set make it possible for the simulation to be used by a non-expert programmer such as a process engineer in a mill. This is no small matter. The utility and ease of dissemination of a simulation are at least minimum requirements when assessing its merit, in addition of course to its validity.

The development of a modular simulation is a five step procedure. First the process flow sheet must be converted into an information flow diagram which is a graphical representation of information flow through the model. This is done by drawing system boundaries about the process units. A system boundary defines the physical phenomena to be modelled in a module. In addition modules are added to control interative calculations about process loops. Figure 4-1 is an information flow diagram of the process described by Figure 2-2. In this case replicate units are described by only one module. It is also possible to completely disaggregate the information flow diagram and simulate replicate units by replicate modules (26). Table 4-1 lists the functions of the modules defined in Figure 4-1.

The second step is to decide what information will flow from module to module. Table 4-2 lists the components and format of all stream vectors in the simulation. There are two types of streams, gaseous and non-gaseous. The format is fixed for each of these types with three exceptions. The exceptions are made to allow conformity with the formats used by operating mills for these process feed streams. The definition of two types of streams is simply a space saving device. As shall be seen in the next chapter the stream components chosen strongly affect the level of complexity of the simulation.

The third step requires the development of the causal relationships within the modules and will be discussed in the next chapter. The fourth step is writing of the computer coding for the modules (Appendix A). Finally the data set is created which realizes the information flow diagram and is consistent with the computer coding (Appendix A). The data set consists of the sequencing of module execution, the flagging of streams for permanent or temporary storage (a space saving device), initialized system input streams, the stream interconnection of modules and the parameter sets for each module. Table 4-3 lists the standard format of the first fifteen elements of the module equipment vectors. Here the stream interconnections for each module are specified. The sixteenth and subsequent elements of each equipment vector contain the physical parameters of the module causality in an order specified in the module coding. There is one equipment vector for each module in the information flow diagram and if Figure 4-1 were disaggregated to show four furnace modules (FURN02) what would be required is four equipment vectors operating on the same module (FURN02) and no additional coding. Thus, the only steps that need be repeated when applying the model to a different Kraft mill are the first and fifth.

If the simulation is to be used to study the impact of an excursion from a base operating point one more step must be taken. The simulation must be "tuned" to the base operating condition. The tuning procedure fits the simulation to the base operating point. The external process inputs are set as well as the controlled operating conditions. The latter requires the setting of some flow rates, temperatures and densities as well as other fixed process parameters. The empirical or semi-empirical predictive causality may also be tuned by adjusting the coefficients of the equations, if necessary, to match the measured outputs. This tuning procedure generally involves several iterations as inconsistencies between the simulation statement and measurements, and among the measurements themselves,arise.

Table 4-1

Purpose of Simulation Modules

MODULE	DESCRIPTION
CHIP01	Calculates wood charge to batch digesters
CHIP02	Calculates wood charge to continuous digesters
DIGES3	Simulates batch digesters. Predicts yield, and chemical and energy consumption
DIGES4	Simulates continuous digester. Predicts yield, and chemical and energy consumption
BLOW01	Calculates amount of water flashed from liquor upon discharge from digester
WASH01	Simulates brown stock washing
EVAP01	Simulates multieffect evaporator
SBL01	Simulates strong black liquor evaporation
DCVP01	Simulates direct-contact evaporator
FURN02	Simulates a kraft recovery furnace
SMELT1	Simulates smelt dissolving tank
SLACA2	Simulates slaking and causticizing tank
CLAR01	Simulates white liquor clarifier
MUDDE1	Simulates lime mud washing and dewatering
KILN02	Simulates lime kiln
MAKUP1	Calculates NaOH and Na_2SO_4 make-up requirements
MAKUP2	Calculates water make-up requirement in white liquor preparation loop
JUNC01	Generalized mixer and splitter
JUNC02	Special purpose splitter
ENREP	Prints out EN vectors
QREP	Reports mill energy balance

Table 4.1 continued

DIGREP	Digester report
LIQREP	Evaporator, Recovery furnace report
PREREP	White liquor preparation loop report
LOSREP	Chemical loss report
CONTB1	Convergence control module
L999	Control module to initiate final pass for printout

Table 4.2: Components and Format of Stream Vectors

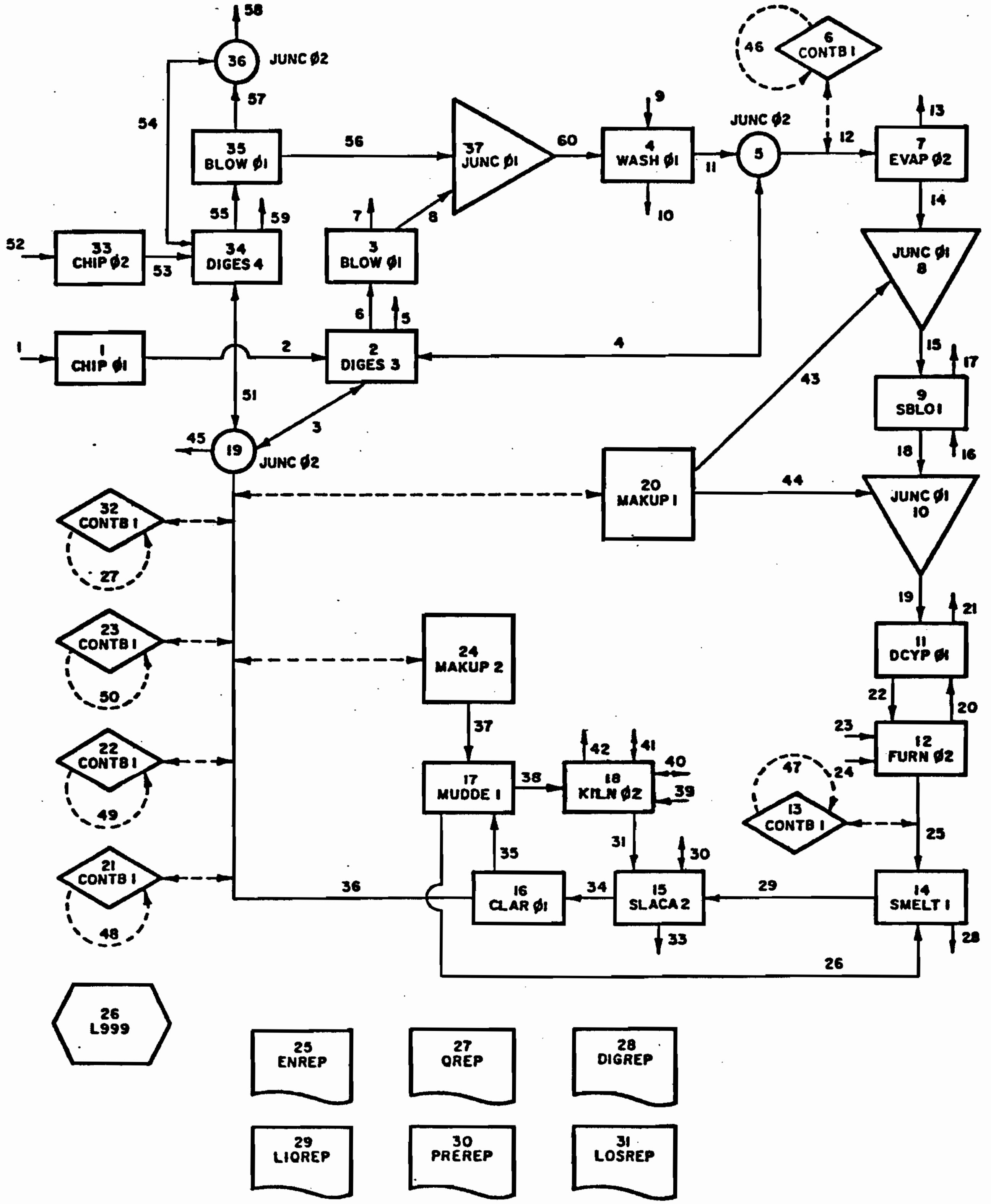
```
C
C             THE FOLLOWING STREAM FORMATS ARE COMMON TO ALL STREAMS O
C             THE SAME TYPE (INPUTS,SI(,), OUTPUTS, SO(,) & STORAGE,
C             SN(,)) WITH THREE EXCEPTIONS.
C
C
C                   STREAM FORMAT
C
C      SO( , 1) - STREAM NUMBER AS IN INFO. FLOW DIAG.
C      SO( , 2) - TYPE (NON-GASEOUS, 1/ GASEOUS, 2)
C      SO( , 3) - TOTAL FLOW (TONS/HR)
C      SO( , 4) - STREAM TEMPERATURE (DEGREES F)
C      SO( , 5) - STREAM PRESSURE (PSIG)
C
C COMPONENTS OF FLOW FOR NON-GASEOUS STREAMS
C
C      SO( , 6) - WOOD                              (TONS/HR)
C      SO( , 7) - DISSOLVED LIGNIN (C10H1203.3)   (TONS/HR)
C      SO( , 8) - WATER        (TONS/HR)
C      SO( , 9) - NAOH         (TONS/HR AS NA2O)
C      SO( ,10) - NA2S         (TONS/HR AS NA2O)
C      SO( ,11) - NA2SO4       (TONS/HR AS NA2O)
C      SO( ,12) - NA2CO3       (TONS/HR AS NA2O)
C      SO( ,13) - CAO          (TONS/HR)
C      SO( ,14) - CACO3        (TONS/HR)
C      SO( ,15) - INERTS       (TONS/HR)
C
C COMPONENTS OF FLOW FOR GASEOUS STREAMS
C      SO( , 6) - O2           (TONS/HR)
C      SO( , 7) - CO2          (TONS/HR)
C      SO( , 8) - H2O          (TONS/HR)
C      SO( , 9) - N2           (TONS/HR)
C      SO( ,10) - H2S     (LBM/HR) .........
C      SO( ,11) - NA2SO4       (TONS/HR AS NA2O)
C      SO( ,12) - NA2CO3       (TONS/HR AS NA2O)
C      SO( ,13) - CAO          (TONS/HR)
C      SO( ,14) - CACO3        (TONS/HR)
C
C    ******************************************************************
C    *
C    *        THE EXCEPTIONS TO THE ABOVE STREAM FORMATS ARE AS
C    *        FOLLOWS:
C    *        1) THE WOOD STREAM TO CHIPO1 HAS UNITS (TONS/BATCH)
C    *        2) WOOD STREAM TO CHIPO2 HAS UNITS;
C    *                                 SO( ,3) - CHIP METER RPM
C    *                                 SO( ,6) - WOOD FRACTION
C    *                                 SO( ,8) - WATER FRACTION
C    *        3) FUEL TO KILNO2 CALCULATED TOTAL FLOW IN TONS/HR
C *                                      NO COMPONENTS
C    *
C    *  N.B.      FLOW OF H2S IN GASEOUS STREAMS IN (LBM/HR)
C    *
C    ******************************************************************
```

Table 4.3: Format of the Equipment Vector

```
C
C         THE FORMAT OF THE FIRST FIFTEEN ELEMENTS OF THE
C         EQUIPMENT VECTOR IS COMMON TO ALL MODULES.
C
C
C               EN VECTOR FORMAT ( FIRST 15 ELEMENTS)
C
C         EN( 1) - MODULE NUMBER (AS IN INFO. FLOW DIAG. )
C         EN( 2) - MODULE TYPE
C         EN( 3) - NUMBER OF ELEMENTS IN EN VECTOR (15 + ?)
C         EN( 4) - TEMPERATURE (DEGREES F)
C         EN( 5) - PRESSURE (PSIG)
C         EN( 6) - NUMBER OF INPUT STREAMS (NIN)
C         EN( 7) - STREAM NO.  OF FIRST INPUT STREAM (SN( ,1))
C         EN( 8) - STREAM NO.  OF SECOND INPUT STREAM (SI(2,1)
C         EN( 9) - STREAM NO.  OF THIRD INPUT STREAM (SI(3,1))
C         EN(10) - STREAM NO.  OF FOURTH INPUT STREAM (SI(4,1))
C                                 -ZERO IF NOT USED
C         EN(11) - NUMBER OF OUTPUT STREAMS (NOUT)
C         EN(12) - STREAM NO.  OF FIRST OUTPUT STREAM (SO(1,1))
C         EN(13) - STREAM NO.  OF SECOND OUTPUT STREAM (SO(2,1))
C         EN(14) - STREAM NO.  OF THIRD OUTPUT STREAM (SO(3,1))
C         EN(15) - STREAM NO.  OF FOURTH OUTPUT STREAM (SO(4,1))
C                                 -ZERO IF NOT USED
C
C
```

FIGURE 4.1:

INFORMATION FLOW DIAGRAM



5 - THE PREDICTIVE CAUSALITY OF THE SIMULATION

The simulation consists mainly of simple material balances that result from only a few predictive equations. For example the extent of conversion of one component of a reaction is predicted by a single equation and subsequent calculations to determine the amount of other components in the product are the result of simple stoichiometric considerations. In those cases where the predictive equations are derived from the material balances the full development will be shown. The simulation User's Manual in Appendix A will serve as a supplement to this presentation.

The simulation is not simply an aggregation of algebra which has been encoded in a computer language. It has been designed specifically to take advantage of the GEMCS system and is constrained by the environment in which it is to be used. There are three main factors defining that environment: first, the simulation is intended to be used for the study of overall process behaviour and not for detailed study of individual subprocesses; second, it is intended to be used on small computers that are available in pulp mills. In such computers program execution time is far less important than storage requirements; and third, the type and quantity of data available plays a decisive role in tuning the simulation and in defining the scope of a prediction. An additional constraint on the simulation complexity might be the desire to facilitate portability and dissemination. The key to satisfying these restrictions is to achieve a balance between causal simplicity and predictive accuracy.

With the above statement in mind it will be shown how the components of the stream vectors have been selected and how they define the limits of complexity of the causality. The predictive causality can be characterized by classification into three groups: first, equations predicting product yields; second, the energy balances of the model; and third, the chemical loss causality which can be divided into two sub-groups; the loss of sulphur only, through emission of malodorous gases and the loss of sodium in aqueous streams or entrained particulates in gas streams which may also involve loss of sulphur bound to sodium.

5.1 The Stream Components

The complexity of the chemical constituents of the Kraft process is due mainly to the non-homogeneity of wood. The components of wood may be classified into three groups; cellulose, hemi-cellulose and lignin of which the last two are most susceptible to dissolution in alkaline solutions. Even within these groupings there are non-homogeneities and irregularities in molecular structure causing differing reactions with the Kraft reagent. The relative amounts of the three basic components and irregularities within these groups varies among wood species and particularly between wood types (i.e. hardwood and softwood). The result is a large and to date indeterminate number of reactions going on in a digester (136,pp.559-609). A cooking model appealing directly to reaction kinetics, even when considering only the three basic components, is therefore a highly complex proposition (150,93) and is unsuitable in an overall simulation. The most successful of these models by Lundquist (105) assumes three different forms of lignin and requires determination of three rate constants per wood species. The variety of species used in North America and even within any one mill argues against such a model due to the mass of data required to tune it.

This complexity extends to the inorganic constituents also. The combination of sodium and hydroxyl ion with organic products will vary from species to species and in particular the combination of sulphur from Na_2S will vary both in the pulping reactions to solubilize lignin and in the emission reactions producing differing mixtures of the malodorous gases CH_3SH, $(CH_3)_2S$ and $(CH_3)_2S_2$ and under certain conditions H_2S. The amount and relative composition of these malodorous gases is subject not only to wood type but to the degree of hydrolysis of Na_2S by the reaction

$$Na_2S + H_2O = NaSH + NaOH \tag{5-1}$$

which is dependent on the pH and temperature of reagent. Since there is no agreement in the literature on the degree of hydrolysis of Na_2S (10,156,108) and the acidity of the SH^- ion is not known with any certainty (137,p.584) even a simple equilibrium model for this aspect of the pulping reaction would be difficult to apply.

Similar difficulties are encountered in other process units. Oxidation of Na_2S in black liquor produces mainly $Na_2S_2O_3$, Na_2SO_4 and Na_2SO_3 however there is no apparent agreement on which is the dominant product (69). Baur and Dorland (15) considered twenty different reactions in the gas and solid phases in order to predict the composition of smelt exiting a recovery furnace and composed of only three components. In the white liquor preparation loop of a mill various calcium compounds are generated including combinations with silicon and rare earths as a result of degradation of the brick lining of the kiln.

The most severe restraint on the number of stream components is the limitation on available computer space. A reduced component set must allow a physical analogue of the process sufficient for description of over-all system behaviour and sub-system interactions. Table 5-1 lists twenty-seven basic components of the process and the 13 analogues actually used in the stream vector of the simulation (see also Table 4-2). The twenty-seven components are themselves a simplification of the true state. The analogous components are believed to be the simplest set that will allow an accurate representation of the process causality. The main advantage of this set of components is that the process is described in terms of these components in pulp mills. The physical analogue for the pulping process is seen as one in which wood fiber is separated from other organics which are subsequently burned to generate steam for the chemical recovery process. The organic components are reduced to two, insoluble wood and soluble wood for which the chemical model is $C_{10}H_{12}O_{3.3}$ a model for softwood lignin (4). The emission reactions producing CH_3SH, $(CH_3)_2S$, $(CH_3)_2S_2$ and SO_2 are seen as a mechanism for the separation of sulphur atoms from sodium atoms and the reaction analogue will be

$$Na_2S + 2H_2O = 2NaOH + H_2S \tag{5-2}$$

or

$$Na_2S + H_2O + CO_2 = Na_2CO_3 + H_2S \tag{5-3}$$

in the case of the recovery furnace. Clearly there will be some discrepancy between the actual and predicted mass of organics because the methyl groups are not taken into account but the resulting simplification of the model justifies this approximation especially when considering the relatively small amount of gas that is generated. Note that H_2S emission is reported in lbm/hr while all other components are in tons/hr (see Table 4-2).

The objective of the system chemical balance is to determine at any point how much sodium and sulphur are in a stream and to know what portion is free and therefore able to take part in reactions in subsequent units. No differentiation between free and bound inorganics is made in the stream vector. Thus, NaOH and Na_2S pass through the digester unchanged by the pulping reactions. An independent equation is used to calculate the amount of residual NaOH and Na_2S in a stream wherever required obviating the need for derivative lignin components bonded to sodium and sulphur as a result of pulping.

The oxidation of Na_2S to Na_2SO_4, $Na_2S_2O_3$ and Na_2SO_3 in the black liquor oxidation system, handled by the reaction

$$Na_2S + 2O_2 = Na_2SO_4 \tag{5-4}$$

is also an oversimplification but nevertheless allows computation of active residual Na_2S which is deemed to be the most important factor in subsequent process units. Lumping calcium compounds into CaO and $CaCO_3$ is a convenient way of distinguishing between active and inactive calcium available for causticization of green liquor. Similarly, NaOH and Na_2CO_3, and Na_2S and Na_2SO_4 may be thought of as active and inactive pairings. These sodium compounds are expressed as equivalent mass of Na_2O in the simulation to conform to the traditional way in which a sodium balance is made in North American pulp mills.

An alternative component set might be composed of elemental or ionic groups (13). The only disadvantage of this option is the lack of conformity with the terms in which measurements are reported in mills.

Due to the abbreviated component set and sweeping analogues of real reactions the simulation causality will of necessity be semi-empirical in many cases. In the context of an overall simulation which is bound to be complex because of the size of the process this can be a desirable feature. This is particularly valid here since a major premise of this work is that these relationships or the data required to develop them already exist in the literature.

The causality to be presented is the result of three passes at simulating the process. The first attempt by Boyle, Treiber and Vadnais (26) was a modular version of an earlier ad-hoc model by Boyle and Tobias (25) and featured very simple causality. This effort bears a strong similarity to the more recent work of Baldus and Edwards (13). The causality was shown to be inadequate in many areas as a result of a four month long testing and observational period in a southern U.S. pulp mill. This led to a more complex model using the twenty-seven stream components shown in Table 5-1. Unfortunately the inherent complexity led to serious difficulties in tuning and implementation as well as taxing the limited computer facilities available in the mill. The simulation presented here is a compromise between the simple structure of the first attempt while retaining the more comprehensive causality of the second.

5.2 A Parametric Description of the Process Performance

As in the case of many large and complex processes the overall operating and economic performance of a Kraft mill is described by a concise set of parameters that can be calculated from reasonably simple measurements of the process streams. These parameters are indicative of reactor efficiencies, the mill energy balance and the chemical losses.

The yield of pulp from wood cooked in the digesters is the most important parameter. The furnace reduction ratio, defined by

$$Rd = \frac{Na_2S}{Na_2S + Na_2SO_4} \tag{5-6}$$

all expressed as Na_2O and measured in smelt exiting the furnace indicates the efficiency of Na_2S production from Na_2SO_4. The caustic conversion efficiency, E_c,

$$E_c = \frac{NaOH}{NaOH + Na_2CO_3} \times 100 \qquad (5\text{-}7)$$

all expressed as Na_2O and measured in the white liquor indicates the efficiency of the slaking and causticizing system in producing NaOH from Na_2CO_3. The lime availability, A_v,

$$A_v = \frac{CaO}{\text{Total Lime}} \times 100 \qquad (5\text{-}8)$$

measured in the reburned lime exiting a kiln indicates the efficiency of CaO production, from $CaCO_3$, for the recausticization of green liquor in the slaking and causticizing system.

The basic energy balance is composed of the steam demand of the digesters, washers, multi-effect evaporators and the steam production by burning organics in recovery furnaces. There is also a fuel demand in the kiln.

The sodium losses with washed pulp are usually the only regular loss measurements made in pulp mills. The sodium losses from the recovery furnaces, dregs washers and kilns are small but play an important role in the chemical make-up requirements in the mill. The emission of sulphurous gases from the digesters, blow tanks, evaporators, direct-contact evaporators and recovery furnaces are small and difficult to measure but are extremely important environmentally and as they affect the chemical make-up requirements. Lime losses from the kiln and in the dregs are almost never measured but are the determining factor in calculation of the lime make-up requirement.

The predictive causality of the simulation focuses on these operating parameters. In addition there are a number of ancillary predictions made which are related to the dependency of the major variables to be predicted.

5.3 Reactor Efficiency

For the sake of convenience the variables in the following equations are mnemonically coded.

5.3.1 Digesters

The yield of pulp from the cooking reaction in both continuous and batch digesters is predicted by a relation due to Hatton (79,80,81).

$$Y = a^* - b \log (H) (EA)^n \tag{5-9}$$

where Y is the percent yield, H is the H-factor of Vroom (170) which expresses the relative reaction rate as a function of the temperature-time profile of a cook and EA is the initial pounds effective alkali per pound of oven dry wood. The coefficients a and b are specific to the wood species cooked while the exponent n is more strongly dependent on wood type (hardwood and softwood). Hatton provides a table of values for a number of wood species commonly cooked.

The Vroom H-factor is defined by

$$H = \int_0^{t_f} e^{\left(A - \frac{B}{T(t)}\right)} dt \tag{5-10}$$

where T is absolute temperature and t is time in hours. A and B are the coefficients of the Arrhenius type rate constant. The H-factor does not define the reaction absolutely, it merely relates the effects of different temperature-time profiles on the delignification reaction.

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* The coefficients of all equations may be found in Appendix C and in the sample data set of the simulation "User's Manual", Appendix A, Table 5.

The effective alkali is defined as the mass of

$$\text{NaOH} + \frac{1}{2}\text{Na}_2\text{S} \tag{5-11}$$

expressed as Na_2O. The concept is that of the two sodium atoms in one molecule of Na_2S only one atom will be available, through reaction 5-1, for delignification.

In pulp mills the temperature-time profile and effective alkali to wood ratio are used to control the pulp yield. In North American mills it is common to control the active alkali rather than effective alkali in the white liquor reagent. The active alkali is defined as the mass of

$$\text{NaOH} + \text{Na}_2\text{S} \tag{5-12}$$

expressed as Na_2O and is related to the effective alkali by the equation

$$\text{EA} = \text{AA}(1 - \frac{S}{2}) \tag{5-13}$$

where S is the white liquor sulphidity, defined as

$$S = \frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{NaOH}} \tag{5-14}$$

all expressed as Na_2O.

The advantage of Hatton's model over the kinetic models of Smith (150), Johnsson (93), and Lundquist (105) is its simplicity. Hatton has shown that the exponent, n, of equation 5-9 is more strongly dependent on wood type than wood species and has recommended general values of n for the two types. Thus, if the species of interest is not among the group for which he has listed values for the coefficients a and b as few as two experimental cooks would be required to fit the relationship.

For most wood species equation 5-9 is limited to the sulphidity range, 20% to 60% (136,p.624). The model predicts yield independent of sulphidity purporting to take it into account through the effective alkali which states that one mole of Na_2S is equivalent to one half mole of NaOH, as effective cooking chemical, through the hydrolysis reaction 5-1. This is not true out of the above sulphidity range (note that kraft cooks are carried out in the applicable range). In the sulphidity range 0 to 20% addition of Na_2S to the basic NaOH reagent drastically accelerates the delignification reaction (136,p.624). NaOH also attacks cellulose and results in a weakened fibre so this acceleration of delignification is desirable and is the reason why the kraft process is the pre-eminent pulping process world-wide. While the delignification reaction is not well understood and the exact structure of lignin unknown (102,p.86), it is believed that the NaSH formed by reaction 5-1 aids in the break-up of the lignin polymer into smaller components that are more soluble in alkaline solution. In the sulphidity range 60 to 100% a pH dependent reaction results in reprecipitation of lignin on the pulp (136,p.624). In delignification much more NaOH is consumed than NaSH and at very high sulphidities this will result in a significant lowering of the liquor pH as the reaction proceeds to conclusion. This last effect can occur even at lower sulphidities if there is insufficient residual chemical at the end of a cook.

Edwards and Norberg (47) have proposed an alternate model which specifically includes the effect of sulphidity. The model, like Hatton's, is fit to data which unfortunately does not include variation of sulphidity. There is also some question as to the validity of their sulphidity dependency. Tasman (155) has recently shown that the Hatton model does not fit one particular species in any range of sulphidity and has proposed a modfication. Even in this particular case the error is quite small, also there is some question as to validity of the algorithm by which Tasman estimated the H-factor which possibly compromises his model.

In batch digesters black liquor is recycled as a diluent. The black liquor contains some residual chemical which may take part in the pulping reaction. This residual chemical also takes part in the emission reactions in subsequent units. In order to reduce the size of the stream vector NaOH and Na_2S are unchanged by the reaction so it is necessary to independently distinguish between that which has been consumed in the pulping reaction and that which is free. The equations predicting residual NaOH and Na_2S are based on a datum from Rydholm (136,p.603) for a Kraft cook at 30% sulphidity.

$$NaOH_{active} = NaOH_{in\ stream} - 0.2413\ Lignin \qquad (5\text{-}15)$$

$$Na_2S_{active} = Na_2S_{in\ stream} - 0.0417\ Lignin \qquad (5\text{-}16)$$

where Lignin refers to all dissolved organics. These equations can be applied to any stream containing dissolved organics (i.e. any black liquor stream).

5.3.2 Recovery Furnace

In the recovery furnace the organics are separated from inorganics by burning. Air flow is controlled so as to supply an insufficient amount of oxygen for complete combustion in the primary or bottom zone. In this reducing atmosphere Na_2SO_4 is reduced to Na_2S.

Bauer and Dorland (15) drew phase diagrams for the components of twenty reactions in the gas and solid phases and from these generated a set of curves predicting the furnace reduction ratio as a function of char bed (i.e. solid phase) reaction temperature and the oxygen deficiency in the primary zone.

The oxygen deficiency as defined by Sillen and Andersson (148) is

$$\Delta = \frac{O_A - O_R}{O_A} X_{o_2} \qquad (5\text{-}17)$$

where Δ is the oxygen deficiency in percent and is negative, X_{o_2} is the percent oxygen in air, O_A is the oxygen available for combustion in the primary zone from the fresh air input, and O_R is the oxygen required to burn the organics, modelled by $C_{10}H_{12}O_{3.3}$, less that liberated by lignin and the complete reduction of Na_2SO_4. It is assumed that all organics sprayed into a furnace burn in the primary zone.

Galtung (57) partially linearized the curves of Bauer and Dorland and used a tabular search technique in his model of a recovery furnace. Here an equation has been fit to one portion of that graph in the region, $-1 \leq \Delta \leq -11$ and $1500^{o}F \leq T \leq 2000^{o}F$[a], that at least four mills are known to be operating their furnaces (27,57,32,19). This region is also recommended by Bauer and Dorland. The relationship is

$$Rd = a_3 + \sqrt{a_2(a_4 - \Delta - a_1T)} \quad /a_2 \qquad (5\text{-}18)$$

where Rd is the reduction ratio as defined by equation 5-6, Δ is the oxygen deficiency in %, T is the smelt temperature in ^{o}F, and a_1 to a_4 are the coefficients of the fit (see Appendix C). In the applicable region the reduction ratio increases with increasing T and $|\Delta|$. All sulphur bound to organics becomes Na_2S and all non-sulphur bearing sodium compounds become Na_2CO_3.

The limitation on equation 5-18 is that while Rd is quite properly dependent on the smelt temperature, T, the temperature, as shall be seen

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[a] $1^{o}F = 0.5556^{o}C$

in the section presenting the energy balances, is fixed. The temperature is not explicitly controlled in the actual operation. The smelt temperature has been measured by the author in four different furnaces at a single mill on at least a dozen different occasions over a two year period and was consistently within the range 1750°F to 1800°F. The temperature in three of the four furnaces never deviated by more than 20°F. While this causes very little change in Rd (see Figure C-3, Appendix C) Galtung indicates that the bed burning characteristics are very sensitive to temperature. Too low a temperature will result in a bed black-out extinguishing combustion while too high a temperature will result in a bed burn-down. Apparently control of the solids firing rate and primary air flow to avoid the latter extremes results in tight control of temperature.

5.3.3 Rotary Lime Kiln

The purpose of the lime kiln is to regenerate $CaCO_3$ mud for the recausticization of green liquor in the slaking and causticizing system. The conversion of $CaCO_3$ to CaO by the reaction

$$CaCO_3 = CaO + CO_2 \tag{5-19}$$

is predicted by the equation

$$Y = 1. - \frac{a\ TA^n}{\log Q} \tag{5-20}$$

$$n = n\ ,\ TA > 1.$$

$$n = o\ ,\ TA \leq 1.$$

where Y is the molar fraction converted, TA is the percent total alkali (as Na_2O) in dry $CaCO_3$ mud fed to the kiln, Q is the Q-factor analogous to the H-factor for wood pulping, and a and n are coefficients of the fit to data from a lime kiln experiment (see Appendices B and C) and the data of Hughey et al (89).

The Q-factor was developed by assuming an Arrhenius form of rate expression for the calcining reaction and is defined by

$$Q = \int_{o}^{t_f} e^{(A - \frac{B}{T(t)})} dt \qquad (5\text{-}21)$$

where the definition of terms is the same as that for the H-factor (see equation 5-10), and A and B were determined for $1650^{o}F \leq T \leq 2400^{o}F$, the reaction initiation temperature is $1650^{o}F$ by a fit to the data of Hughey et al who calcined samples of mud from two Kraft mills at various temperatures and for differing lengths of time (see Appendix C). The value for the activation energy, B, compares very favorably with that determined by Satterfield and Feakes (142).

The Q-factor like the H-factor is an expression of the relative effects of the temperature-time profile on the calcining reaction. It is not an absolute expression of the reaction rate. Attempts at simulation of the reaction as simply a first order reaction with a Arrhenius form for the rates expression by Jacobi (90) and Chase and Koivo (35) have been unsuccessful. Satterfield and Feakes suggest that the rate of diffusion of CO_2 from the particles also affects the reaction rate. Niggli (120) suggested that the presence of sodium compounds in the mud to a kiln can cause a smelting reaction in the lime which will plug the pores of the particulates at temperatures as low as $814^{o}F$. The mechanism he suggested was

$$CaCO_3 + Na_2CO_3 = Na_2(Ca(CO_3)_2) \qquad (5\text{-}22)$$

Hughey et al calcined mud with up to 12% sodium chemical as Na_2O and found that below 1% there was no appreciable retardation of the reaction thus the form of equation 5-20.

The calculation of Q by equation 5-21 applies only in the temperature region $1650^{o}F \leq T \leq 2400^{o}F$. Calcining at temperatures above $2400^{o}F$ results in a retardation of the reaction (142,89,139) possibly as a result of partial melting of $CaCO_3$ which results in pore plugging. This phenomenon is modelled by the reversible reaction

$$CaCO_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CaO + CO_2 \qquad (5\text{-}23)$$

and the Q-factor is calculated by the equation

$$Q = \int_{t_{2400}}^{t_f} e^{(A_1 - \frac{B_1}{T})} - e^{(A_2 - \frac{B_2}{T})} \, dt \qquad (5\text{-}24)$$

where A_1, A_2, B_1 and B_2 result from from a fit to the data of Hughey et al (see Appendices B and C). There are only four data points available for the fit but this phenomenon is so important in most pulp mill operations that inclusion of this causality is warranted.

The causality represented by the above equations is also adaptable to fluid bed calciners. The basic difference between fluid bed and rotary calciners, with respect to the reaction, is in the temperature profile (42). The major drawback in this causality is that a temperature profile must be assumed. Based on the temperature profiles shown by Jacobi, and Chase and Koivo a particular profile is estimated from known inlet and outlet lime temperatures. This causality suffers from the inadequacy of the energy balance. Unfortunately, a model calculating a dependent temperature profile would be extremely complex and would conflict with the major objectives of this work.

5.3.4. Causticization

Regenerated lime from the kilns is used to recausticize Na_2CO_3 in green liquor by the reactions

$$CaO + H_2O \longrightarrow Ca(OH)_2 + Na_2CO_3 \longrightarrow 2NaOH + CaCO_3 \qquad (5\text{-}25)$$

The causticizing efficiency, E_c , as defined by equation 5-7 is predicted by an empirical equation developed by Hughey et al and modified by Carroll (31).

$$E_c = \eta - a\,TTA - B\,TTA^2 - c\,S - d\,A \qquad (5\text{-}26)$$

where E_c is in percent and η is a constant and is considered to be limiting causticizing efficiency (less than 100%) which takes into account factors such as the physical characteristics of the regenerated lime which will affect settling and decomposition rates in the slakers. TTA is the total titratable alkali concentration in incoming green liquor

$$TTA = NaOH + Na_2S + Na_2CO_3 \qquad (5\text{-}27)$$

as lbm Na_2O/ft^3[(a)], S is the Na_2S concentration in green liquor lbm Na_2O/ft^3 and A is the concentration of Na_2SO_4 in green liquor in lbm Na_2O/ft^3. The coefficients a, b, c and d are constants derived by Hughey et al (see Appendix C). It should be clear that E_c is not really a conversion efficiency as it is calculated from the outlet white liquor only and there is normally NaOH in the green liquor (see Table B.6, Appendix B). E_c is most strongly dependent on TTA. Jacobi has suggested an equation dependent only on TTA, however, both Kobe and Wilkinson (100) and Hughey et al have shown that sulphur compounds have a significant effect in the reaction. Rydin (139) has suggested that the presence of Na_2S shifts the equilibrium

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(a) 1 lbm/ft^3 = 16.03 kg/m^3

of reaction 5-25 to the left through hydrolysis by reaction 5-1. Equation 5-26 has been tested with mill data and seems quite adequate.

It would seem that this type of reaction would be more suitably described by an equation which is temperature and time dependent. The optimum temperature of approximately 185°F is well established (89,139) and the temperature is controlled. The reaction proceeds very rapidly going to 85% of completion within 30 minutes while the residence time in industrial units is typically between 90 and 120 minutes. One such model does exist. Rydin has had success with a multi-path model of the causticizing reaction that involves five rate constants of the Arrhenius form. The model is quite involved and there is uncertainty about some of the assumptions. Rydin assumes that all Na_2S in the green liquor is hydrolysed and affects the equilibrium of equation 5-26 while Martin (108) has shown that Na_2S is only 40% hydrolysed in solutions more dilute than those of Rydin. Further, Rydin assumes that all NaOH in green liquor results from hydrolysis of Na_2S when in most mills a significant amount of NaOH is recycled to the green liquor in the wash water used to wash sodium compounds out of mud (see Figure 4-1 and Table B-6). This is the case in the mill from which Rydin acquired his data. As an alternate to this approach it might be possible to make the limiting constant, η, dependent on temperature and time, however, the data required are unavailable.

A more serious drawback of equation 5-26, related to time dependency, is the effect of physical properties of the lime on its settling and decomposition rate and therefore on the causticization rate. It is known (89,90,139) that lime which is overburned in the kilns (i.e. $T > 2400^{\circ}F$) or contains too high an Na_2O concentration in the mud to the kilns results in retardation of causticization. This is likely to be related to smelting in the kilns, unfortunately the quantitative information on this problem is meagre. Another factor is the effect of lime excess on the reaction. Kinzner (98) and Rydin have shown that E_c increases with increasing lime excess. In the test mill mentioned previously this plays a small but significant role in the control of causticization. Unfortunately, the effect of lime excess is related to the physical properties of the lime and there are no data available to allow distinction between the two effects.

In the remaining reactor, the strong black liquor oxidation system, the conversion efficiency of Na_2S to Na_2SO_4 is a specified fraction and is defined by

$$\frac{Na_2SO_4}{Na_2SO_4 + Na_2S} \tag{5-28}$$

all expressed as equivalent Na_2O in the outlet black liquor stream.

5.4 Chemical Losses

The chemical loss causality can be segregated into two groups, the loss of sulphur through emission of H_2S and the loss of sodium through loss of NaOH, Na_2S, Na_2SO_4 and Na_2CO_3 in the liquid streams and solid particulates in gas streams. There are also particulate losses of calcium compounds and purges of inerts from the system.

5.4.1 Emission of Sulphur Bearing Gases

Sulphurous gases are emitted in four major operating areas, the digesters, multi-effect evaporators, direct-contact evaporators and recovery furnaces. In some mills the gases from the digesters are incinerated in the kilns and some of the sulphur is recovered as usable chemical.

5.4.1.1 Digesters

Douglass and Price (44) conducted experimental cooks using three wood species and measured the amount of sulphur in the gases released. A linear relationship has been fit to the part of their data which falls in the applicable region of industrial Kraft cooking (see Appendices B and C).

$$TRS = a_1 + a_2S + a_3T + a_4\theta \tag{5-29}$$

where TRS is emitted sulphur (lbm H_2S/lbm oven dry wood)

S is reagent sulphidity

T is the top cooking temperature (^oF)

θ is the cooking time (min.)

The coefficients a_1 to a_4 are specific to wood type. The data for Pine was used as the softwood model and Birch for the hardwood model. The equation is applicable in the ranges, $320^oF \leq T \leq 356^oF$, $120 \leq \theta \leq 480$ min. and the experiments were carried out at 15% and 31% sulphidity. The amount of gas emitted increases with increasing S, T and θ.

There is some question as to the validity of the experimental technique of Douglass and Price. Their work is the most comprehensive available and the causality has been included because of its importance in the process. The dependence of emission on sulphidity and cooking conditions is well established (140,116,117) and actual use of the model should establish the suitability of the coefficients a_1 to a_4.

5.4.1.2 Multi-Effect Evaporators

The emission of sulphurous gases from multi-effect evaporators is predicted by

$$TRS = a\left[\frac{0.5Na_2S}{NaOH + 0.5Na_2S}\right]_{active} \tag{5-30}$$

where TRS is emitted sulphur (lbm H_2S/lbm dissolved organics in liquor)

Na_2S_{active} is the active residual Na_2S in black liquor (lbm Na_2O/ft)

$NaOH_{active}$ is the active residual NaOH in black liquor (lbm Na_2O/ft^3)

a is an adjustable parameter

As the reagent sulphidity to the digesters is increased the active residual Na_2S increases and the active residual NaOH decreases causing increased emission of sulphur from the system. The residual chemicals in the incoming black liquor are calculated using equations 5-15 and 5-16.

Sarkanen et al (140) have suggested that the emission reactions in multi-effect evaporators are similar to those in the digesters. No temperature dependency is included in the relationship as little is known about these reactions at these relatively low temperatures (viz. relative to digesters) however the temperatures in the various effects are strongly dependent on the solids concentration which is controlled. The dependence on active residual chemical is obvious and use of only one-half of the Na_2S suggests itself from the hydrolysis reaction 5-1. The reaction is also believed to be pH dependent (176) thus the inclusion of NaOH in the denominator. In some mills NaOH make-up is added to the weak liquor prior to evaporation in order to take advantage of this effect.

5.4.1.3 Direct Contact Evaporator

The emission of sulphurous gases from a direct contact evaporator is predicted by a relationship due to Murray and Rayner (114)

$$C_e = K_1 \left(\frac{Na_2S}{NaOH}\right)_{active} \qquad (5\text{-}31)$$

$$C_o = C_e - \frac{(C_e - C_i)}{K_2} \qquad (5\text{-}32)$$

where C_e is the equilibrium concentration of H_2S (lbm H_2S/lbm gas)

C_i is the inlet concentration of H_2S (lbm H_2S/lbm gas)

C_o is the outlet concentration of H_2S (lbm H_2S/lbm gas)

Na_2S, NaOH are the active residual chemicals in black liquor (lbm Na_2O) /ft^3)

K_1, K_2 are parameters fit to data

As before the active residual chemicals are calculated by equations 5-15 and 5-16. A dependency similar to equation 5-31 has been suggested by Walther and Anberg (176).

5.4.1.4 Recovery Furnace

Recovery furnace emissions are predicted by a relationship due to Blosser et al (22).

$$TRS = a \left(\frac{AIR}{SOLIDS}\right) + b \qquad (5\text{-}33)$$

where TRS is H_2S concentration (lbm H_2S/lbm gas)

AIR is primary air flow rate (lbm/hr)$^{(a)}$

SOLIDS is black liquor solids to furnace (lbm/hr)

a, b are parameters of the fit

The parameter a is negative resulting in decreasing emission with increasing AIR:SOLIDS ratio. Bhada et al (19) agree with the dependency but suggest that the emissions are also dependent on Na_2S content of the liquor however Thoen, DeHaas and Austin (158) provide data which indicate that air distribution between the primary, secondary and tertiary air ports of a furnace is the most important parameter.

(a) 1 lbm/hr = 1636 kg/s.

5.4.1.5 Blow Heat Recovery

In order to reduce malodourous emissions a growing number of pulp mills are collecting digester and evaporator gases for incineration in the lime kilns. The term "blow heat recovery" refers to the recovery of low temperature energy from blow tank water vapor and does not have anything to do with the sulphur recovery in the kilns but is now a widely accepted term to describe this process.. The anomolous name derives from the fact that the phenomenon of sulphur recovery was neither widely recognized nor well understood. Though recovery reactions occur in the kiln and slaking and causticizing system,the process is simulated here as a separate phenomenon in an individual module (see Appendix A).

The purpose of incineration of the gases is to generate SO_2 which is easily absorbed by hot lime thus reducing a pollution hazard. Haigh (78) has suggested that the major reactions are

$$\begin{aligned} CaO + SO_2 &= CaSO_3 \\ CaO + SO_2 + \tfrac{1}{2}O_2 &= CaSO_4 \end{aligned} \qquad (5\text{-}34)$$

It is further suggested here that the $CaSO_4$ will react preferentially with Na_2CO_3 in the slaking and causticizing system

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4 \qquad (5\text{-}35)$$

resulting in the recovery of sulphur in the form of Na_2SO_4. Since the causticizing mechanism is primarily through $Ca(OH)_2$ and because $CaSO_4$ is much more soluble in aqueous solution this mechanism seems reasonable. The $CaSO_3$ is highly insoluble and there is no recovery of this sulphur. Experiments performed in this work seem to confirm this mechanism (see Appendix C).

Since there is no $CaSO_4$ component in the stream vector of the simulation the reaction is modelled as

$$H_2S + 2\frac{1}{2}O_2 + CaO + Na_2CO_3 = CaCO_3 + Na_2SO_4 + H_2O \qquad (5\text{-}35)$$

Very little is known about the nature of this reaction and so the fraction of H_2S which is recovered from incoming gas is simply a specified constant in the simulation.

5.4.2 Solids Losses

The loss of sodium based chemical and calcium compounds is distributed throughout the mill. In most areas the causality treats the losses as simple fractions of the flow. In the case of the green liquor dregs washers, mud washing and lime kiln flue gas particulates the solids losses are a specified, adjustable fraction of the flow. In the case of direct-contact evaporators and electrostatic precipitators, and recovery furnaces the losses are also a specified fraction of the load but non-sulphur bearing sodium, as Na_2CO_3, and sulphur bearing sodium, as Na_2SO_4, are lost preferentially. That is

$$(Na_2SO_4)_{lost} = a_1\ (Na_2S + Na_2SO_4)_{in\ liquor} \qquad (5\text{-}36)$$

$$(Na_2CO_3)_{lost} = a_2\ (NaOH + Na_2CO_3)_{in\ liquor} \qquad (5\text{-}37)$$

where the parameters a_1 and a_2 are independently tunable.

The loss causality in the brown stock washers and by the smelting reaction in kilns mentioned in section 5.3.3 is slightly more involved.

5.4.2.1 Brown Stock Washers

The loss of chemical from multi-stage, counter-current, pulp washers is predicted by a single parameter model similar in approach to that of

Norden (122). The fraction of chemical lost with pulp is

$$F = (\frac{W_{pulp}}{W_{TOT}}) / \eta \qquad (5\text{-}38)$$

where F is the fraction of total flow lost with pulp

W_{pulp} is the water leaving with washed pulp (lbm/hr)

W_{TOT} is the total water entering the system (lbm/hr) including that with unwashed pulp

η is the washing efficiency (> 100%)

and assuming a constant pulp consistency

$$W_{pulp} = \text{Wood } (\frac{1 - \text{cons}}{\text{cons}}) \qquad (5\text{-}39)$$

where Wood is pulp flow rate (lbm/hr)

cons is the specified outlet consistency $(\frac{\text{lbm pulp}}{\text{lbm slurry}})$

The concept is that partial displacement of black liquor by wash water makes the filter washing process more efficient than dilution washing which is taken to be 100% efficient. The difference in the Norden model is that there complete displacement of liquor by wash water is taken to be 100% efficient. That formulation requires tuning of two parameters while here only, η , need be tuned. Equations 5-38 and 5-39 may be applied to a single stage of a multi-stage system in a modular fashion or can be used to represent the entire system.

The major drawback in the above formulation is the lack of causality predicting the outlet pulp consistency as a function of flow conditions. An experiment carried out on a three stage washing system (see Appendices B and C) showed that while the dependency of equation 5-38 is reasonably satisfactory the assumption of constant consistency, when wash water flow rates are varied, is not. There were insufficient data for the development of a simple relationship to predict consistency. Jacobi (90) has developed an extremely complex simulation predicting consistency in mud filter cakes. The problem is much more complex for pulp fibres because unlike lime mud particles they are highly asymetrical and compressible.

The experiments were carried out in a system washing low yield pulp (Kappa = 26, see Appendix C). Baldus et al (13) have indicated that loss of sodium compounds by adsorption to pulp can be a significant contribution in high yield systems (Kappa = 80) and have modified the Norden model by adding a term to include adsorption of sodium compounds as a function of outlet liquor sodium concentration. The data of Rosen (134) and Rydin (139) though sparse in the concentration region of interest indicate that adsorption is only slightly dependent on concentration and strongly dependent on pulp Kappa number, species and liquor pH. Adsorption is a much less important phenomenon in low Kappa than high Kappa system (70,71).

5.4.2.2 Lime Kiln

As stated earlier Niggli (120) suggested that sodium compounds carried into the lime kilns will react to form an inert smelt by reaction

$$2NaOH + 2CO_2 + CaO = Na_2Ca(CO_3)_2 + H_2O \qquad (5\text{-}40)$$

or by reaction 5-22. Hughey et al carried out calcining experiments with lime containing zero to 12% sodium compounds as Na_2O in dry mud and a relationship has been fit to that data. Any $Na_2Ca(CO_3)_2$ formed is reported in the stream vector as an inert and represents both a sodium and calcium loss.

$$Na_{out} = Na_{in} (1. - (Na_2O - 0.01)F) \qquad (5\text{-}41)$$

where Na is the flow of Na_2O (lbm/hr)

Na_2O is the fraction of Na_2O in incoming solids

F is the fraction of chemical reacted

and $F = 0.5$ if $Na_2O > 0.01$

$F = 0$ if $Na_2O \leq 0.01$

Thus, if the Na_2O concentration is greater than 1% half the sodium chemical above the 1% limit is lost. For accounting purposes the loss is ascribed completely to NaOH in the inlet mud flow.

5.5 Energy Balances

All the energy balances are based on specified outlet temperatures that must be entered as measured values. This is a good assumption in all units except the recovery furnace and kiln. Treatment of temperatures as variables dependent on flow rates and stream compositions would represent a very large increment in the complexity of the overall simulation (57). As it stands the simulation already involves a rather large computer programme (see Appendix A) and a large step up in complexity would exceed the mandate of this work.

5.5.1 Digesters

The energy required by a digester is the sum of that required to heat the wood to the top cooking temperature and that required to heat the reagent to the top cooking temperature divided by a fractional heat loss due to radiation.

$$Q_{req'd} = \left\{ (mC_{P_L}(T_o - T_i))_{wood} + (mCp_L(T_o - T_i))_{liquor} \right\} \frac{1}{(1-Q_L)} \qquad (5\text{-}42)$$

where m is mass (lbm)

C_p is specific heat (BTU/lbm-°F)[a]

T_o is the controlled top cooking temperature (°F)

T_i is the specified inlet temperature (°F)

Q_L is the specified fraction of heat lost by radiation

5.5.2 Blow Tanks

The slurry of pulp and black liquor from the digesters is blown into large tanks where some of the water is flashed off.

$$y_{H_2O} = \frac{[mC_p(T_i-T_o)]_{\text{wood}} + [mC_p(T_i-T_o)]_{\text{liquor}}}{\Delta H_{vap}} \qquad (5\text{-}43)$$

where y_{H_2O} is water vapourized (lbm/hr)

ΔH_{vap} is the heat of vaporization of water (BTU/lbm)[b]

T_i is the blow line temperature (°F)

T_o is the blow tank temperature (nominally 212°F)

5.5.3 Brown Stock Washers

Wash water is preheated to a specified temperature before being showered on the pulp.

$$Q_{req'd} = [mC_p(T_o-T_i)]_{\text{water}} \qquad (5\text{-}44)$$

where T_o is the specified wash water temperature (°F)

5.5.4 Multi-Effect Evaporators

The outlet solids concentration desired from the final effect is specified and the heat required to evaporate the required amount of water is calculated.

(a) 1 BTU/lbm-°F = 1308 joule/kg-°K

(b) $1 \frac{\text{BTU}}{\text{lbm}} = 2324.4 \frac{\text{joule}}{\text{kg}}$

$$m_{vap} = (m_{b.l.} - m_w) \left(\frac{1-conc}{conc}\right) \qquad (5\text{-}45)$$

where m_{vap} mass of water to be vapourized (lbm/hr)

$m_{b.l.}$ mass of black liquor in (lbm/hr)

m_w mass of water in black liquor in (lbm/hr)

conc specified outlet concentration

$$Q_{req'd} = \frac{m_{vap}\,\Delta H_{vap}}{E_c} \qquad (5\text{-}46)$$

where ΔH_{vap} ~ heat of vaporization of water (BTU/lbm)

E_c ~ steam economy $\frac{\text{lbm vaporized}}{\text{lbm steam used}}$

and

$$E_c = aP + b$$

where P ~ vacuum in the final effect (in. of Hg)(a)

a,b ~ coefficients of a fit to experimental data (see Appendices B and C)

The steam economy is a commonly used parameter to specify evaporator efficiency (178,2,121). It is however more strongly dependent on inlet flow rate and solids concentration than on final effect vacuum (73,74). There is little data on the effects of the first two variables though the former is limited by design criteria and the final effect vacuum is used to control evaporator efficiency.

5.5.5 Recovery Furnace

The net heat generated by a recovery furnace is the heat from burning organics plus the sensible heat in black liquor less the sensible

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(a) 1 inch Hg = 3384 N/m^2

heat in smelt, the heat to fuse smelt, the heat to reduce Na_2SO_4, the heat to vapourize water in black liquor and the sensible heat in flue gas and flue gas particulate all less a fractional heat loss due to radiation. The reactions and vapourization of water occur at 78°F.

$$
\begin{aligned}
Q = \Big\{ & m_{lig}\,\Delta H_c + (mC_p(T_i-78))_{b.l.} \\
& -(mC_p(T_o-78))_{smelt} - (m\Delta H_f)_{smelt} - (m\Delta H_R)_{Na_2SO_4} \\
& -(m\Delta H_{vap})_{H_2O} - (mC_p(T_o-78))_{F.g.} \\
& -(mC_p(T_o-78))_{F.g.p.} \Big\} (1 - Q_L)
\end{aligned}
\tag{5-47}
$$

where m ≈ mass flow rate (lbm/hr)

C_p ~ specific heat (BTU/lbm-°F)

T_i ~ inlet temperature (°F)

T_o ~ specified outlet temperature (°F)

ΔH ~ heat of reaction or state change (BTU/lbm)

Q_L ~ fractional radiation loss

and subscripts

lig ~ lignin

b.l. ~ black liquor

smelt ~ smelt

vap ~ vapourization

F.g. ~ flue gas

F.g.p. ~ flue gas particulates

c ~ combustion

f ~ fusion

R ~ reduction

5.5.6 Lime Kiln

The purpose of the energy balance is to determine the amount of fuel required in the furnace. The energy required is the sum of the heat required to react the incoming $CaCO_3$ to a previously determined extent (see section 5.3.3), the sensible heat lost with exiting lime and flue gas, the energy required to evaporate water in mud and a radiation loss term less the sensible heat in with mud. The fuel and air enter the system at 78°F and the reactions and vaporization occur at 78°F.

$$\begin{aligned} F\,\Delta H_{Fuel} = {} & [\,m\,\Delta H_R]_{CaCO_3} + [mC_p(T_o-78)]_{lime} \\ & + [(m_{fg} + F)\;C_p(T_o-78)]_{fg} + UA\Delta T_{ave} \qquad (5\text{-}48) \\ & - \Big\{ [mC_p(T_i-78)]_{solids\ in} + ([m(C_p(T_i-78)] - \Delta H_{vap})_{water} \Big\} \end{aligned}$$

where F is fuel flow (lbm/hr)

m is mass flow (lbm/hr)

C_p is specific heat (BTU/lbm-°F)

ΔH is heat of reaction or change of state (BTU/lbm)

T_o is specified outlet temperature (°F)

T_i is inlet temperature (°F)

ΔT_{ave} is the arithmetic mean temperature difference across the kiln wall (°F)

and

$$UA = \pi D^{a_1} L^{a_2} \qquad (5\text{-}49)$$

a relationship due to Bowers and Read (24) where D is kiln diameter and L is length in feet.

Note that in equation 5-48 the mass flow of fuel is segregated from other sources of flue gas (third term). Rearranging equation 5-48 yields a solution for the Fuel flow F

$$F = \frac{\left\{ m \Delta H_{R\ \mathrm{CaCO_3}} + mC_p(T_o-78)_{\mathrm{lime}} + mC_p(T_o-78)_{\mathrm{fg}} + UA\Delta T_{\mathrm{ave}} - mC_p(T_i-78)_{\mathrm{solids\ in}} + (m(C_p(T_i-78) - \Delta H_{\mathrm{vap}}))_{\mathrm{water}} \right\}}{\Delta H_{\mathrm{Fuel}} - C_p(T_o-78)_{\mathrm{fg}}} \qquad (5\text{-}50)$$

There are two remaining units in which significant energy transfer occurs. In the strong black liquor oxidation towers air bubbled through the black liquor vaporizes some of the water in the liquor. In the model the difference in water burden between incoming and outgoing air is a specified parameter determined from psychrometric charts. The mass of water evaporated is the air flow multiplied by this parameter. In the direct contact evaporator model the strong black liquor outlet concentration is a specified parameter.

5.6 Chemical Make-up Calculation and Convergence

Some comment is warranted here on the procedure for making up for lost chemical and water, the convergence procedure and how these two factors are related to the simulation causality. In the pulp mill simulation shown in Figure 4-1 the NaOH and Na_2SO_4 make-ups are calculated as dependent variables by module 20, MAKUP1, and the water make-up is calculated by module 24, MAKUP2. In contrast all other external inputs to the simulation are independent variables (e.g. wood chips to digesters). Module 20 samples the white liquor, stream 36, and then calculates the additional Na_2SO_4

required in make-up stream 44 to achieve a desired sulphidity and the additional NaOH required in stream 43 to supply the required active alkali flow. Similarly module 24 calculates the water required in make-up stream 37 to control the active alkali concentration in stream 36. These make-up flows must be calculated as dependent variables because the process is not self-regulatory with respect to these flows. That is, setting the make-up streams arbitrarily will not necessarily result in a steady-state. In the process the mass flow of chemical to the digesters, streams 3 and 51, is rigidly controlled. This chemical flow will determine the sodium losses at the brown stock washers assuming unvarying operation of the brown stock washers. The chemical make-up is added down stream of the washers. The brown stock washers represent approximately 90% of the system sodium losses. Due to the control of chemical flow to the washers (through the digesters) a change in make-up flow will not necessarily result in a commensurate change in the sodium losses. If the sodium make-up in streams 43 and 44 is greater than the loss, more white liquor will be produced in stream 36 than is used in streams 3 and 51 (the digester streams). In the process this manifests itself as rising storage tank levels that will eventually result in overflows. Similarly, an incorrect water make-up in stream 37 will result in changing storage tank levels. For this reason these make-ups must be calculated as dependent variables. All other process inputs will result in a new steady-state if a change is made.

The decision to determine the make-ups as dependent variables also has a profound effect on the procedure for iterative computations about the process loops. It can be seen from Figure 4-1 that in addition to a main loop there are a number of internal loops, some of which are also nested within each other. The convergence about each of these loops must be controlled individually by a separate convergence testing module, CONTB1 (see Appendix A, Figure 3). Module 24, MAKUP2, determines the amount of additional water required in stream 37 in order to provide the specified active alkali concentration in stream 36. Before this can be done the loop comprised of modules 14, 15, 16, 17 and 18 must be converged (i.e. the material balance must close). If module 24 makes its decision based on an unconverged solution for stream 36 the water flow will be incorrect and will perturb convergence about the main outer loop. In addition, the caustic conversion efficiency in module 15, SLACA2, is strongly dependent on input liquor density so a change in water make-up may cause a significant change in the reaction efficiency for the production of NaOH. This would modify the previous decision on water make-up requirements. The computational loop comprised of modules 14, 15, 16, 17, 18 and 24 must be converged before module 20, MAKUP1, can make a decision on the NaOH and Na_2SO_4 make-ups. If this procedure is not followed these make-ups may perturb convergence about the outer loop. Finally, the NaOH make-up in stream 43 can have a significant effect on the H_2S emission reaction in the direct contact evaporator, module 11, DCVP01 and both NaOH and Na_2SO_4 make-up can have a small effect on the furnace reduction efficiency in FURN02 and the causticizing efficiency in SLACA2. For this reason a computational loop comprising all the modules from 8 to 20 must be converged before proceeding to another pass beginning at the digester modules.

The alternate approach would be to have only one convergence tester which would allow a pass through every module before a decision on convergence is made. This results in very slow convergence if the make-up streams are not carefully initialized. The procedure described above results in positive, stable convergence even when the iterative computations involve only simple successive substitution.

5.7 The Effect of Data Availability

As stated earlier the causality presented here evolved from earlier simulation passes and an observational period in a mill. The latter had a profound effect on the causality. Most of the predictive equations involve only one and occasionally two adjustable parameters. The most compelling reason for this approach is that analysis of several years of mill data produced only two distinct overall operating points. One of the operating points was used to tune the simulation to the mill and the other was used for partial validation of the causality. Inquiry at other mills yielded the information that a simulation user in most mills would probably have only one set of data with which to tune the simulation causality.

5.8 Conclusion

It should be clear from the preceding sections that the individual sub-process models are not intended to be used to optimize the behaviour of individual units. The equations taken one by one are quite simple, however their interdependency becomes extremely complex in the context of a process with many recycle loops. The modularity of the simulation results in prediction of all the stream flow rates and compositions through the simple material balances derivative from the predictive equations in the previous sections.

A strong appeal to empiricism has the advantage that the causality may be easily tuned to different physical plants by adjusting coefficients to match plant data. The disadvantage of models of an empirical or semi-empirical nature is that their applicability over a range of operating conditions is suspect due to their relative simplicity. The causal dependency can only be evaluated by direct experiment in a real process. Such an experiment is the subject of the next three chapters.

Table 5-1 Model Stream Components

Model Stream Components	27 Components +	
Undissolved Wood	Carbohydrate	$C_6H_{10}O_5$
Dissolved Wood, $C_{10}H_{12}O_{3.3}$	Softwood Lignin	$C_{10}H_{12}O_{3.3}$
	Hardwood Lignin	$C_{10}H_{11.5}O_{3.3}(OCH_3)_{0.5}$
	Extracts	
	Dissolved Lignins (3 each hard and softwood)	
	Dissolved Carbohydrates	
H_2O	H_2O	
NaOH	NaOH	
Na_2S	Na_2S	
	NaSH	
Na_2SO_4	Na_2SO_4	
	Na_2SO_3	
	$Na_2S_2O_3$	
Na_2CO_3	Na_2CO_3	
CaO	CaO	
	$Ca(OH)_2$	
$CaCO_3$	$CaCO_3$	
	$CaSO_4$	
gas O_2	O_2	
N_2	N_2	
CO_2	CO_2	
	CO	
H_2S	SO_2	
	H_2S	
	CH_3SH	
	$(CH_3)_2S$	
	$(CH_3)_2S_2$	

6 - THE SIMULATION AS A VEHICLE FOR PROCESS IMPROVEMENT

In order to be meaningful, a study of alternate operating points must be bounded by external operational constraints such as the market demand for the product and acceptable limits on pollution. Because raw material costs amount to less than half the cost of bleached pulp, the most obvious target of an optimization is the maximization of production. Such strategies were proposed by Boyle and Tobias and Rogers et al. (133) and have been rejected here because of the depressed market demand for paper and because both strategies involve an increase in air pollutants emitted and probably an increase in water pollution caused by increased bleach plant loading resulting in increased waste water treatment demand.

The study carried out here and previously reported by Boyle and Treiber (27) was the effect of white liquor sulphidity on malodourous emissions and process economics. The range of sulphidity considered was 21% to 33%. The criterion for acceptability at an alternate operating point in this range is that there be no change from the base condition in production rate and yield.

In order to satisfy the criterion, a basic strategy must be established. Three strategies are possible to compensate for decreasing sulphidity: the cooking time may be reduced, the cooking temperature may be reduced or the initial chemical loading (active alkali on wood) may be reduced. Simulation studies for all three strategies were carried out and while all predicted substantial reduction of malodourous emissions with decreasing sulphidity the third strategy was found to be the most cost effective because the small decreases in cooking time or temperature produced very small energy savings compared to the chemical savings possible by the third strategy.

Figure 6-1 shows the effect of white liquor sulphidity on production costs and malodourous emissions (as Total Reduced Sulphur) by the third strategy. The study showed that TRS emissions are reduced by 30% over the range and intriguingly an operating cost reduction of $1.83 per ton[a] of pulp. It should be pointed out that since there is no change in production rate and yield the important factors of wood cost, pulp value and fixed operating costs are not included. The benefit in operating cost is an intriguing result because traditionally high sulphidity has been associated with profit. When compared to the value of bleached pulp ($300/ Air dry Ton)[b] the cost reduction is less than 0.5%; however, in a pulp mill, such as that considered here, where the annual production is approximately 500,000 tons of pulp per year, the saving amounts to nearly one million dollars before taxes. The significance of this result is further enhanced by a survey of North American mills which shows that most operate at the high end of the sulphidity range.(89)

The basis for the strategy of reducing chemical charge (active alkali on wood) to compensate for reduced sulphidity is equation (5-6) which predicts constant yield at constant effective alkali and equation (5-9) which shows that as sulphidity is reduced active alkali must be reduced in order to maintain constant effective alkali. Figure 6-2 provides a breakdown of the elements of the economic analysis. As sulphidity is reduced, the salt cake make-up requirement is reduced and the caustic make-up is increased. While caustic is approximately twice as effective as salt cake (as equivalent Na_2O) it is also approximately twice as expensive. These factors cancel each other with the exception that since the total active alkali

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(a) 1 Ton = 0.91 metric Tons
(b) 1 Ton Air Dry = 0.9 Tons Oven Dry

charge to the digesters is reduced the mass flow of sodium bearing chemical in the system is reduced and by the equations in section 5.4.2 the sodium losses and therefore total sodium make-up (salt-cake and caustic) requirement is reduced. Lower sulphidity implies a greater Na_2CO_3 concentration in green liquor requiring more regenerated lime from the kilns. Though partly compensated for by reduced active alkali charge, the net result is higher kiln fuel and fresh lime make-up requirement.

The above factors basically cancel each other out. The key element in the economic improvement is increased generation of steam in the recovery furnace which replaces steam that would otherwise be generated by burning fuel oil. The interesting aspect here is that the installation of a strong black liquor oxidation system and rising fuel costs radically changed the operating economics. It can be seen from the furnace energy balance (equation 5-26) that energy is required to reduce oxidized Na_2S. With the addition of the strong black liquor oxidation system to the process 95% of residual Na_2S is oxidized to $Na_2S_2O_3$, Na_2SO_4 and Na_2SO_3. Thus as sulphidity and active alkali are reduced, the residual Na_2S in black liquor is decreased. A lower concentration of Na_2S results in a lower level of the oxides and therefore less heat is lost in the reduction reaction. A minor factor is that there is also less Na_2SO_4 make-up to be reduced.

Figure 6-1 shows a unimodally decreasing cost and begs the question, "Why not reduce sulphidity below 21%?" The answer is partially related to the range of validity of the Hatton pulp yield model (equations (5-6)). While Hatton does not indicate a range of validity the data of Rydholm (136,pp.625-6) indicates that for most species constant initial effective alkali will not produce a constant yield of pulp below approximately 20% white liquor sulphidity. In fact, below that value there will be a sharply rising demand for alkali. Beyond any economic considerations, the most important effect will be increased attack by the reagent on the cellulose, producing pulp with unacceptably low strength properties.

The results of this study were presented to the owners of the Kraft mill with a proposal for an experiment to take advantage of the economic benefits indicated by the simulation.

FIGURE 6.1:

PRODUCTION COST AND EMISSIONS VS. SULPHIDITY

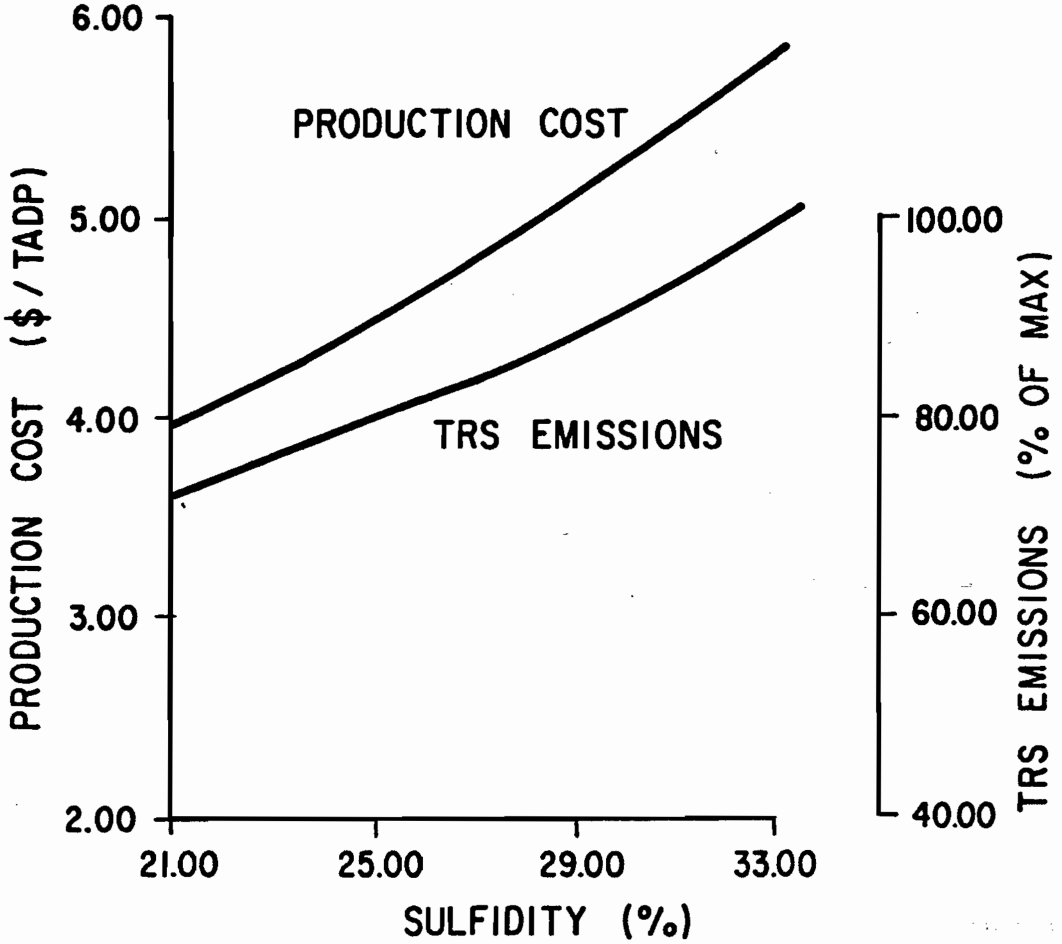
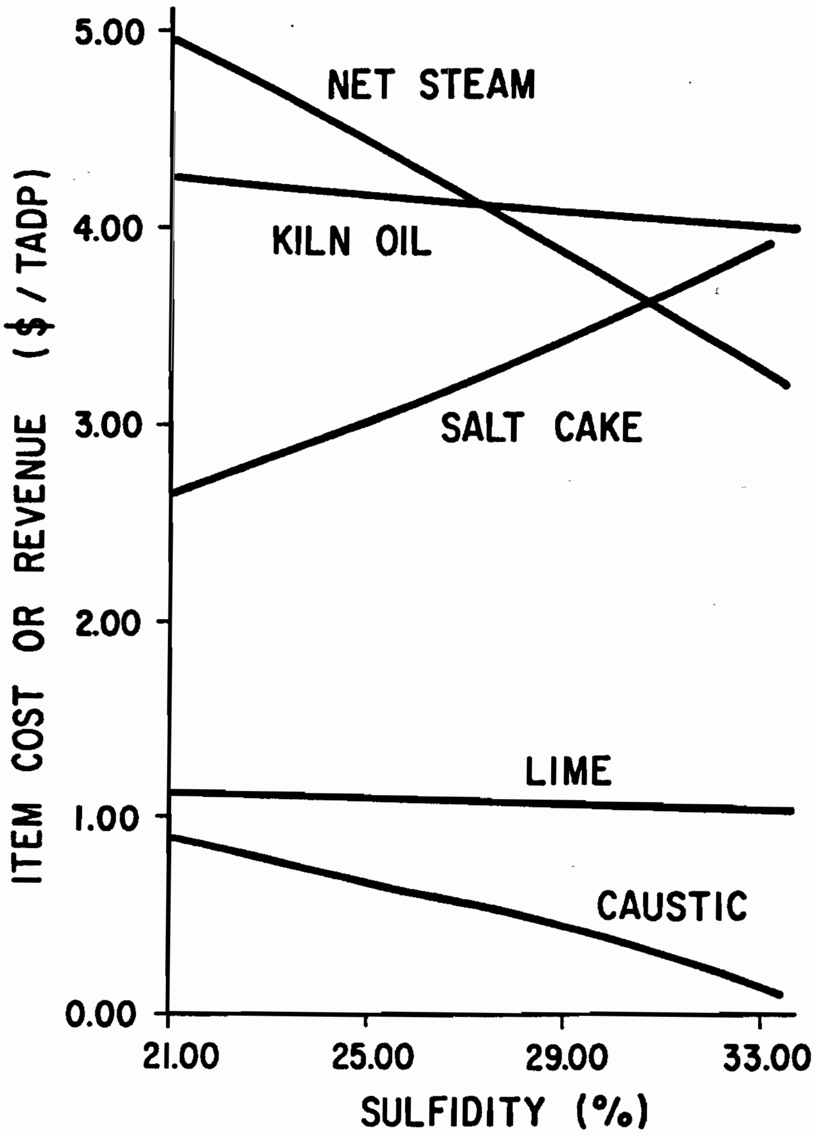


FIGURE 6.2:

PARAMETERS OF ECONOMIC PERFORMANCE



7 - RESULTS OF THE MILL TRIAL

An experiment to reduce white liquor sulphidity from 29% to 24% was carried out at the test mill (see Figure 2-2 and insert in back cover) in February and March of 1977. As in the case study discussed in the last chapter, the key constraint was that pulp yield and production rate remain invariant. The operational changes made are presented in Table 7-1. The reduction of sulphidity was compensated for by reducing the active alkali on wood in both types of digester but because such changes are made in quantum steps (standard operating procedure) partial compensation in the continuous digester was made by lowering the cooking temperature by one Fahrenheit degree.

The sulphidity reduction occurred as a result of a four day breakdown of the strong black liquor oxidation system which resulted in a sharp increase in loss of system sulphur (viz. H_2S emission) and a chemical make-up control strategy calculated by a dynamic model developed for this purpose. That model and the nature of the control problem are developed in subsequent chapters. Here the concern is comparison of the predicted and actual changes in steady-state values.

The experiment did not test all elements of the model causality. Twelve parameters of comparison are listed in Table 7-2. The actual changes reported are the difference in mean values of data taken from the operating log sheets. The caustic, salt cake and fresh lime make-up data are monthly average values for the period July to December 1976 (defined as before the trial) and March to September 1977 (defined as after the trial). All other data are daily average values from the periods immediately prior to and after the experiment (January 20 to February 11 and February 21 to March 11, 1977 respectively). As can be seen the changes that occurred are generally quite small by comparison to the base values. The most stringent test of validity of the predictions is a comparison of the predicted and actual changes. The test of significance is carried out in two stages. First the significance of the measured change, $\Delta\overline{X}$, is tested by a two-sided t-test to the 90% confidence level.

$$\text{Hypothesis:} \quad \Delta\overline{X} = 0$$

$$t = \frac{\Delta\overline{X}}{s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \tag{7-1}$$

where the best estimate of the population variance, s^2, is defined as

$$s^2 = \frac{n_1 s_1^2 + n_2 s_2^2}{n_1 + n_2 - 2} \tag{7-2}$$

In each case, if the null hypothesis is rejected, another test is carried out to compare the predicted change, ΔX, to the measured change, $\Delta\overline{X}$.

$$\text{Hypothesis:} \quad \Delta X - \Delta\overline{X} = 0$$

$$t = \frac{\Delta X - \Delta\overline{X}}{s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \tag{7-3}$$

where s is defined by equation 7-2. It should be clear that the desired result of this second test is that the null hypothesis cannot be rejected. For this reason, a low confidence limit is more stringent than a high confidence limit. The confidence level chosen for this second two-sided test was the 90% limit.

In all twelve cases in Table 7-2, the null hypothesis tested by equation 7-3 above could not be rejected. In other words, the predicted change compares favorably with the measured change in each case. For the case of items which are annotated by an asterisk the null hypothesis test by equation (7-1) cannot be rejected. This weakens any statement made by the subsequent test of significance (equation 7-3) of those parameters. With the exceptions of lime and salt-cake, this occurs in the case of minor parameters only. Table 7-3 lists the measured means (before and after the trial), the sample sizes and standard deviations for the tests of significance.

The costs of the changes listed in Table 7-2 are presented in Table 7-4 to calculate the net operating cost change. The predicted change is a cost reduction of $0.63 per ton of air dry pulp and the measured cost reduction was $1.02 per ton of air dry pulp. The elements of the comparison are as in the previous chapter. Since there is no production rate or yield change there is no cost change in these parameters. A reduction in sulphidity results in higher caustic usage and lower salt cake usage. In addition, there is a reduction in total cost of sodium chemical due to reduction of total sodium losses as a result of lowering the active alkali change and because NaOH is cheaper than Na_2SO_4 in dollars per pound as Na_2O. The gain here is cancelled by an increased use of kiln fuel and lime make-up. As before, the major benefit lies in increased steam generation from the recovery furnaces. The measured values indicate that the economic benefits may be greater than predicted. While the steam and caustic make-up compare favorably, the measured reduction of salt cake requirement is greater than predicted and the measured lime requirement decreased when it was forecast to increase.

Because of the scatter in the data it is not unreasonable to say that the model provides a good estimate for the problem posed here. Scatter in data from industrial processes is not uncommon. The tests of significance have been fairly and conscientiously applied and it is tempting to accept the analysis as proof of the virtue of the simulation.

As a result of this successful trial, a proposal has been made to the host company for a further reduction in white liquor sulphidity which will yield comparable cost benefits. In view of this and the implication of this work for the rest of the industry it would be profitable to know if the discrepancy between the measured and predicted cost benefits is real. The simulation is one of the first attempts in this area and the causality is heavily constrained by requirements of practicality. Errors would therefore not be surprising. In addition, there is some question as to the source of scatter in the chemical make-up data which may be partially due to operational practice and not measurement error.

It is therefore proposed that the statement of the statistical analysis be taken literally (i.e. the analysis does not give grounds for rejection of the predictions) but that the measured difference in mean values be accepted. It is then necessary to explain the discrepancies in the chemical make-up either by finding fault with the causality or with the method of analyzing the data.

Table 7-1

Operational Changes

	Before	After
White liquor sulphidity	29%	24%
Batch pine active alkali on wood	16.25%	16.0%
Continuous hardwood active alkali on wood	16.35%	16.0%
Continuous digester lower heater temperature	320°F	319°F

Table 7-2

Parameters of Comparison for the Trial

Parameters of Comparison	Base Values	Predicted Change	Actual Change
Caustic make-up	$16.33\frac{\text{lbm}}{\text{TADP}}$	$+3.90\frac{\text{lbm}}{\text{TADP}}$	$5.23\frac{\text{lbm}}{\text{TADP}}$
Salt cake make-up	$45.5\frac{\text{lbm}}{\text{TADP}}$	$-8.40\frac{\text{lbm}}{\text{TADP}}$	$-13.94\frac{\text{lbm*}}{\text{TADP}}$
Fresh lime make-up	$33.28\frac{\text{lbm}}{\text{TADP}}$	$+1.9\frac{\text{lbm}}{\text{TADP}}$	$-5.97\frac{\text{lbm*}}{\text{TADP}}$
Recovery furnace steam	$12.5\text{x}10^{9}\ \frac{\text{BTU}}{\text{DAY}}$[a]	$+433\text{x}10^{6}\ \frac{\text{BTU}}{\text{DAY}}$	$+428\text{x}10^{6}\ \frac{\text{BTU}}{\text{DAY}}$
Mud flow to kilns	214.2gpm[b] (us)	+9.73gpm (us)	+9.91usgpm
Kiln fuel	18gpm (us)	+0.5gpm (us)	+0.28gpm*(us)
Batch pine yields	18.79P	-0.3	-0.2*
Cont. hardwood yields	10.86P	+0.3	+0.36
Titratable brown stock washer losses	$26.4\frac{\text{lbNa}_2\text{SO}_4}{\text{TADP}}$[c]	$-1.3\frac{\text{lbmNa}_2\text{SO}_4}{\text{TADP}}$	$+0.06\frac{\text{lbmNa}_2\text{SO}_4^{*}}{\text{TADP}}$
Furnace reduction	93.1%	+0.1%	+0.43%*
Caustic conversion	84%	0	+1.6%*
Lime availability	87%	0	+0.5%*

* Cannot reject null hypothesis

(a) $1\ \frac{\text{BTU}}{\text{Day}} = 25344\ \frac{\text{joules}}{\text{sec}}$

(b) 1 gpm = $6.309\text{x}10^{-5}\text{m}^3/\text{sec}$

(c) 1 lbm/TADP = 0.5 kg/mTon

Table 7-3

Measurements and Statistical Parameters for Data Analysis

	Measured Values		Number of Samples		Standard Deviation	
	Before Trial	After Trial				
	x_1	x_2	n_1	n_2	sd_1	sd_2
Caustic make-up (lbm/TADP)	15.8	21.1	7	7	2.78	3.64
Salt cake make-up (lbm/TADP)	43.7	29.7	7	7	14.2	15.6
Lime make-up (lbm/TADP)	32.1	26.1	7	7	8.84	5.95
Recovery furnace steam $\frac{\text{BTUx}10^6}{\text{DAY}}$	12504	12932	22	12	270	276
Mud flow to kilns (usgpm)	214.2	224.1	39	66	15.04	9.16
Kiln fuel (usgpm)	18.0	18.28	NA	NA	NA	NA
Batch pine $KMnO_4$	18.79	18.59	124	92	1.08	1.03
Continuous hardwood $KMnO_4$	10.86	11.22	152	96	0.60	0.51
Titratable brown stock washer loss $\frac{lbmNa_2SO_4}{TADP}$	26.48	26.54	25	16	2.57	3.17
Furnace reduction (%)	93.1	93.5	14	9	1.77	1.20
Caustic conversion (%)	84.0	85.6	14	9	3.2	1.7
Lime availability (%)	87.37	87.58	14	9	2.29	1.95

Table 7-4

Parameters of Economic Comparison

Parameters of Economic Comparison		Predicted Production Cost Changes	Actual Production Cost Changes
Wood	$/TADP	0	0
Fixed	$/TADP	0	0
Caustic make-up	$5.50/cwt[a]	+$0.21/TADP	+$0.29/TADP
Salt cake make-up	$3.50/cwt	-$0.29/TADP	-$0.49/TADP
Lime make-up	$2.50/cwt	+$0.05/TADP	-$0.15/TADP
Recovery steam (valued as oil)	$0.35/gal(us)	-$0.78/TADP	-$0.77/TADP
Kiln oil	$0.35/gal (us)	+$0.18/TADP	+$0.10/TADP
Operating cost		-$0.63/TADP	-$1.02/TADP

(a) 1 cwt = 45.45 kg

8 - Analysis of Chemical Make-Up Results

In the last chapter emphasis was placed on comparison of predicted and measured changes between only two of the operating points (i.e. 1976, before the trial and 1977, after the trial). The comparison of predicted and measured values in the last chapter shows that the largest discrepancies were in the chemical make-up predictions. Here, comparison of the absolute values of the chemical make-up for all four operating points will also be made with the objective of detecting sources of error.

In Chapter 7, the statistical tests applied did not allow rejection of the hypothesis that the predicted and measured changes are equal. This indeterminacy is due to the scatter in the data. Evidence will be presented to support the thesis that:

1) The scatter in the NaOH and Na_2SO_4 make-up data is not primarily due to measurement noise;
2) That average chemical make-up as calculated from chemical purchases over a one year period is a good estimate of make-up usage; and
3) That the discrepancies between predicted and measured values should therefore be treated as more accurately reflecting the true state of affairs than the statistical analysis indicates.

Finally, the model causality will be examined for the purpose of adjustment or modification so as to improve the fit to all the make-up data for the four different operating conditions.

8.1 Error in the Na_2SO_4 and NaOH Make-up Predictions

Table 8-1 presents make-up data and simulation results at four different operating conditions. The 1974 condition is for the test mill prior to the installation of environment protecting systems. The 1975 data are the result of installation of electrostatic precipitators to reduce particulate losses from the recovery furnaces and a strong black liquor oxidation system to suppress H_2S emissions from the direct contact evaporators. The simulation loss relationships were tuned to the 1975 and 1974 data prior to its application to the mill trial of 1977. The 1976 data are the result of addition of a system to collect malodorous gases from the digesters and incinerate them in a kiln (viz. blow heat recovery, BHR) and an increase in the efficiency of the strong black liquor oxidation system. This point was the initial condition for the trial discussed in the last chapter. The 1977 data represent the endpoint of the trial. It should be noted that in addition to differences in process configuration, there are also significant differences in operating white liquor sulphidities among the four conditions.

The most glaring error shown in Table 8-1 is that the simulation statement of make-up requirement does not match the measured make-up usage of the 1976 condition which was the starting point of the trial to test the model. Since the intention of the trial was to test whether or not the simulation could predict a new steady state operating condition, starting from the wrong point was rather awkward. Time did not allow resolution of this problem before the trial began so it was decided that the trial would test the accuracy of the simulation predictions of <u>changes</u> in the make-ups. As will be shown shortly, the error in the starting point has subsequently been traced to a clerical error in data handling. Therefore, the judgment to proceed on the basis of a test of model changes was a good one.

Since the model causality was tuned to the 1975 condition, the 1976 trial starting point also serves as a test of the model validity. Recently, the 1975 make-up data was re-analyzed and it was found that a large error had been made in calculating the average make-up usage for that year.

The model has been re-tuned to match the correct data for 1975. The procedure was to adjust the coefficients of the brown stock washer loss equation so as to match the total sodium make-up as Na_2O. The coefficients of the direct contact evaporator emission equations were then adjusted so as to match the NaOH and Na_2SO_4 make-up of 1975 and so that the NaOH make-up for the 1974 condition would be zero. This new information is presented in Table 8-2. It can be seen that the 1974 Na_2SO_4 make-up prediction matches the measured value better in Table 8-2 than in Table 8-1. As before, the model was then used to predict the 1976 and 1977 make-up requirements <u>without</u> readjusting the causal coefficients. Table 8-2 shows that in general, the absolute values, while still different, now compare more favorably with the measured values. However, the predicted differences between 1976 and 1977 have not improved.

In the analysis of model errors now to be presented, Table 8-2 will be taken as the basis rather than Table 8-1.

8.2 Reliability of Chemical Make-up and Loss Measurements

It has been shown that a t-test to the 90% confidence limit does not allow rejection of the hypothesis that the predicted changes equal the measured changes. It should be noted that in the cases of the Na_2SO_4 and CaO make-up the hypothesis that no change has occurred also cannot be rejected. However, the fact remains that in the period March to September 1977 (defined as after the trial), the mill purchased 3,865,138 lbm Na_2SO_4 less, 1,470,600 lbm NaOH more and 1,673,181 lbm CaO less than in a comparable period before the trial (June to December 1976) while the pulp production was essentially the same (see Table B-3, p.B.12) these differences in the chemical purchase are approximately equal to the total chemical contained in the liquors in the on-line storage tanks.

The lack of statistical determinacy is due to the large variation in make-up data from month to month. An argument will now be developed which concludes that the variation is in fact mainly due to process behavior and cannot be treated as scatter.

Table 8-3 presents the values for an analysis of the make-up data and a comparison to predicted values. The salt-cake and caustic make-up, and the total Na_2SO_4 and NaOH expressed as equivalents of Na_2O are tabulated for the before and after trial periods. The lime make-up data is also presented and in addition the Na_2SO_4 and NaOH make-up is also expressed as <u>make-up</u> sulphidity defined as,

$$\frac{Na_2SO_4}{NaOH + Na_2SO_4} \qquad (8\text{-}1)$$

all expressed as Na_2O equivalents. This last term reflects the relative loss of sulphur and sodium from the system. In addition to the above information, the 1975 base condition is presented. At the bottom of the table is a comparison of the measured and predicted changes for the trial. Numbers accompanied by an asterisk indicate that the hypothesis of no change cannot be rejected to the 90% confidence limit. In all cases the hypothesis, that predicted and measured changes are equal, cannot be rejected to the 90% limit. While three of the five comparisons are compromised by failure of the first test, caustic make-up and make-up sulphidity survive both tests despite a 20% and 40% error respectively. The large standard deviations cause the indeterminacy of the test.

In Figure 8-1 the monthly NaOH and Na_2SO_4 data, calculated as Na_2O, which was used for the analysis, is plotted for the period June 1976 to September 1977. It is believed that the large monthly variation is caused by storage manipulation. The density of stored liquors is controlled and the mill staff manipulate storage tank levels by varying the chemical make-up. The test mill appears to have insufficient storage capacity to satisfactorily damp out process upset. In order to maximize the use of storage capacity,tank levels are maintained so high that there is insufficient spare capacity to accommodate process unit volumes in the event of a shut-down. Therefore, in the month prior to a major shut-down, the storage tank levels are reduced. Clearly, if the liquor concentration is maintained constant and the make-up chemical is less than that required to replace losses the net result is a reduction in over-all liquor volume. After a start-up, the storage levels are raised during the following month by making up with more chemical than is required to replace losses.

There are three major shut-downs each year. These are indicated in Figure 8-1 and it can be seen that the chemical make-up is below the mean in the month prior to each shut-down and above the mean afterward. Thus the mill is being cycled hydraulically and the standard deviations overemphasize the indeterminacy of the data.

A corrollary of this hypothesis states that if the chemical make-up were maintained at the mean value (viz. the amount required to replace losses only) there would be no change in the total liquor volume. The hypothesis can be tested by an example. During the trial the storage tank levels were monitored and the total liquor volume has been tabulated as equivalent white liquor at a concentration of 6 lbm Na_2O/ft^3 in Table B-10, p.B.18. The total storage volume decreased by 27336 ft^3 during the trial, equivalent to 164016 lbm Na_2O of chemical. Figure 8-1 shows that during the trial the average make-up was less than the approximate mean of 30 lbm Na_2O/TADP required for no change in volume. From Table B-3, p.B-12 it can be calculated that the average for the period was approximately 26 lbm Na_2O/TADP and the pulp production was approximately 38000 TADP. The difference from the "no volume change" case is therefore 152000 lbm Na_2O which is equivalent to a volume decrease of 25333 ft^3 (expressed as white liquor of concentration 6 lbm Na_2O/ft^3). This accounts for most of the monthly deviation from the mean and supports the previous argument about the significance of the variation in the monthly chemical make-up data.

The discussion above argues for acceptance of the measured changes as being truly representative of a change in the process. A comparison of the predicted and measured changes leads to the conclusion that the simulation is seriously in error with regard to chemical make-up. Accepting this, the response must be improvement of the simulation causality with the purpose of making a better fit to all the make-up data now in hand.

Comment should be made here as to the relative merits of measured make-up and loss data. Appendix B provides a detailed discussion of the source of chemical loss data and its reliability. It is sufficient to say here that the only chemical loss which is monitored regularly is the brown stock washer loss. With respect to the practicalities of mill operation this might be justified because the sodium loss at the washers represents approximately 90% of the total sodium lost and the other losses are small and difficult to measure. However, the washer loss data is extremely suspect because of the measurement technique used. There is reason to believe that the losses are as much as three times greater than measured. Since chemicals are purchased from an external source and the costs play a vital role in the economics of the operation, these quantities along with total pulp produced are the most highly scrutinized variables in a pulp mill. Furthermore, the amount of chemical purchased in a one year period is approximately ten times that contained in the process units and liquor storage tanks so chemical purchases over the seven month periods used here should reflect the losses fairly accurately.

8.3 Improvement of the Chemical Loss Causality

The strategy used in considering causal changes to improve the fit to data was to reconsider all four operating points of Table 8-2 rather than merely the 1977 experimental results. The procedure followed was first to readjust the coefficients of the equations to improve the overall fit to data without changing the number of coefficients of the fit nor the functional dependency of the equations. In cases where this proved unsatisfactory, the functional dependency of the equations has been changed without increasing the number of empirical parameters. Finally, where the latter failed the chemical loss causality has been changed, more radically, to improve the fit to the make-up data. These last changes have generally been based on physical arguments rather than on hard data and should thus be viewed as suggestions to be tested by future work. Thus the entire model development process has been repeated and extended.

The chemical loss causality can be divided into three major areas: 1) The loss of sodium in liquor streams (i.e. brown stock and flue gas particulates where this sodium loss is also accompanied by the loss of sulphur in Na_2S and Na_2SO_4 ; 2) The loss of sulphur by emission of H_2S; and 3) The loss of calcium as CaO and $CaCO_3$. Tables 8-2 and 8-3 can be used to focus on each of these areas separately.

8.3.1 Improvement of Sodium Loss Causality

The total NaOH and Na_2SO_4 make-up expressed as Na_2O represents the system sodium losses. From the tabulation of make-up as Na_2O in Table 8-3 it can be seen that beginning from the 1975 base case to which the sodium losses were tuned the simulation first underestimated the change in sodium losses as a result of the process changes that led to the 1976 condition and then again as a result of the process change to the 1977 condition.

Looking at the first error, the difference in the 1976 operating condition from the 1975 condition is that: 1) The strong black liquor oxidation efficiency was increased from 95% to 99.9% (based on outlet composition); 2) the start-up of the blow heat recovery system in which sulphurous gases emitted by the digesters are passed to the kilns; and 3) the daily pulp production was increased by approximately 30 TADP per day (see Table B-1, p.B.8. The first two changes mainly affect the loss of sulphur as CH_3SH, $(CH_3)_2S$ and H_2S. The third factor will affect sodium loss from the brown stock washers because there was no comparable change in washing capacity. Note also that due to the comparative size of the sodium losses from the washers (see Table 8-4) this is the most likely single area for causal adjustment. To this point, all simulation was based on a daily production of 1400 TADP. Incorporating the change of production (at constant yield) in the 1975 and 1976 simulations does not improve the Na_2O make-up comparison sufficiently. The change in production is small but the conclusion must be that the washer loss causality is not sufficiently sensitive to a change of this kind. The washer loss equation presented in Chapter 5 is shown below.

$$F = \frac{W_{pulp}}{W_{TOT}} / \eta$$

where W_{pulp} is the water leaving with washed pulp, W_{TOT} is the total water into the washer including wash water and water in entering pulp, η is the washing efficiency and F is the fraction of the total input of chemical that is lost with washed pulp. The equation simulates a multi-stage counter-current washing system and is clearly an oversimplification. It might be more appropriate to use the equation to simulate only one stage of a washing system. With such dissaggregation the simulation of the test mill would require 15 modules to simulate washing as well as 10 modules to control convergence about the computation loops. This would double the size of the simulation and does not seem justified for this particular problem though it would be a valuable study for future work.

Short of complete disaggregation and without attempting to create completely new causality, which would require testing by experiment, another form of the above equation suggests itself which reflects the higher order of the system but is no more difficult to tune to the system;

$$F = \left[\frac{W_{pulp}}{W_{TOT}}\right]^m / \eta \qquad (8\text{-}2)$$

where m is the number of stages in series in the washer system. In the case of the process change from 1975 to 1976, the pulp flow increases without an increase in wash water flow. The ratio W_{pulp}/W_{TOT} increases and the change is accentuated by the power relationship. Retuning this new relationship to the 1975 condition so as to give the same value for F as with the former relationship and then predicting forward to 1976 gives a total make-up prediction of 31.0 lbm Na_2O/TADP as compared to the measured mean of 31.4 from Table 8-3.

Applying equation (8-2) to prediction of the 1977 condition results in only a small improvement. The predicted change in make-up from 1976 to 1977 is a reduction of 0.85 lbm Na_2O/TADP as compared to a measurement of 2 lbm/TADP. It would seem that this modification of the washer loss causality is insufficient. Following along the same lines in search for causal modifications which do not change the complexity of the model the furnace particulate loss causality may be modified. From Table 8-4 it can be seen that after the brown stock washer losses the furnace losses are the only losses of sufficient magnitude to allow a rectification of 1.15 lbm Na_2O/TADP which is the remaining discrepancy.

As presented in Chapter 5, the loss of Na_2SO_4 and Na_2CO_3 is proportional to the total inflow of Na_2S and Na_2SO_4, and NaOH and Na_2CO_3 respectively. The major process change from 1976 and 1977 was the addition of the blow heat recovery system in which sulphurous gases from the digesters are collected and then passed to the lime kilns for incineration. As a consequence, sulphur from the gas is being recovered and returned to the liquor system as Na_2SO_4 resulting in an increase in the flow of Na_2SO_4 through the system. If the furnace loss causality were made dependent on the free chemical rather than the total chemical these loss equations would become more sensitive to this change. Thus,

$$\begin{aligned} Na_2SO_{4\,\text{lost}} &= a[Na_2S + Na_2SO_4]_{\substack{\text{free}\\ \text{residual}}} \\ Na_2CO_{3\,\text{lost}} &= b[NaOH + Na_2CO_3]_{\substack{\text{free}\\ \text{residual}}} \end{aligned} \qquad (8\text{-}3)$$

The physical argument for this causality is related to the mechanism of chemical loss, which is entrainment of fine droplets of liquor sprayed into the furnace. Black liquor at a solids concentration of approximately 60 to 65% is sprayed into the furnace. The spray nozzle atomizes the liquid and the large droplets fall to the bottom of the furnace or strike the opposite wall. The droplets dry as they fall and then the organics begin to burn releasing the sodium and sulphur attached in the pulping reaction, to re-form primarily Na_2S, Na_2CO_3 and Na_2SO_4. Now, at these high solids concentrations the organics are not completely dissolved and form a suspension in the liquor (1). It is not unreasonable to expect that the suspended matter will form large droplets which will not be entrained and that the smaller droplets will contain a higher concentration of dissolved free inorganic matter. Since most of the chemical is attached to the organics a small change in the free inorganic content of the liquor could cause a relatively large change in the furnace particulate loss. Incorporating the above equations and retuning to the 1975 data the predicted change in make-up as Na_2O from 1976 to 1977 becomes 1.05 lbm Na_2O/TADP, a slight improvement but still insufficient. As in the case of the washer loss causality, it is unlikely that the relationship should be proportional; however, lacking data any greater change in causality would be unreasonably speculative.

The modifications have been suggested within the framework of present level of complexity. These two areas deserve further study. Baldus et al. (11) have surveyed the field of washing models and Galtung (57) has presented a rather complex model of entrainment but there is no data for testing of these models at present.

8.3.2 Improvement of H_2S Emission Causality

The H_2S emission causality can be examined independently of the other loss causality. The make-up sulphidity reflects the balance of sodium and sulphur loss in the system. Table 8-3 shows that the model was in error in predicting the make-up sulphidity at the end of the trial (i.e. 1977). The model predicted a make-up sulphidity of 51% and the measured value was 44%. In effect, this means that the model should have predicted lower Na_2SO_4 and higher NaOH make-up at the end of the trial, but without disturbing the sodium balance. In other words, for the 1977 condition equation (8-1) should equal 0.44 and from Table 8-3

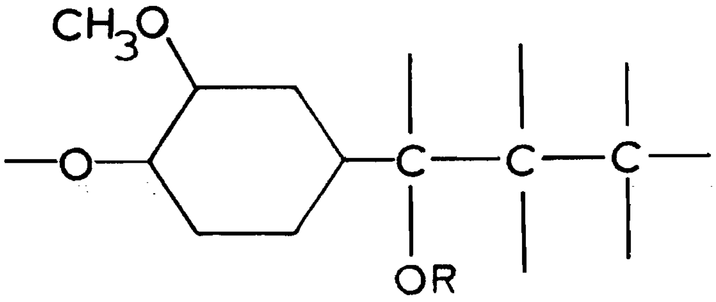
$$(Na_2SO_4 + NaOH)_{\text{make-up}} = 28.87 \frac{\text{lbmNa}_2\text{O}}{\text{TADP}}$$

Solving the two equations the Na_2SO_4 make-up should be reduced by 2 lbm/TADP as Na_2O and NaOH make-up increased by the same amount as Na_2O. The mechanism for changing this balance is the emission of sulphurous gases. The simulation analogue is

$$Na_2S + 2H_2O = 2NaOH + H_2S$$

Since Na_2SO_4 is replacement for lost sulphur, the H_2S emission in the model must be reduced by an amount equivalent to the desired reduction in Na_2SO_4 make-up. That is, the total emission of H_2S for the 1977 condition should be 1.1 lbm H_2S/TADP less, than is now the case.

In order to adjust the causality accordingly, it is necessary to determine where this adjustment should be made (e.g. digester, evaporator emissions). The major operating difference between 1976 and 1977 was a reduction in white liquor sulphidity so it is required that the emission dependency on white liquor sulphidity be adjusted. From the loss report in Table 8-4 it can be seen that in terms of magnitude the digester emissions are the most viable candidates for reduction by 1.1 lbm H_2S/TADP. The data originally used to fit the digester emissions causality (Table B-7, p.B.15) is due to Douglass & Price (44) and is somewhat suspect. The experiments were carried out in digesters of 7 ml. volume using 1 mg. of wood and a synthetic reagent. As shown in Chapter 5, the emission of H_2S is a function of sulphidity, top temperature and cooking time. For the comparison of 1976 and 1977 data the important variable is sulphidity. In Figures 8-2 and 8-3 the H_2S emission has been plotted as a function of sulphidity with the temperature and time dependency lumped into a constant. As can be seen, the fit to softwood data gives a large positive intercept and to hardwood data a very small negative intercept. While the mechanics of the delignification reaction are not completely understood (102) there is reason to disbelieve the behavior shown in Figures 8-2 and 8-3. The pulping reaction is basically an attack on the lignin in wood rendering it soluble in the aqueous reagent and leaving separate wood fiber. Lignin is thought to be made of substituted phenyl propane units (102,p.167).



(8-4)

The Kraft reagent is composed of NaOH and Na_2S which hydrolyzes to form NaOH and NaSH (156,10). The NaOH is thought to attack the benzene ring and the NaSH attacks the -OR group. Up to approximately 20% white liquor sulphidity the delignification reaction is strongly dependent on the sulphide content of the reagent but above this level, the reaction becomes almost completely independent of sulphidity (136,p.624-5). It would then seem that above this saturation level more and more SH^- ion would be available to form CH_3SH which gives Kraft mills their characteristic odor and is simulated here as an emission of H_2S. Thus it would appear that a linear model of emissions at sulphidities greater than 20% should have a significant negative intercept. Since this fits the requirements here for a reduction in the emissions at 24% sulphidity (i.e. 1977 case), the required reduction has been distributed proportionately between hard and softwood and the modified equations are shown in Figures 8-2 and 8-3 for comparison. This adjustment involves only a change in dependency on sulphidity in the digester emission equation.

$$\text{Emission} = a + bS + cT + d\theta$$

where S is sulphidity (%), T is top cooking temperature (^{o}F) and θ is cooking time (minutes). From Table 8-2 it should be clear that adjusting this causality will worsen the fit to the 1974 data as the sulphidity then was only 21%. In order to compensate, the coefficients of the direct contact evaporator emissions causality must be retuned to the 1974 and 1975 conditions.

Having made all of the adjustments discussed in the last two sections the simulation runs were repeated for all four cases. The results are tabulated in Table 8-5 along with the measurements for comparison. It can be seen that a very significant improvement has been made. It should be remembered that the four points represent very different operating conditions and process configurations.

A further note on the digester emissions is appropriate. A recent application of this equation to a Swedish pulp mill (164) gave poor results until the temperature and time dependency of the equation was combined by using the H-factor of Vroom (170). Thus the equation becomes

$$\text{Emission} = a + bS + cH \tag{8-5}$$

The experiments in the U.S. mill did not test the temperature and time dependency. The most probable source of error in the previous equation was the use of only one temperature from a temperature-time profile (i.e. the top cooking temperature). In readjusting the above equation to the U.S. data, only the coefficient, c, was manipulated. The equation thus adjusted then fit the Swedish mill.

8.4 Scatter in the Lime Make-up Data

The worst performance of the simulation is in the prediction of lime make-up usage. Table 8-3 shows that for the trial the model predicted an increase in lime usage of 1.7 lbm/TADP while measurement indicates a decrease of 6 lbm/TADP. A mitigating factor is that lime make-up was not a controlled parameter of the trial but was left to the operators discretion.

As shall be seen in the next section, attempts to modify the causality so as to fit all four operating points failed. Here an argument will be made that: 1) Unlike the NaOH and Na_2SO_4 make-up, the scatter in the lime make-up data is the result of process noise; 2) The indeterminacy of the statistical tests on lime make-up precludes a fit to all four years of data; and 3) Despite the indeterminacy of the data the radical difference in the trends predicted for the trial requires some phenomenological explanation which might be tested in some future work.

There is evidence that the procedures in the test mill for controlling the feeding of regenerated lime to the slakers are quite inadequate. A material balance about the slaking and causticizing system performed before the trial showed that the charge of lime was up to 50% in excess of the theoretical requirement while the normal value should be approximately 10% (90,139). Operating data shows that there was a reduction in unreacted lime being recycled to the kiln after the trial. This would indicate that less excess lime was being charged into the slakers. It is estimated that the excess was reduced to only 30% after the trial. This would translate into approximately a 0.5 lbm/TADP reduction in lime make-up requirement.

As for the NaOH and Na_2SO_4 make-ups, the monthly variation in lime make-up may be partially due to inventory manipulation. However, the case for disregarding the indeterminancy in lime make-up is much weaker than for the other chemicals. Regenerated lime from the kilns is charged to the slaker so as to causticize Na_2CO_3 in green liquor and form NaOH. The operator samples the exiting white liquor to determine the alkali concentration and if it is lower than the set point the rate of feeding lime to the slakers is increased. Lime make-up is added to the lime storage bin to maintain approximate level control. Thus, the lime addition rate is used to control the cauticization reaction. The basic assumption of this control procedure is that the deviation from the causticization setpoint is caused by a change in the composition of the green liquor. This assumption is not necessarily true. The upset can be caused by the lime itself. For example, the calcining efficiency in the lime kiln may change, producing lime with a different percentage of CaO. The most important changes however are changes in physical properties of the lime. Overburning of the lime in the kilns (89,139) or the presence of impurities (120) can change the settling and slaking properties of the lime. The result of an increase in either of the above factors is a retardation of the causticizing rate. By increasing the lime charge, the operator attempts to shift the equilibrium of the causticizing reaction so as to compensate. As a consequence, the lime excess is increased. This unreacted lime will exist as fine suspended particles of $Ca(OH)_2$ (139) which settle slowly in the clarifiers. As a result, more calcium is carried over with clarified white liquor to be purged through the brown stock washer, and form scale in the digesters and evaporators. The net result of this control strategy is random changes in the calcium losses and therefore the lime make-up requirement. A more effective way of controlling this process would be to manipulate the causticization temperature.

Accepting this argument leads to a possible statement that there is insufficient data to test the prediction of lime make-up;however, the difference in the predicted and measured <u>trends</u> for the trial requires an attempt at explanation.

8.4.1 Modification of the Calcium Loss Causality

At first sight, the case for accepting the simulation's statement seems quite strong. During the trial, as the white liquor sulphidity is reduced, the Na_2CO_3 content of green liquor increases requiring more lime for causticization to NaOH resulting in greater losses of calcium as the system load increases. However, it is possible that the trend has been reversed by the action of the blow heat recovery system.

The blow heat recovery system was started-up in early 1976 and is apparently the main cause of the difference in make-up sulphidity between the 1975 and 1976 cases. The function of this system is to collect the malodorous digester gases and pass them to the kiln for incineration. Measurements in the mill (see Table B-1,p.B.8) show that less than 10% of the sulphurous gases leave the kiln stack. While it is known that hot lime will absorb SO_2, there is no certainty as to subsequent reactions. A recent study (78) suggests that the gases are burned to SO_2 which then reacts with CaO to form $CaSO_4$. It is proposed here that when the lime is charged into the slakers, the $CaSO_4$ which is more soluble than $Ca(OH)_2$ will react preferentially with Na_2CO_3.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4 \qquad (8\text{-}6)$$

In this way, some of the sulphur from the digester gases will be recovered. A material balance about the entire slaking and causticizing system of the test mill shows that there is an increase in the Na_2SO_4 content of the liquor passing through the slakers (see Section C-17, Appendix C). Based on the change in the make-up sulphidity from 1975 to 1976 it is estimated that 35% of the sulphur entering the kilns is being recovered. A single set of measurements about the kilns in the test mill indicates that the recovery is 67%. This figure, based on only one measurement, cannot be very reliable as blowing of the batch digesters causes periodic air dilution of the collected gas and the concentration of the gases flowing to the kilns will vary considerably.

As the sulphidity is reduced (1976 to 1977 case), there will be less sulphurous gas entering the kiln and less CaO will be immobilized by reaction 8-6. Unfortunately, as evidenced by comparison of data and prediction this causality was insufficient to cause a reversal in the lime usage trend in the model. Some other reaction must occur to cause this trend. Since less than 10% of the sulphur entering leaves the stack and only 35% is recovered as $CaSO_4$, it remains to account for the rest of the sulphur. Among the many reactions suggested by the study mentioned previously (78) is

$$CaO + SO_2 = CaSO_3 \qquad (8\text{-}7)$$

$CaSO_3$ which is much more insoluble in aqueous solution than either $Ca(OH)_2$ or $CaSO_4$ so any $CaSO_3$ formed in the kilns would be effectively inert. This inert material would eventually be purged from the system. Thus, as the flow of sulphurous gas to the kiln is reduced by a reduction of white liquor sulphidity the $CaSO_3$ production would be reduced and the lime make-up requirement lowered. The causality represented by reaction 8-7 has been incorporated in the model giving the results shown in Table 8-6. As can be seen, the simulation now predicts that the lime requirement would be reduced by 0.7 lbm/TADP from 1976 to 1977. This is still very far from the measured change but is progress since the trend has at least been corrected.

This new causality alone is insufficient to explain the magnitude of the change. It is possible however, that the presence of $CaSO_4$ and $CaSO_3$ in the lime affects the settling characteristics of the lime pellets in the slakers so as to retard dissolution and therefore causticization of the green liquor. In the test mill, an operator would make any increase in causticizing efficiency and would respond by decreasing the flow of lime to the slakers. This would result in lower lime usage as the $CaSO_4$ and $CaSO_3$ content of the lime is reduced and would be consistent with the fact that the excess lime charge was reduced after the trial. The present causticizing causality does not include dependency on the physical characteristics of the lime. There are no data for development of such causality and this is definitely an area where further work would be profitable.

A recent study in a Swedish pulp mill (172) provides some supportive evidence for production of inert material from reactions 8-6 and 8-7. The mill uses oil as fuel in the kilns and at one point converted from oil containing 1.5% sulphur by weight to 2.5%. The standard laboratory analysis provides data for the CaO, $CaCO_3$, and inert content of lime. Analysis of the data from before and after the switch to high sulphur fuel showed a significant increase in the inert content of lime. The CaO and $CaCO_3$ analyses showed no significant change as these values are influenced by other operational factors. The U.S. mill reports only CaO and a similar analysis there also gave indeterminate results.

8.5 Discussion

The chemical loss causality has been modified to give a better fit to the four years of operating data. The method involved adjusting coefficients and changing functional dependency of the equations without increasing the number of coefficients and thus the order of the fit. The procedure was a repetition and extension of the original causal development.

The four data points represent not only significant differences in operating conditions, but significant process changes, specifically additions of important new unit processes to the test mill. The fit to all sodium and sulphur make-up data has improved while the causal modifications for calcium losses have not improved the fit. The latter failure appears to be due to a lack of data; however, suggestions for future testing have been made.

With the application of the causal modifications to the trial of 1977, the simulation would now predict a saving of $0.92/TADP as compared to $1.02 calculated from measured values. The previous prediction was a $0.63/TADP saving.

Table 8-1

Predicted and Measured Average Chemical Make-Up

Yearly Average Process Unit Changes	1974 Pre-environment Protection	1975 Base Case BLO	1976 Before Trial BLO, BHR	1977 After Trial BLO, BHR
White Liquor Sulphidity	21%	29%	29%	24%
Measured Ave. Make-Up				
NaOH(lbm/TADP)	--	6.2	15.8	21.0
Na_2SO_4(lbm/TADP)	73	68.1	43.7	29.7
Total as Na_2O	31.9	34.5	31.3	29.3
CaO (lbm/TADP)	20	35	32	26
Pred. or Tuned Make-Up	tuned	tuned	predicted	predicted
NaOH(lbm/TADP)	--	6.2	17.2	21.1
Na_2SO_4(lbm/TADP)	78	68.3	50.0	41.6
Total as Na_2O	34.1	34.6	35.2	34.5
CaO (lbm/TADP)	20	35	35.8	37.7

Table 8-2

Predicted and Measured Average Chemical Make-Up

1975 Base Case Corrected

Yearly Average	1974	1975	1976	1977
Process Unit Changes	Pre-Environment Protection	Base Case BLO	Before Trial BLO, BHR	After Trial BLO, BHR
White Liquor Sulphidity	21%	29%	29%	24%
Measured Ave. Make-Up				
NaOH(lbm/TADP)	--	4	15.8	21.0
Na_2SO_4(lbm/TADP)	73	58.2	43.7	29.7
Total as Na_2O (lbm/TADP)	31.9	28.5	31.3	29.3
CaO (lbm/TADP)	20	35	32	26
Pred. or Tuned Make-Up	tuned	tuned	predicted	predicted
NaOH(lbm/TADP)	--	4	14.9	18.2
Na_2SO_4(lbm/TADP)	73	58.2	41.2	33.8
Total as Na_2O (lbm/TADP)	31.9	28.5	29.5	28.9
CaO(lbm/TADP)	20	35	35.8	37.7

Table 8-3

Analysis of Chemical Make-Up

		W.L. Sulph.	Salt Cake Make-Up (lbm/TADP)	Caustic Make-Up (lbm/TADP)	Make-Up Sulphidity %	Total Make-Up $\frac{\text{lbm Na}_2\text{O}}{\text{TADP}}$	Lime Make-Up (lbm/TADP)
1975	Average and Simulation Set Point	29%	58.2	4	89.1	28.5	35
Before Trial		29%					
	Monthly Average, $\overline{X}_1$		43.7	15.8	60.8	31.3	32.1
June '76 to	Stand. Dev.$\overline{S}_1$		14.2	2.78	7.21	7.01	8.84
Dec. '76	Pred. Ave.,X_1		41.2	14.9	60.8	29.5	35.8
After Trial		24%					
	Monthly Average, X_2		29.7	21.1	44.3	29.3	26.1
March '77 to	Stand. Dev.,S_2		15.6	3.64	11.9	8.11	5.95
Sept. '77	Pred. Ave.,X_2		33.1	17.8	51.1	28.9	37.7
	$\overline{X}_2-\overline{X}_1$		-13.9*	5.2	-16.5	-2.*	-6 .0*
	X_2-X_1		-8.8	3.1	-10.2	-0.67	1.9

Table 8-4

Simulation Loss Report

Chemical Losses and Make-Up Report

Sulphurous Emissions as H_2S:

	LBM/HR	LBM/TADP
Batch Softwood Digesters	225.3	3.9
Continuous Digester	146.1	2.5
Multi-Effect Evaporators	75.5	1.3
Direct Contact Evaporator	89.4	1.5
Total Emissions	536.4	9.2
As Equivalent Salt Cake	2240.4	38.6

Brown Stock Washer Losses:

	TONS/HR	
Actual Losses:		
$NaOH$ =	0.743	
Na_2S =	0.272	
Na_2SO_4 =	0.053	
Na_2CO_3 =	0.180	
As Equivalent Salt Cake		72.5
Titratable Losses:		
$NaOH$ =	0.091	
Na_2S =	0.159	
Na_2SO_4 =	0.053	
Na_2CO_3 =	0.180	
As Equivalent Salt Cake		25.7
Furnace Particulate Losses:		
Na_2SO_4 =	0.160	5.5
Na_2CO_3 =	0.021	0.7
Green Liquor Dregs:		
$NaOH$ =	0.004	
Na_2S =	0.006	
Na_2SO_4 =	0.001	
Na_2CO_3 =	0.018	
As Equivalent Salt Cake		1.5
Kiln Stack Losses:		
Na_2CO_3 =	0.001	0.0
Na_2SO_4 =	0.003	0.1

Table 8-5

Predicted and Measured Average Chemical Make-Up

After Modification of Causality

Yearly Average	1974	1975	1976	1977
Process Unit Changes	Pre-Environment Protection	Base Case BLO	Before Trial BLO, BHR	After Trial BLO, BHR
White Liquor Sulphidity	21%	29%	29%	24%
Measured Ave. Make-Up				
NaOH(lbm/TADP)	—	4	15.8	21
Na_2SO_4(lbm/TADP)	73	58.2	43.7	29.7
Total as Na_2O	31.9	28.5	31.3	29.3
Pred. or Tuned Make-Up	tuned	tuned	predicted	predicted
NaOH(lbm/TADP)	0	4	16.3	22.5
Na_2SO_4(lbm/TADP)	73	58.2	44.2	30.8
Total as Na_2O	31.9	28.5	31.9	30.92

Table 8-6

Lime Make-Up After Causal Modification

	1974	1975	1976	1977
Measurement				
CaO(lbm/TADP)	20	35	32	26
Simulation	20	35	41.9	41.1
CaO(lbm/TADP)				

FIGURE 8.1:

SIXTEEN MONTH RECORD OF CHEMICAL MAKE-UP

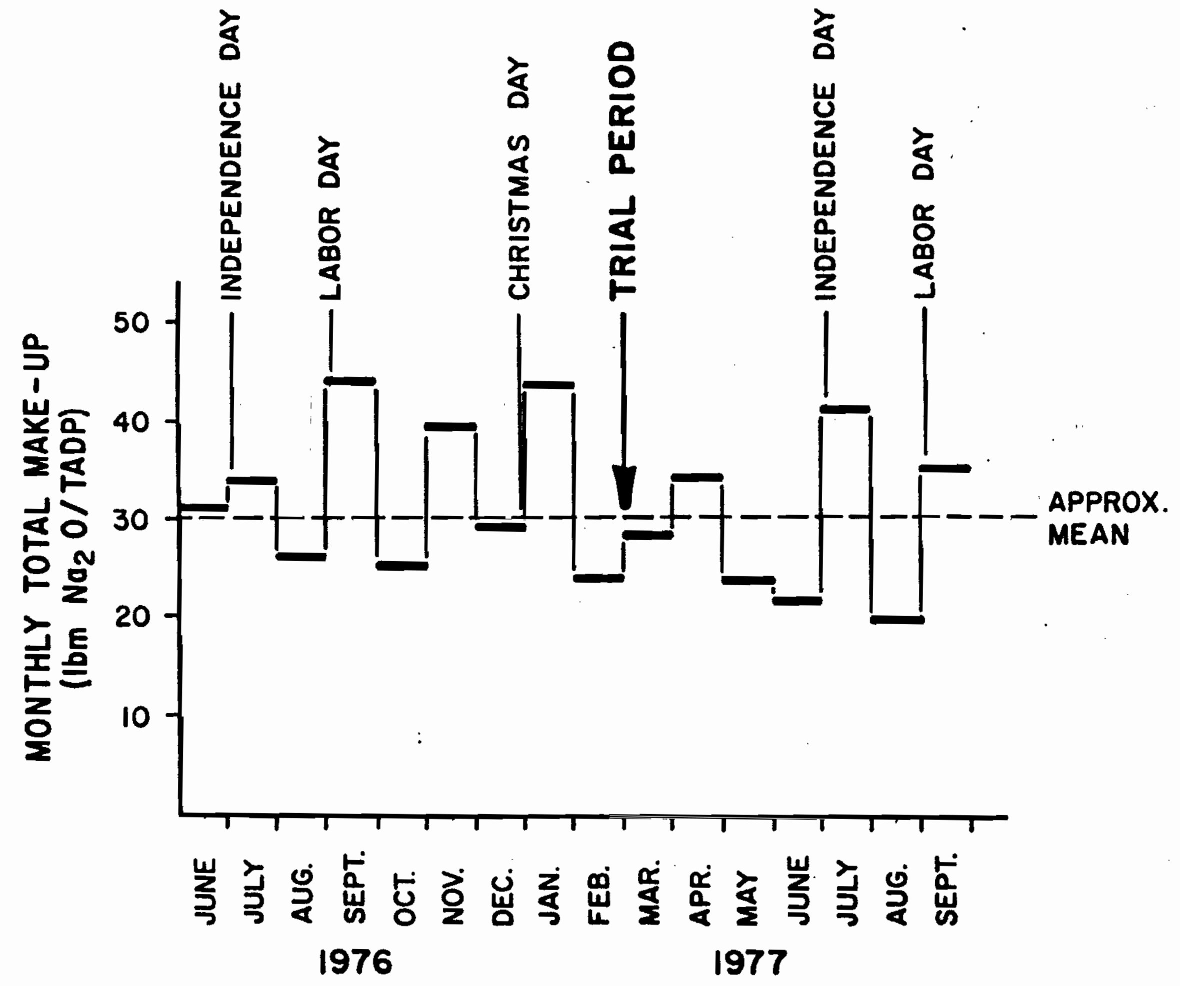


FIGURE 8.2:

PREDICTED H_2S EMISSIONS

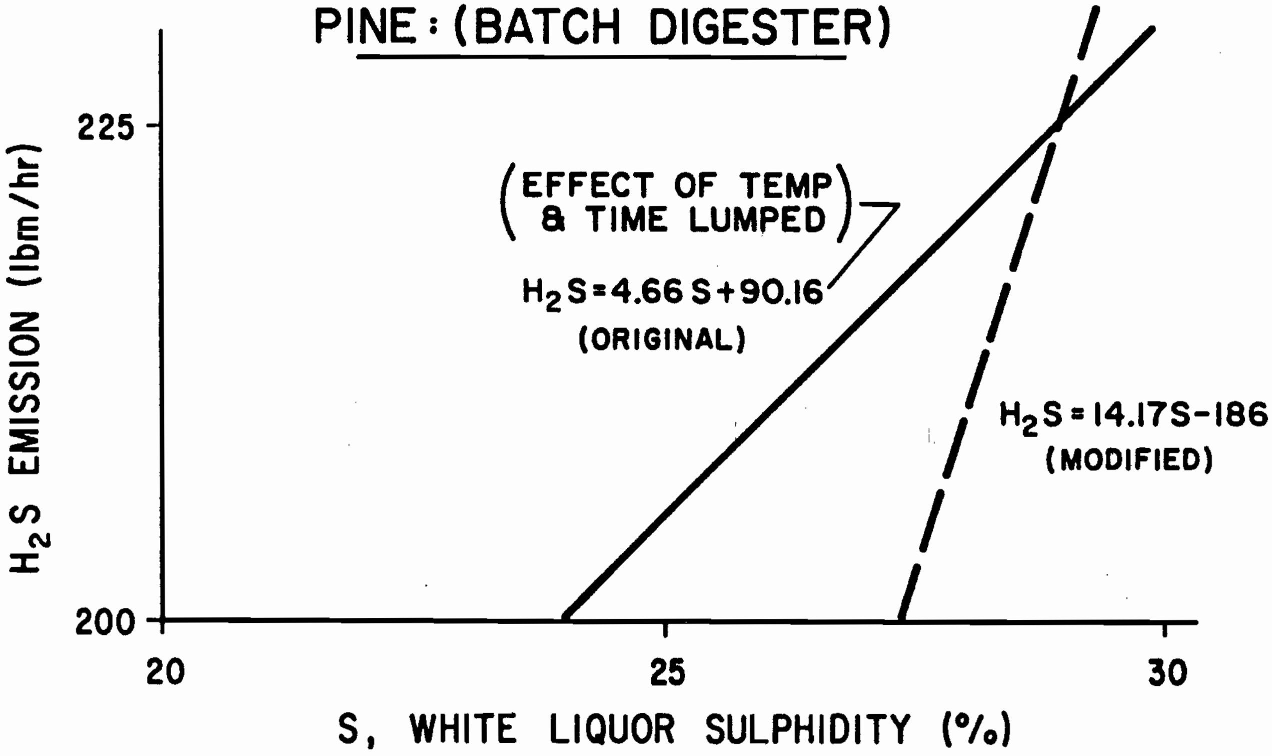
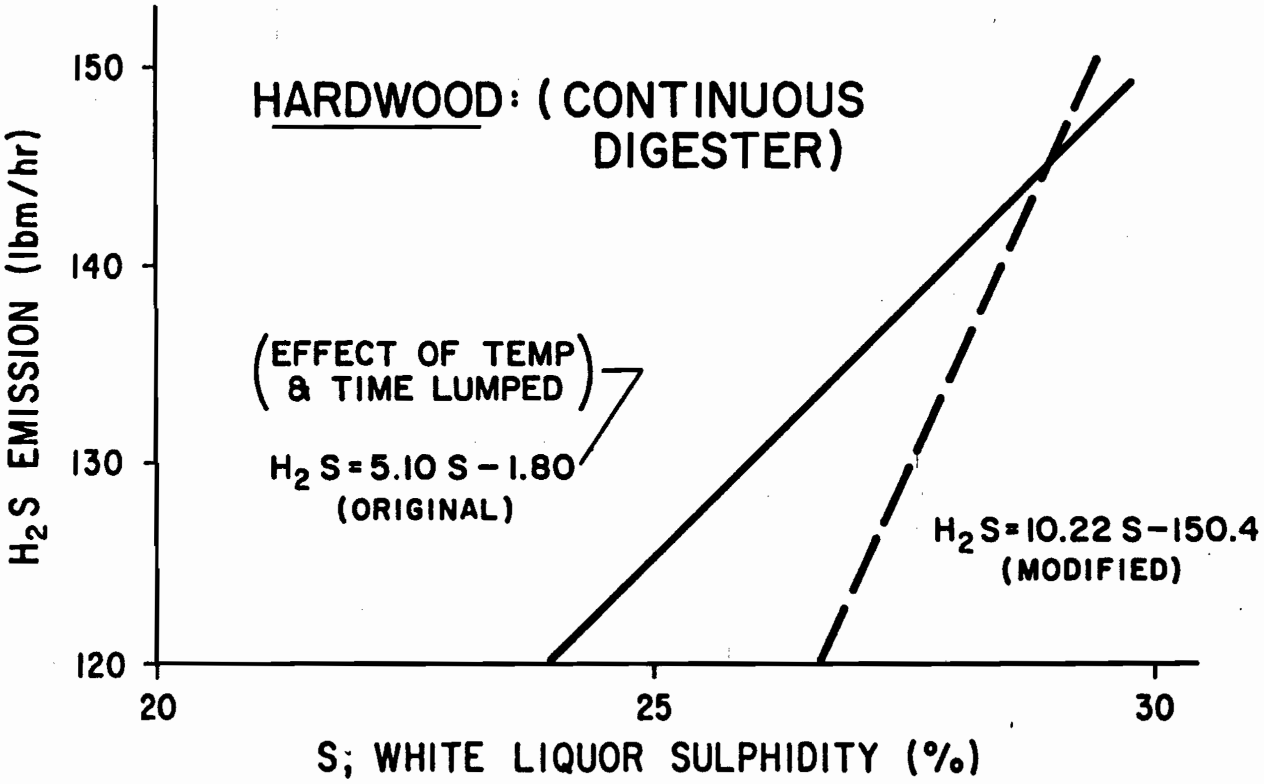


FIGURE 8.3:

PREDICTED H_2S EMISSIONS



9 - A Dynamic Model of the Kraft Mill Chemical Balance

A very simple dynamic model of the kraft mill chemical balance was developed as an aid for calculation of a chemical make-up strategy for the 1977 mill trial to reduce white liquor sulphidity. The model's function is to predict white liquor sulphidity response to the chemical make-up applied. As shall be seen, the model also predicts white liquor sulphidity response to process unit breakdowns which change the mill's chemical balance.

Figure 9-1 is the model flow sheet for the test mill. The fundamental assumption of the model is that dynamic behavior occurs only in storage. Tank V_1 is the volume of the entire white liquor preparation system, from the recovery furnaces to white liquor storage tanks, all expressed as equivalent white liquor at a specified active alkali concentration. Tank V_2 is the volume of the black liquor system, from the digesters to the strong black liquor storage tanks, expressed as equivalent volume of strong black liquor at a specified solids concentration. Tank V_3 is volume of the black liquor oxidation system, including all tanks downstream of these units, up to the recovery furnaces, all expressed on the same density basis as V_2.

Reactions to produce Na_2S in the furnace and NaOH in the causticizers occur at specified efficiencies. The model is a simulation of the mill chemical balance only. The process units function as losers of chemical only. In Figure 9-1 unit I represents the instantaneous loss of chemical from all process units in the black liquor system and unit II represents the loss of chemical from units processing white liquor. The loss of chemical is dependent on the flow and the dependency is determined by force fitting the coefficients of the loss relationships to the endpoints of a process change as determined by the steady-state model presented in the previous chapters. Neither unit I nor II exhibit dynamic behavior and have no volume. Stream 1 is fresh white liquor prepared from furnace smelt, stream 2 is white liquor from storage going to the digesters, stream 3 is strong black liquor from the evaporators, stream 4 is black liquor to the oxidation system and stream 5 is black liquor fired into the furnace.

There are three stream components: 1) non-sulphur bearing sodium, Na, which is NaOH + Na_2CO_3; 2) sulphur bearing sodium, S, which is Na_2S + Na_2SO_4 and; 3) an inert material. The first two are expressed as equivalent Na_2O. NaOH is distinguished from Na_2CO_3 by a specified caustic conversion efficiency, Ec, where,

$$E_c = \frac{NaOH}{NaOH+Na_2CO_3} \tag{9-1}$$

and Na_2S is distinguished from Na_2SO_4 by a specified furnace reduction efficiency, R_D, where,

$$R_D = \frac{Na_2S}{Na_2S+Na_2SO_4} \tag{9-2}$$

NaOH make-up, M_{N_a}, is added to V_3 and Na_2SO_4 make-up, M_S, to unit I, where both are expressed as equivalents of Na_2O. The liquor densities are assumed to be constant and the volumetric flow rate of NaOH make-up is considered to be negligibly small.

An overall material balance about V_1, V_2 or V_3 yields

$$Q_i - Q_o = \frac{dV_j}{dt} \tag{9-3}$$

where Q is volumetric flow rate in ft^3/hr and j=1, 2 or 3, and i=in, o=out, and refer to the stream numbering in Figure 9.1 .

Species balances for V_1, V_2 and V_3 can be made for sulphur-bearing sodium, s,

$$C_{i_s} Q_i - C_{o_s} Q_o = \frac{d(C_{o_s} V_j)}{dt} \tag{9-4}$$

where C is concentration in $lbmNa_2O/ft^3$. Similarly, for non-sulphur bearing sodium, Na, but only for V_1 and V_2 (i.e. j=1,2),

$$C_{i_{Na}} Q_i - C_{o_{Na}} Q_o = \frac{d(C_{o_{Na}} V_j)}{dt} \tag{9-5}$$

Because NaOH is added to V_3 the special Na balance for V_3 is

$$C_{4_{Na}} Q_4 + M_{Na} - C_{5_{Na}} Q_5 = \frac{d(C_{5_{Na}} V_3)}{dt} \tag{9-6}$$

where M_{Na} is the NaOH make-up in $lbmNa_2O/hr$. Now, substituting equation (9-3) into each of equations (9-5) to (9-6) and rearranging yields: a sulphur-bearing sodium balance for each of V_1, V_2 and V_3

$$(C_{i_s} - C_{o_s}) \frac{Q_i}{V_j} = \frac{dC_{o_s}}{dt} \tag{9-7}$$

where j=1,2,3, i=in and o=out; a non-sulphur bearing sodium balance for two tanks, V_1 and V_2,

$$(C_{i_{Na}} - C_{o_{Na}}) \frac{Q_i}{V_j} = \frac{dC_{o_{Na}}}{dt} \tag{9-8}$$

where j=1,2, i=in and o=out; and a non-sulphur bearing sodium balance for tank V_3

$$(C_{4_{Na}} + \frac{M_{Na}}{Q_4} - C_{5_{Na}})\frac{Q_4}{V_3} = \frac{dC_{5_{Na}}}{dt} \qquad (9\text{-}9)$$

giving a total of six species balances and three overall balances (i.e. equation 9-3).

The outlet flow rates of all storage tanks, Q_2, Q_4 and Q_5 are specified independent variables. In the process the flow rate of black liquor to the furnace, Q_5, is determined by the exigencies of steam production and Q_4 is set by level control in V_3 (note, however, that equation (9-9) does not assume constant V_3). The flow rate of white liquor to the digesters, Q_2, is directly proportional to the wood flow assuming perfect control of the active alkali concentration.

To complete the model material balances about the static units I and II are required. A species balance about unit I yields

$$C_{1_s} Q_1 = (C_{5_s} Q_5 + M_s)(1+L_{1_s}) \qquad (9\text{-}10)$$

$$C_{1_{Na}} Q_1 = C_{5_{Na}} Q_5 (1+L_{1_{Na}}) \qquad (9\text{-}11)$$

where L_1 is the fraction of each chemical lost in unit I and M_s is the Na_2SO_4 make-up in $lbmNa_2O/hr$.

In addition to density control in the case of stream 1 the active alkali concentration (i.e. $NaOH+Na_2S$) is held constant. Thus

$$C_{1_{Na}} E_c + C_{1_s} R_D = AAC \qquad (9\text{-}12)$$

where AAC is the active alkali setpoint and E_c and R_D are defined in equation 9-1 and 9-2. In the process the control of AAC in stream 1 results from the strong dependency of the caustic conversion efficiency on liquor density.

A material balance about unit II yields

$$\rho_3 Q_3 - \rho_2 Q_2 = (C_{2_{\mathrm{Na}}} L_{2_{\mathrm{Na}}} + C_{2_s} L_{2_s}) Q_2 \tag{9-13}$$

where L_{2_s} and $L_{2_{\mathrm{Na}}}$ are the fractional losses of each species passing through unit II. A species balance about unit II yields

$$C_{3_s} Q_3 = C_{2_s} Q_2 (1+L_{2_s}) \tag{9-14}$$

and

$$C_{3_{\mathrm{Na}}} Q_3 = C_{2_{\mathrm{Na}}} Q_2 (1+L_{2_{\mathrm{Na}}}) \tag{9-15}$$

Now, substituting equations (9-10) and (9-11) into (9-12) yields a solution for Q_1.

$$Q_1 = ((C_{5_s} Q_5 + M_s)(1+L_{1_s}) R_D + C_{5_{\mathrm{Na}}} Q_5 (1+L_{1_{\mathrm{Na}}}) E_c)/AAC \tag{9-16}$$

and rearranging equations (9-10) and (9-11)

$$C_{1_s} = \frac{(C_{5_s} Q_5 + M_s)(1+L_{1_s})}{Q_1} \tag{9-17}$$

$$C_{1_{\mathrm{Na}}} = \frac{C_{5_{\mathrm{Na}}} Q_5 (1+L_{1_{\mathrm{Na}}})}{Q_1} \tag{9-18}$$

which are the three equations describing unit I.

Rearranging equation (9-13) gives

$$Q_3 = (\rho_2 + C_{2_{\mathrm{Na}}} L_{2_{\mathrm{Na}}} + C_{2_s} L_{2_s}) Q_2/\rho_3 \tag{9-19}$$

The terms $C_{2_s} L_{2_s}$ and $C_{2_{\mathrm{Na}}} L_{2_{\mathrm{Na}}}$ are very small by comparison to ρ_2 and ρ_3 and while L_{2_s} and $L_{2_{Na}}$ change in response to a composition change the effect on the term before Q_2 in equation (9-19) is extremely small thus

$$Q_3 = KQ_2 \tag{9-20}$$

is a reasonable approximation to equation (9-19) where K is a constant.

Rearranging equations (9-14) and (9-15) completes the balance for unit II

$$C_{3_s} = C_{2_s} Q_2 (1+L_{2_s})/Q_3 \tag{9-21}$$

$$C_{3_{Na}} = C_{2_{Na}} Q_2 (1+L_{2_{Na}})/Q_3 \tag{9-22}$$

The process model consists of equations (9-3), (9-7) to (9-9), (9-16) to (9-18) and (9-20) to (9-22) for a total of fifteen equations (note multiple application of 9-3, 9-7 and 9-8) for a system of five units with three components of flow. In addition, the fractional losses are themselves functions of the stream compositions.

$$L_{1_s} = a_1 (C_{5_s} + \frac{M_s}{Q_5}) + a_2 \tag{9-23}$$

$$L_{1_{Na}} = a_3 C_{5_{Na}} + a_4 \tag{9-24}$$

$$L_{2_s} = a_5 C_{2_s} + a_6 \tag{9-25}$$

$$L_{2_{Na}} = a_7 C_{2_{Na}} + a_8 \tag{9-26}$$

where $a_1, \ldots, a_8$ are constants. The loss coefficients cannot be simple constant coefficients because of the complication introduced by the H_2S emission reaction

$$Na_2S + H_2O = 2NaOH + H_2S$$

as C_{1_s} increases more H_2S is lost but the reaction generates NaOH, $C_{1_{Na}}$.

The dynamic model is slaved to the steady-state simulation through equations 9-23 to 9-26. If for example the white liquor sulphidity is to be changed from 29% to 24% the tuning procedure for the dynamic model is to run the steady-state simulation at the two endpoint conditions. Then, using the black and white liquor flow information from the steady state model, equations 9-17, 9-18, 9-21 and 9-22 are solved at each condition for L_{1_s}, $L_{1_{Na}}$, L_{2_s} and $L_{2_{Na}}$. Note that at steady-state $C_{2_s}=C_{1_s}$, $C_{2_{Na}}=C_{1_{Na}}$, $C_{4_s}=C_{3_s}$, $C_{4_{Na}}=C_{3_{Na}}$, $C_{5_s}=C_{4_s}$ and $C_{5_{Na}}=C_{4_{Na}}+M_{Na}/Q_4$. Also, $Q_2=Q_1$ and $Q_5=Q_4=Q_3$. Finally equations 9-23 to 9-26 can be solved for $a_1,\ldots,a_8$.

In previous chapters, mention was made of various systems which have been added to the Kraft process to reduce chemical losses. If one of these systems were to break down, the process chemical balance could change quite radically. In this situation, the steady-state model could be executed at two endpoint conditions without the unit that has broken down. A new set of values for the parameters, a_1 to a_8, can be determined for this new configuration. For the period of the breakdown, the dynamic model would use these new values of the parameters and then would switch back to the original values when the full system is back on line. In this way, the dynamics of the process during such an upset can be studied.

A more important application would be to use the dynamic model to calculate a make-up strategy to control reagent (i.e. white liquor) composition during such an upset. In the next section a very simple control algorithm is presented.

9-1 A Chemical Make-Up Control Algorithm

The purpose of NaOH and Na_2SO_4 make-up is to control white liquor sulphidity and replace system sodium losses so as to supply sufficient reagent for pulping. The former is stated by

$$\frac{C_{1_s} Q_1 R_D}{C_{1_s} Q_1 R_D + C_{1_{Na}} Q_1 E_c} = \text{Targ} \qquad (9\text{-}27)$$

where Targ is the desired white liquor sulphidity. Substituting equation 9-10 and 9-11

$$\text{Targ} = \frac{R_D (C_{5_s} Q_5 + M_s)(1 + L_{1_s})}{R_D (C_{5_s} Q_5 + M_s)(1 + L_{1_s}) + E_c C_{5_{Na}} Q_5 (1 + L_{1_{Na}})} \qquad (9\text{-}28)$$

Further, substituting equations 9-23 and 9-24 and rearranging to solve for M_s

$$M_s = \frac{-B + \sqrt{B^2 - 4AC}}{2A} \qquad (9\text{-}29)$$

where

$$A = \frac{a_1}{Q_5}$$

$$B = 1 + a_2 + 2a_1 C_{5_s}$$

$$C = E_c C_{5_{Na}} Q_5 (1 + a_3 C_{5_{Na}} + a_4) \frac{\text{Targ}}{(1-\text{Targ}) R_D}$$

$$+ (1 + a_2 + a_1 C_{5_s}) C_{5_s} Q_5$$

The second requirement may be stated by a steady-state material balance about unit I and V_1.

$$(R_D C_{2_s} + E_c C_{2_{Na}})Q_2 = R_D (C_{5_s} Q_5 + M_s)(1+L_{1_s})$$

$$+E_c C_{5_{Na}} Q_5 (1+L_{1_{Na}}) \qquad (9\text{-}30)$$

During an upset equation 9-27 does not necessarily hold and the NaOH make-up requirement is

$$M_{Na}(k+1) = M_{Na}(k) + (R_D C_{2_s} + E_c C_{2_{Na}})Q_2 \qquad (9\text{-}31)$$

$$-R_D (C_{5_s} Q_5 + M_s)(1+L_{1_s})$$

$$-E\, C_{5_{Na}} Q_5 (1+L_{1_{Na}})$$

where $M_{Na}(k)$ is the old and $M_{Na}(k+1)$ is the new value of the caustic make-up. Note that the lag in V_3 is being ignored and the calculation is simply arithmetic. The make-up strategy of equations 9-29 and 9-31 can be stated as making up with salt cake to control sulphidity and with caustic to supply the additional sodium required for control of the white liquor storage volume V_1. The strategy of lowering and raising storage levels before and after a mill shut-down, as described in Chapter 8, involves a relaxation of equation 9-31.

Edlund and Johansson (46) and Pettersson (131) have taken a similar approach in developing a dynamic model for the purpose of storage volume manipulation to minimize disruption of pulp production during partial, emergency shut-downs. In their cases the liquor is handled as a completely inert material which is pumped from tank to tank. Their models consist of equation 9-3 only and implementation has apparently been successful. The introduction of chemical stream constituents here allows handling of reagent composition control which is the main purpose of this model.

Figure 9-2 presents the results of a sample application of the dynamic model. It is desired to lower the sulphidity of the white liquor to the digesters, stream 2, from 29% to 24%. Three strategies are applied. In the first case the NaOH and Na_2SO_4 are set to their endpoint values, as determined from the steady-state simulation. After twenty-four days, the sulphidity is reduced to 25.3% and will require a further sixty days to arrive at the endpoint. This is not a satisfactory strategy as uncontrolled upsets will likely interfere during such a long period. Also a drifting sulphidity will complicate the control of the pulping reaction in the test mill.

In the second case, the algorithm presented in this section is applied to calculate a make-up strategy. In case 2, the sulphidity reaches the endpoint in fifteen days. The basic make-up strategy is to supply the maximum caustic flow allowable, which is determined by equation 9-28 or by a limit on the caustic pumping capacity, until the sulphidity reaches the endpoint followed by a gradual adjustment down to the make-up endpoint values.

While the make-up algorithm is not "optimal" in the strictest sense, it becomes clear that the only way to significantly reduce the time required for the change in sulphidity is to change the systems sodium-sulphur loss balance. Case 3 is the result of such a procedure. This strategy involves shutting down the strong black liquor oxidation system for five days. This action so radically alters the sodium-sulphur loss balance that even when all sodium is supplied as Na_2SO_4 make-up the sulphur input is insufficient to maintain 24% sulphidity (viz. the 1977 operating condition). The sulphidity overshoots the target and reaches steady state after eight days. Faster response might be attainable by starting up the oxidation system after three days. Case 3 is handled by calculating a set of loss coefficients a_1 to a_8 for each condition (i.e. with and without black liquor oxidation) using the steady-state simulation, as described in section 9-1.

This approach adds a new dimension to the control of a pulp mill chemical balance. Extremely complex situations can be treated with a very simple model.

9-2 Application of the Dynamic Model to the Mill Trial

The dynamic model was used for off-line calculation of a make-up strategy for the purpose of a reduction in the white liquor sulphidity. The approach was that of case 2 in the last section and the trial was scheduled to begin on February 18, 1977. The objective was to reduce sulphidity from 29% to 21%. On February 11 a unit breakdown forced the shutdown of the strong black liquor oxidation system for six days. This caused an uncontrolled reduction of sulphidity. The simulation was used to monitor the process change until February 18, then the make-up strategy was applied to control the sulphidity. After one week, it became apparent that the strategy was driving the white liquor sulphidity to 24%. The dynamic model loss parameters were then readjusted to fit this situation but the make-up strategy was not changed. The dynamic model loss causality is fit to the steady-state model. As has been shown in Chapter 8, the steady-state model was in error; this caused the error in the dynamic model. Figure 9-3 shows the measured response and the simulation response, with correction of the loss coefficients, to the applied make-up strategy. The sulphidity is a function of Na_2S and active alkali concentration. The latter was controlled independently by the operators and is subject to variations independent of the controlled variables thus the Na_2S concentration in white liquor is plotted rather than sulphidity. A sulphidity of 29% is equivalent to 1.74 lbm Na_2S/ft^3 with an active alkali concentration of 6 lbm/ft^3, both calculated as equivalent Na_2O. The NaOH make-up is shown as U.S.G.P.M. of 50% solution and the Na_2SO_4 as lbm Na_2SO_4/hr. Samples of white liquor were taken daily in addition to regular mill samples which are composites of a day's operation and are taken three times each week. As can be seen, the model response compares quite favorably with the measured response.

The make-up feed rates vary drastically from shift to shift. The almost constant adjustment was a necessary response to the 32 process unit breakdowns that occurred during the trial. Figure 9-4 is a repeat of Figure 9-3 but with a time history of the major breakdowns. The breakdowns caused up to 25% loss of processing capacity in the areas affected and were of up to 16 hours in duration. The basic strategy was calculated with the dynamic model assuming a production rate of 1400 Tons Pulp/Day and no storage volume modification. A simple rule was applied to adjust the make-ups from these base values in response to storage volume exigencies. For example, as a result of a recovery furnace breakdown an additional 100 ft^3/hr of white liquor was required. At an active alkali concentration of 6 lbm Na_2O/ft^3, this translates into an additional 600 lbm Na_2O/hr to be supplied from the make-up. By the rule applied an additional 300 lbm Na_2O/hr is supplied by each make-up. The actual shift by shift strategy was calculated in this way and then entered as independent variables to the dynamic model, which was then used to monitor the process response. Data from the mill up to

September 1977 indicates that this strategy continues to hold the mill at the setpoint of 1.4 lbm Na_2S/ft^3 (i.e. 24% sulphidity).

The prediction of the storage volume behavior is not nearly as successful. During the trial the storage tank volumes were measured daily. These values have been converted into equivalent volumes of white liquor at an active alkali concentration of 6 lbm Na_2O/ft^3 and are tabulated in Table B-10, p.B.18. Figure 9-5 presents a comparison of the predicted and measured total storage volume. Note that the two plots have been shifted to a starting point of 200000 ft^3 for ease of comparison of the change in volume. The simulation volumes V_1, V_2 and V_3 contain process unit volumes as well as storage volumes (approximately 450000 ft^3 total) while only storage volumes have been measured. With the exception of the batch digesters, white liquor clarifiers and recovery furnaces all process units are full when operated. The furnaces can cause large temporary changes in storage volume when a bed burn-down occurs as the result of a furnace shut-down. The peaks in the plot of measured storage volume are a consequence of such upsets.

It can be seen from Figure 9-5 that while the volume prediction is never very good, the trends are similar until February 26 when the measured volume leveled off while the predicted volume continues to decline. The discrepancy at the end of the trial is 55000 ft^3, approximately 12% of the total volume. Approximately 12000 ft^3 of the discrepancy can be accounted for by a change in liquor density leaving 43000 ft^3. The volume reduction is due to the fact that the total sodium made up was less than was being lost. This was an intentional strategy of the mill operators. In the simulation the chemical losses are a function of chemical flow and concentration through the loss units. The liquor flow rates and compositions were not carefully monitored during the trial (with the exception of white liquor) because the simulation was not originally intended as an inventory controller and such monitoring would have required a large support staff which was unavailable. The only meters which were checked were those for the make-up flow rates. The liquor flow rates used in the simulation were estimated from the steady-state simulation and were adjusted for process unit breakdowns and changes in pulp production from the nominal 1400 Tons/Day. If all the flow rates used were reduced by 10% an additional 20000 ft^3 of the discrepancy could be accounted for. Adjustment of the density would have a similar effect;however, such sweeping adjustments are quite unsatisfactory as they could not account for the deviation in trends from February 26 onward.

The data required for such an adjustment is unavailable and could only be acquired by a repetition of the experiment. The dynamic model is a significant advance in the understanding of the chemical dynamics of the process; however, its capability in the area of volume prediction is in doubt. An additional experiment to provide a definitive test of the latter would be extremely useful. The success of Edlund and Johansson in storage volume control seems to encourage the belief that a more carefully monitored experiment would provide positive results. Due to its simplicity, the model would be an excellent basis for the design of a system for the control of both liquor composition and storage volume during upsets caused by process unit breakdowns.

The dynamic model could make a very important contribution to the pulp and paper industry today. Mills that add process units to suppress emission of sulphurous gases find that these units change the chemical balance in the system. The net result is a rise in sulphidity which increases the tendency to emit sulphurous gas and has resulted in serious corrosion problems in some units. The dynamic model in conjunction with the steady-state model, to which it is slaved, can be used to plot a make-up strategy to counter the trend to rising sulphidity and can lead to a better understanding of the chemical dynamics of the new configuration of the process.

FIGURE 9.1:

PROCESS MODEL FLOWSHEET

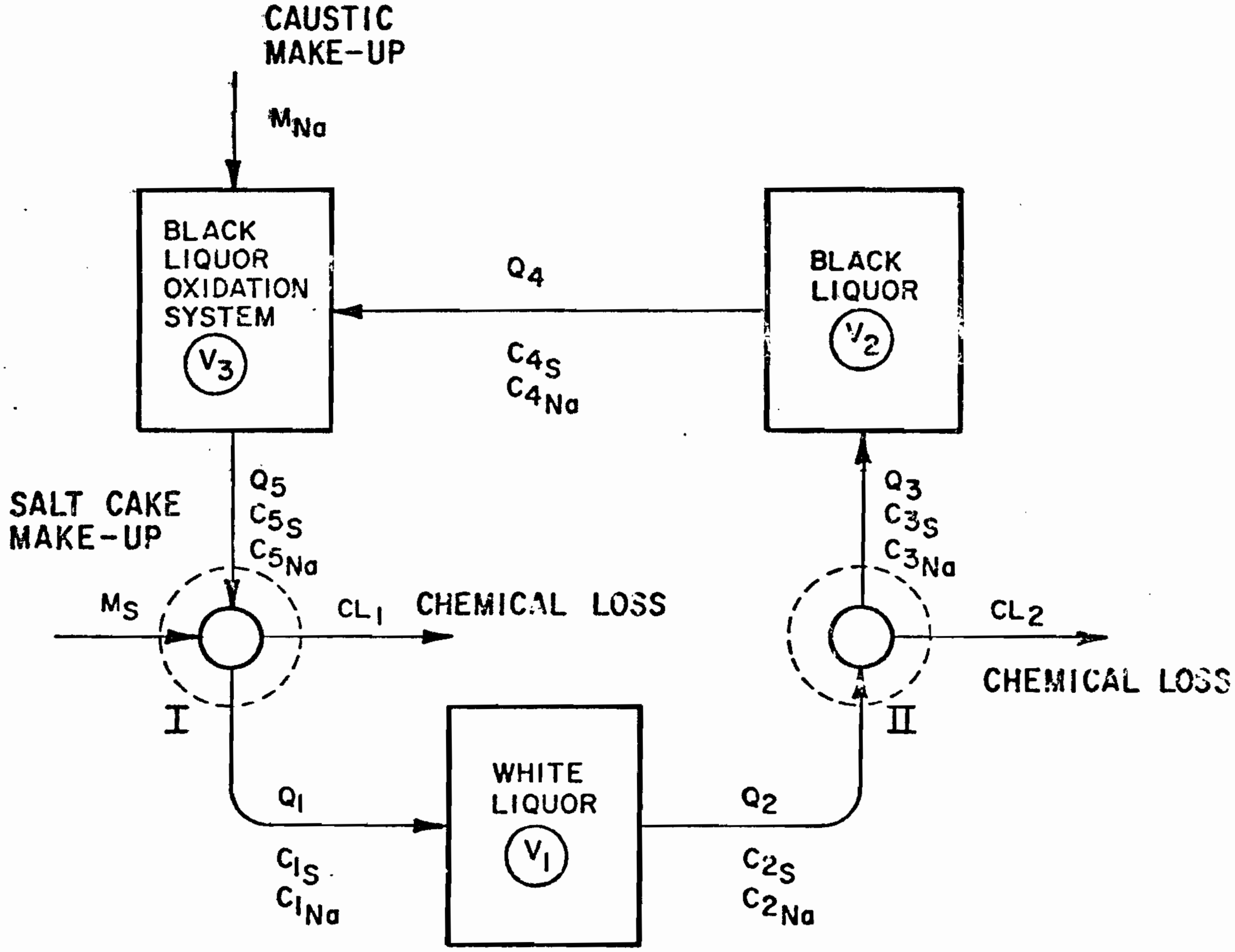


FIGURE 9.2 :

SULPHIDITY RESPONSE TO THREE MAKE-UP STRATEGIES

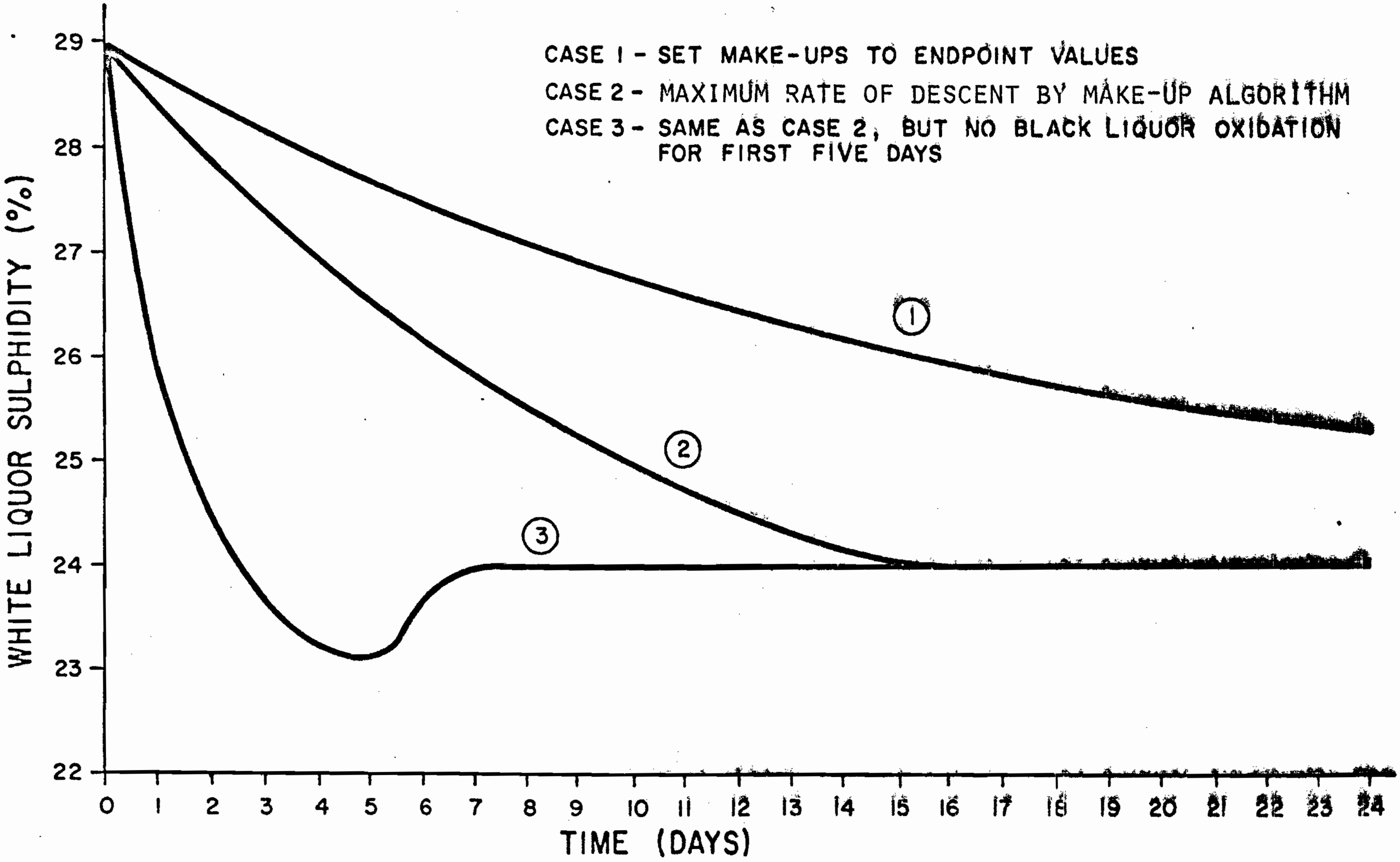


FIGURE 9.3:

PROCESS AND MODEL RESPONSE TO MAKE-UP STRATGIES

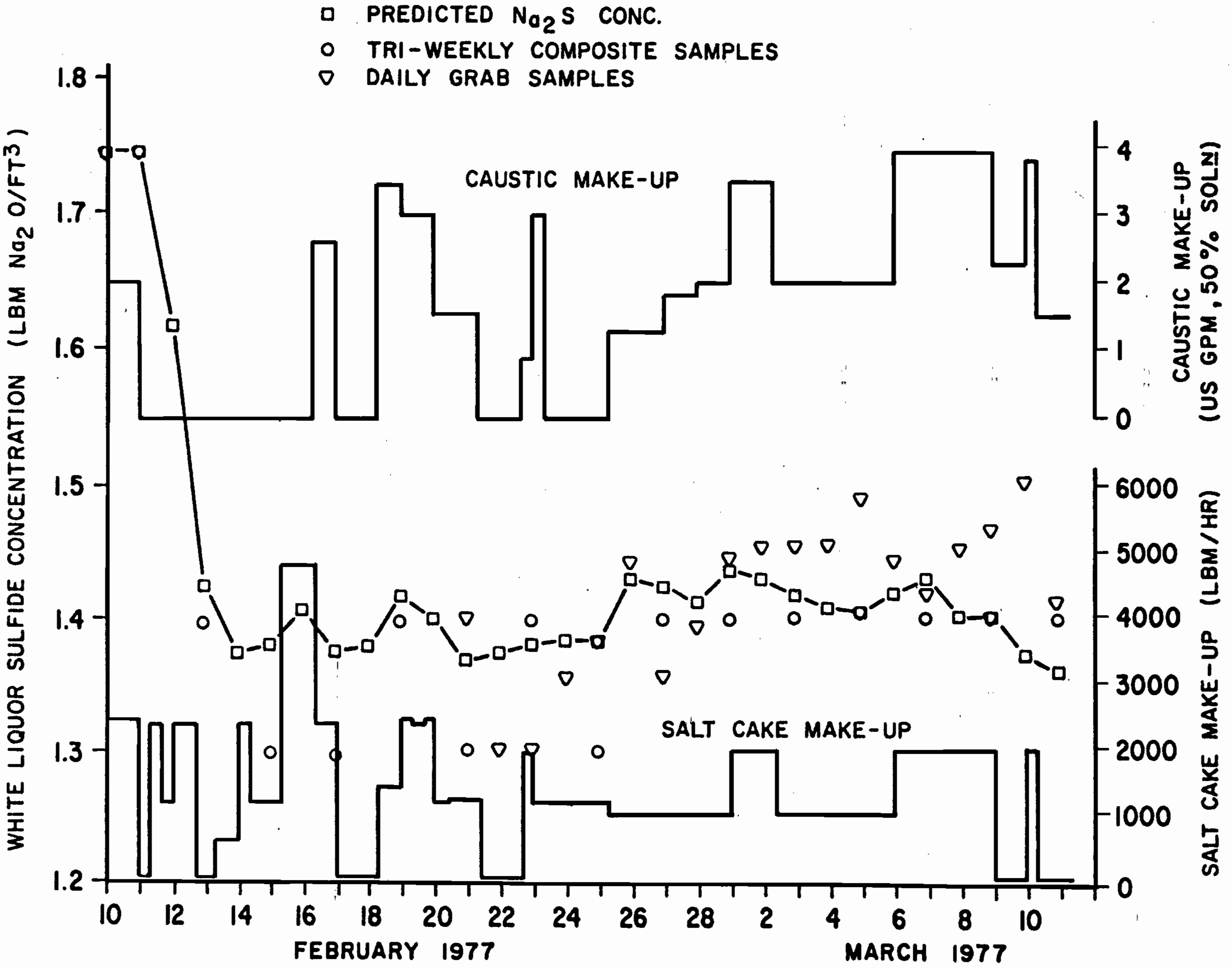


Figure9.4: Effect of Major Process Upsets on Mill Trial

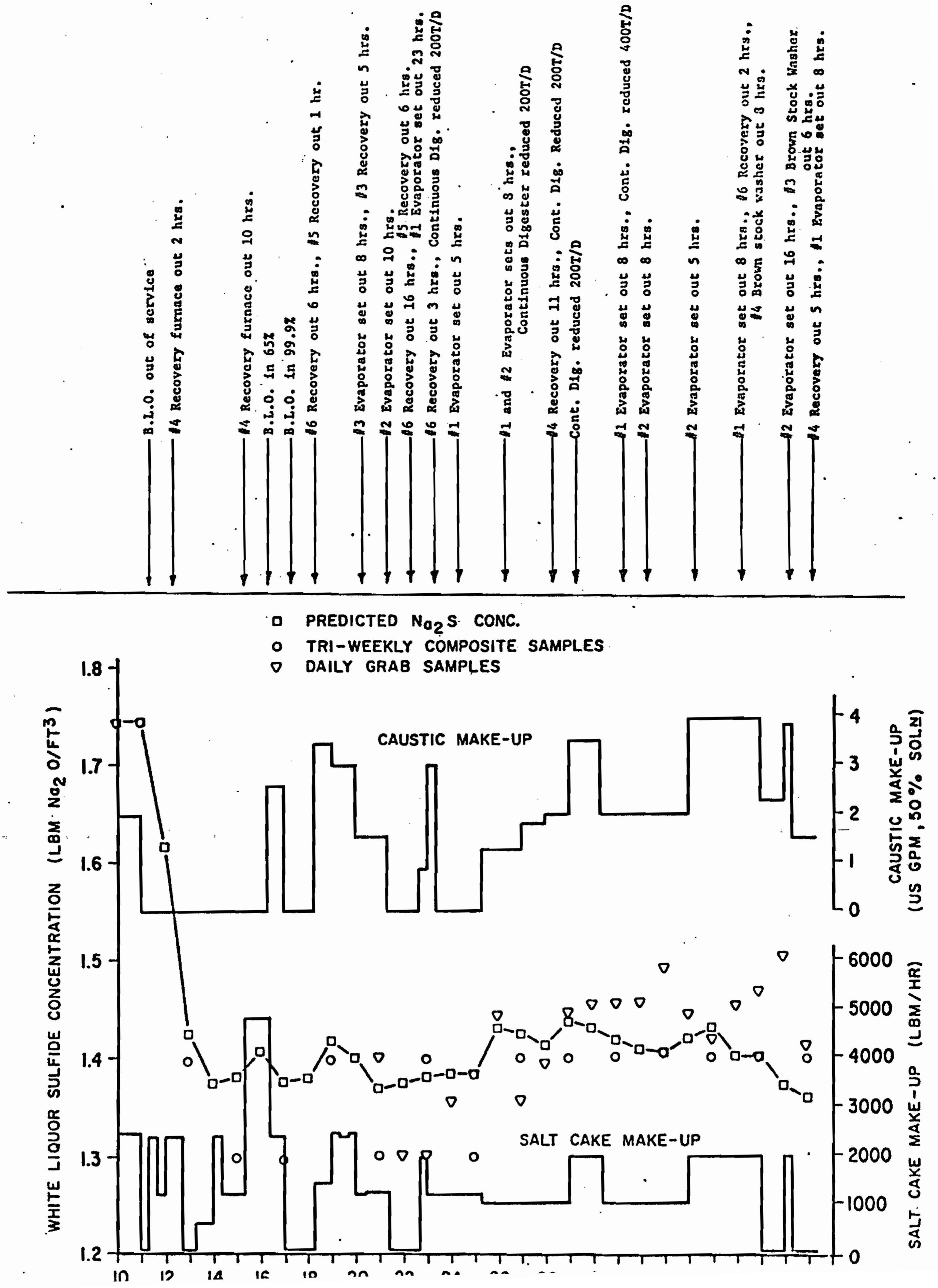
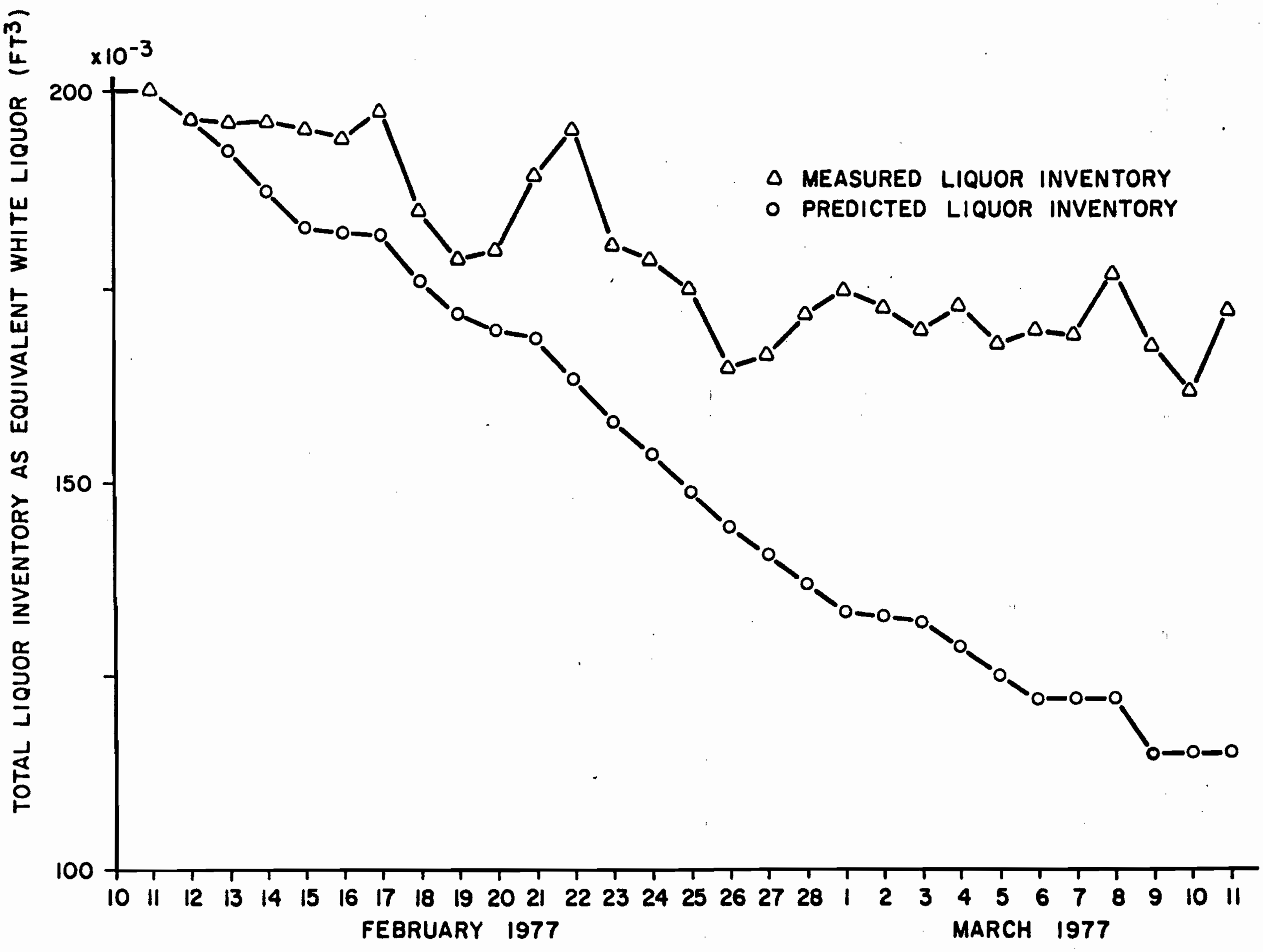


FIGURE 9.5:

EVALUATION OF SYSTEM CHEMICAL INVENTORY PREDICTION



10 - Conclusions

A modular, steady-state simulation of the Kraft pulping and recovery process has been developed. The simulation has been used to model a number of operating conditions as well as different process configurations resulting from occasional addition, over a number of years, of new unit processes to a test mill in the United States.

The test mill is one of the largest and most complex Kraft mills in North America featuring a process cycle with at least four replicate process units, at each stage, operating in parallel. The spent chemical used in pulping of wood is reprocessed with approximately 95% being recovered and recycled for further use. A simulation study of the mill revealed that a change in composition of the reagent would result in economic benefits to the mill. This proposal was subsequently implemented and the data from this implementation was used as a test of the simulation's efficacy. The simulation predicted a saving of $300,000 per year while the measurements indicate a saving of $500,000 per year.

A traditional statistical analysis gave no grounds for rejection of the hypothesis that the predictions equaled the measurements. However, an analysis of the data most in error (i.e. the NaOH and Na_2SO_4 make-up) was used to show that the variation in the data, which causes the indeterminacy of the tests, was due mainly to process cycling. The discrepancies between prediction and measurement for these values was then treated as error and a pass at improvement of the causality was made.

In support of the mill trial a very simple dynamic model of the process was developed to allow calculation of a control strategy to manipulate the reagent composition. The strategy was successfully applied through a series of major process upsets. An ancilliary benefit of the dynamic model may be its application to the manipulation of storage volumes to minimize disruptions caused by process unit breakdown. This last use remains to be proven.

11 - Recommendations

The following recommendations for future work are made with the object of extending and strengthening what has been done here:

1) Implement the simulation at another pulp mill of different configuration than the test mill used here. This should involve another experiment similar to the one carried out here to allow testing of the causal modifications suggested in Chapter 8.
2) Improve the energy causality by treating the outlet temperatures from the multi-effect evaporators, direct-contact evaporators, recovery furnace and kiln models as dependent variables.
3) Develop new causality to predict matte consistency from the brown stock washers.
4) Develop new modules for bleaching and paper machines to extend the applicability of the simulation.
5) Carry out a new experiment to test the applicability of the dynamic model for prediction of storage tank levels.
6) Reformulate the dynamic model in a modular format to allow more disaggregation of the model and more flexible application. Incorporation of simple energy causality may allow the use of the model as a device to control the mill during periods of process upset so as to minimize the loss of pulp and steam production.

BIBLIOGRAPHY

1. Anonymous, "Solubility Limits in Black Liquor," Project 3136, Report No. 1, Institute of Paper Chemistry, Appleton, Wisconsin (February 22, 1974).

2. Adler, L.S., "An Economic Optimization of a Kraft Process," Ph.D. Thesis Purdue University, (1972).

3. Ahlgren, P. and J. Olausson, "Vapor Phase Kraft Cooking," "Part 1. Effect of Uneven Distribution of Cooking Chemicals," Svensk Papperstid., 76 (15):573 (1973).

4. Annergren, G. and A. Backlund, "Neutral Sulfite Semichemical Pulping with Diffusion Washing in a Kamyr Digester," TAPPI, 51 (5):92A (1968).

5. Annergren, G.E., A. Haglund, and S.A. Rydholm "On the Composition and Fuel Value of Black Liquor," Svensk Pappstid., 71 (15):497-504 (1968).

6. Arhippainen, B. and E.N. Westerberg, "Kraft Odor Control - Its Effect on Mill Operating Parameters and Costs," Pulp Pap. Mag., Canada, 69 (8): 65 (1968).

7. Arhippainen, B. and B. Jungerstam, "Operating Experience of Black Liquor Evaporation to High Dry Solids Content," TAPPI, 52 (6):1095 (1969).

8. Arhippainen, B. and J. Venho, "Displacement Bleaching and Process Simulation," TAPPI, 57, 11 (1974).

9. Ashorn, T., "On the Degradation of Spruce Lignin under Conditions of Thioligrin Formation," Paperi jo Puu, 43 (11):655 (1961).

10. Aziz, S., M. Rumean, and M. Renand, "A New Method for In-Situ Measurement of Sulfide Ion Concentration in Kraft Pulping Process," Svensk Papperstid., 17, pp.552-556 (November 1977).

11. Baldus, R., L. Edwards, and B. Warnquist, "Application of Washing Models to General Material Balance Calculations Including Sorption," CPPA, 62nd Annual Meeting, Montreal (January 27, 1976).

12. Baldus, R.L. and B. Warnquist, "Washing Models for Use in Pulp Mill Material Balance Calculations," P.P. Mag., Canada, 78 (6):TR56-61 (1977)

13. Baldus, R.L. and L.L. Edwards, "Mass and Energy Balances for Complete Kraft Mills," PACHEC Engineering Conference, Denver, (August 1977).

14. Baldus, R.L. and L.L. Edwards, "Multiple Effect Evaporation Systems for Kraft Black Liquor," TAPPI, 61 (3):75-78 (1978).

15. Bauer, T.W. and R.M. Dorland, "Thermodynamics of the Combustion of Sodium-Base Pulping Liquors," Canada J. Technol., 32, 91-101 (May 1954).

16. Beckwith, W.F. and J.E. Owen, "Simulation of the Chemical Recovery System of a Kraft Mill," PACHEC Engineering Conference, Denver (August 1977).

17. Benedict, E.V., Jr., "Counter-current Washing in a Bleach Plant," TAPPI Alkaline Pulping Conference, Houston, pp. 261-269(October 1971).

18. Bentuelzen, J.M., W.T. McKean, J.S. Gratzl, S.Y. Lin and W.P. Tucker, "Kinetics of Methyl Mercaptan Oxidation and Dimethyl Disulfide Hydrolysis in Alkaline Solutions," TAPPI, 58 (1):102-5 (1975).

19. Bhada, R.K., H.B. Lange, and H.P. Markant, "Air Pollution from Kraft Recovery Units - The Effect of Operational Variables," TAPPI Environment Conference, Houston, (May 14-17, 1973).

20. Bingham, L.M., "Startup and Operation of a Fluidized-Bed Calciner," TAPPI, 52 (1):59 (1969).

21. Bjerring, A.K. and J.W.T. Battershill, "Computer Control Concepts for a Continuous Digester," Pulp and Paper, 46 (13):57 (1972).

22. Blosser, R.O. and H.B.H. Cooper, "Current Practices in Thermal Oxidation of Noncondensable Gases in the Kraft Industry," NCSI Technical Bulletin, Atmospheric Pollution Technical Bulletin, No. 34 (November 1967).

23. Borg, A. and B. Warnquist, "Matematisk Modell for Svavelutslapp frau sodahusaggregregat," Svensk Papperstid., 77 (1);4 (1974).

24. Bowers, T.G. and H.L. Read, "Heat Transfer in Rotary Kilns," Chem. Eng. Symp. Series, G57, 61:340-6 (1965).

25. Boyle, T.J. and M.G. Tobias, "A Kraft Mill Mathematical Model," TAPPI, 55, 8, 1247 (1972).

26. Boyle, T.J., S.S. Treiber and P. Vadnais, "A Modular Simulation of the Kraft Pulping Process," TAPPI Engr. Conference, Toronto (October 1975).

27. Boyle, T.J. and S.S. Treiber, "A Modular Simulation Study of Sulfidity, Emissions, and Production Cost in Kraft Pulping," A.I.Ch.E. Forest Products Symposium Series (December 1977).

28. Brewster, D.B., "Economic Gains from Improved Quality Control," Pulp Pap. Mag. Can., 71 (6):1127 (1970).

29. Burgess, T.L. et al., "Incineration of Malodorous Gases in Kraft Pulp Mills," Pulp Pap. Mag. Can., 75 (5):92 (1974).

30. Canovali, L.L. and Suda S., "Case History of Selection and Installation of a Kraft Recovery Odor-Reduction System," TAPPI, 53 (8):1488 (1970).

31. Carroll, C.W., "An Operations Research Approach to the Economic Optimization of a Kraft Pulping Process," TAPPI, 43, 4, 305 (1960).

32. Chamberlain, R.E. and C.E. Cairnes, "Analysis of Recovery Unit Operation and Control," Pulp and Paper Mag. Can., 73, 1, 97-101 (January 1972).

33. Chamberlain, R.E., A.R. Smith, G. McFarlin and D.W. Chose, "Control of Recovery Furnace Disturbances," CPPA 60th Ann. Meeting (January 29, 1974).

34. Chiari, N.C.S., "Integrated Control System Approach for Batch Digester Control," TAPPI, 56, (7):65 (1973).

35. Chase, P.M. and A.J. Koivo, "Determination of a Mathematical Model for a Lime-Kiln," 3rd IFAC/IFIP Conf. on Dig. Comp. Applic. to Proc. Control, Helsuiki, Part 2, XII-3 (June 1-6, 1971).

36. Choi, P.M.K., W.Q. Yean and D.A.I. Goring, "Removal of Lignin from Kraft Pulp Fibers During Washing," 62nd Ann. CPPA meeting, Mtl., (January 27, 1976).

37. Clement, J.L., J.H. Coulter and S. Suda, "B & W Kraft Recovery Unit Performance Calculations," TAPPI, 46 (2); 153A (1963).

38. Cliffe, W.R., "Rotary Lime Kiln Practice," Pulp Pap. Mag., Canada, p. T88 (September 1947).

39. Collins, T.T., Jr., "The Ventri-Scrubber on Lime Kiln Stack Gases," TAPPI, 42 (1); 9 (1959).

40. Coleman, A.A., "The Combustion of Noncondensable Blow and Relief Gases in the Lime Kiln," TAPPI, 41 (10); 166A (1958).

41. Copeland, G.G., "Process of Regenerating Pulping Liquor from Cellulose Digestion Waste Liquor for Heat," U.S. Pat. 3,414,468 (December 1968).

42. Dalley, O.T., "Comparison of Rotary Kiln and Fluo-Solids Lime Reburning System," Judian Pulp and Paper, 22 (1):91 (1955).

43. DeHaas, G.G. and G.A. Hansen, "The Abatement of Kraft Pulp Mill Odors by Burning," TAPPI, 38 (12):732 (1955).

44. Douglass, I.B. and L. Price, "A Study of Methyl Mercaptan and Dimethyl Sulfide Formation in Kraft Pulping," TAPPI, 49 (8):335 (1966).

45. Ducar, G.J. and P. Levin, "Mathematical Model of Recalcination of Lime Sludge with Fluidized Bed Reactors," A.B.I.P.C., 12 (10):1012 (1972).

46. Edlund, S.G. and K. Johannson, "Experiences with a Multiple Unit Production Control System for the Optimization of Mill Operations," CPPA, International Symposium on Process Control, Vancouver (May 1977).

47. Edwards, L. and S.E. Norbert, "Alkaline Delignification Kinetics," TAPPI, 56 (11):108 (1973).

48. Enkvist, T., T. Ashborn, and K. Hastbacka, "New Aspects on the Reaction of Lignin in Kraft Pulping," Pappieri ja Puu, 44 (8):395 (1962).

49. Fitch, B. and W.H. Pitkin, "Analysis of Brown Stock Washing Systems," TAPPI, 47 (10):1704-24 (1964).

50. Fletcher, R.H. and H.T. Griffin, "Alternate Hardwood/Pine Brown Stock Washing Using Three Element Control of Shower Water," Pulp. Pap. Mag., Can., 70 (11):77-80 (1969).

51. Foster, R.L., "Optimization of the Chemical Recovery Cycle of the Kraft Pulping Process," M.Sc. Thesis, Purdue University (1973).

52. Fuchs, R.E. and G.J. Single, "Advances in Computer Control of Kamyr Continuous Digesters," TAPPI, 59 (2):96-9 (1976).

53. Fuchs, R.E. and C.L. Smith, "Blow Flow Control of Continuous Digesters," TAPPI, 54 (3):368 (1971).

54. Fuller, R.R., "Thoughts on the Liquor Cycle and Cauticizing," South. Pulp. Pap. Mfr., 29 (1) (1969).

55. Galeano, S.F. and C.D. Amsden, "Oxidation of Kraft Weak B.I. with Molecular O ," TAPPI, 53 (11):2142-46 (1970).

56. Galtung, F.L., "A Survey of the Status of the Mathematical Modeling of the Chemical Recovery Section of a Kraft Paper Mill," M.Sc. Thesis, Purdue University (1971).

57. Galtung, F.L., "A Mathematical Model and Digital Computer Based Advanced Control System for a Kraft Mill Recovery Unit," Ph.D. Thesis, Purdue University (1971).

58. Ganguli, B.N., "Linear Programming as an Aid for Pulpwood Procurement and Scheduling," Indian Forester, 96 (10):781-6 (1970).

59. Gibbs, R.E., "Fundamentals of Lime Kiln Thermodynamics," Pap. Ind. and Pap. World, 32 (5):1970 (1949).

60. Gibbs, R.E., "The Development and Transfer of Heat in Rotary Lime Kilns," Pap. Ind., 32 (1):54 (1950).

61. Gibbs, R.E., "Fundamentals of Lime Kiln Thermodynamics," The Paper Industry, 31 (9):501 (1950).

62. Gibbs, R.E., "How to Determine the Economical Length of a Rotary Kiln," Paper Industry, 32 (10):1084 (1951).

63. Gierer, J., "Model Experiments on the Degradation of Lignin by Alkali,"

Paperi Ja Puu, 43 (11):654 (1961).

64. Gierer, J., "The Reactions of Lignin During Pulping," Svensk Papperstid., 73 (18):571 (1970).

65. Glazunov, A.I. and E.A. Egorova, "Expt. Determination of the Dynamic Characteristics of Classifiers," Tr. Vses. N.I.I. Tsellyul.-Bum. Prom., 52:184-91 (1967).

66. Glazunov, A.I., "Appproximate Mathematical Model of Causticization Unit," Tr. Vses. Nauch.-Issled. Just. Tssellyul-Bum. Prom., 52:192-200 (1967).

67. Glazunov, A.T., et al., "Study of the Cauticization Process for the Purpose of Mathematical Description," A.B.I.P.C. 40 (10):871 (1970).

68. Goodwin, L.E. and I.L. Sills, "The Effect of Additions of Sodium Sulphide on the Causticizing Equilibrium. Part II," J. of Soc. of Chem. Ind., 45:p362T (1926).

69. Grace, T.M., "The Impact of Black Liquor Oxidation on Total Energy Recovery," TAPPI, 60 (11):132-5 (1977).

70. Grahs, L.E., "Displacement Washing of Packed Beds of Cellulose Fibers: Part 3. A Comparison of the Washing Behavior of Sodium and Lignin," Svensk Papperstid., 79 (4):123-8 (1976).

71. Gren, U. and L.E. Grahs, "Washing of Cellulose Fiber Beds," Svensk Papperstid., 76 (16):597-601 (1973).

72. Grigorenko, N.A., "Control of the Quality of Sulphate Pulp Washing," Tr. Vses. N.I.I. Tsellyal.-Bum. Prom., 52:235-43 (1967).

73. Gudmundson, C., et al., "Heat Transfer in Industrial Black Liquor Evaporation Plants, Part I," Svensk Papperstid., 75 (19):773 (1972).

74. Gudmundson, C., "Heat Transfer in Industrial Black Liquor Evaporator Plants, Part II," Svensk Papperstid., 75 (22):901 (1972).

75. Gullichsen, J., Symposium on the Recovery of Pulping Materials, Helsinki, May 13-17 (1968):211-34.

76. Gullichsen, J., "Experience Accumulated from Tests with a Pilot Diffuser," Pulp. Pap. Mag. Can., 74 (12):80-91 (73).

77. Gyusumyan, A.M. and E.I. Perlov, "Automation of the Continuous Washing of Kraft Pulp in Vacuum-Filters," Bumazh. Prom., (2):12-14 (1966).

78. Haigh, D.W., "Sulfur Recovery in Lime Kilns," B.C. Research, Project 2320, Jan. 14, 1970.

79. Hatton, J.V., "Development of Yield Prediction Equations in Kraft Pulping," TAPPI, 56 (7):97 (1973).

80. Hatton, J.V., "Application of Empirical Equations to Kraft Process Control," TAPPI, 56 (8):108 (1973).

81. Hatton, J.V., "The Potential of Process Control in Kraft Pulping of Hardwoods Relative to Softwoods," TAPPI, 59 (8):48-50 (1976).

82. Hedberg, B.E. and E.D. Neuberger and W.B. Simmons, "How do Your Pulping Methods Compare to Kraft Mills in the United States and Canada?," TAPPI, 59 (5):52-63 (1976).

83. Hendrickson, E.R., "The Kraft Process," Proceed. of Int. Conf. on Atmospheric Emissions from Sulphate Pulping, Sanibel Island, 28 Apr. 1966.

84. Hendrickson, E.R. and J.E. Roberson and J.B. Koogler, "Control of Atmospheric Emissions in the Wood Pulping Industry," Clearinghouse for Federal Scientific and Tech. Information, U.S., 15 Mar. 1970.

85. Herschmiller, D. and R. Mitchell, "Elk Falls Controls Kraft Odor," Pulp Pap. Mag. Can., 76 (2):74 (1975).

86. Hinrichs, D.D., "The Effect of Kraft Pulping Variables on Deliquification," TAPPI, 50, 4, 173 (1967).

87. Hisey, R.W., "Counter-current Washing in Multi-stage Bleach Plant Operation at Brown Co.," Am. Pap. Inds., 51 (9):43-5 (1969).

88. Hotz, H.J., Sr. and P. Hinkley, and A. Erdman, Jr., "Fluidized Solids Lime Mud Recovery System at S.D. Warren Co.," TAPPI, 47 (11):174A (1964).

89. Hughey, G.B. and L.K. Herndon, and J.R. Withrow, "Causticizing, Reburning, and Settling in Sulphate Lime Recovery," Paper Trade, J., p25 (Feb. 1942).

90. Jacobi, E.F., "A Dynamic Model and Advanced Direct Digital Control System for a Kraft Mill Liquor-Preparation System," Ph.D. Thesis, Purdue Univeristy, 1973.

91. Jernqvist, A.S.H., "Experimental and Theoretical Studies of Thickeners," Svensk Papperstid., 68 (15):506 (1965).

92. Johnson, A.I. and Associates, "GEMCS Manual," University of Western Ontario Press, London, Ontario (1971).

93. Johnnson, L., "Mathematical Models of the Kraft Cooking Process," ACTA Poly. Scand. Math. and Comp. Mach. Ser. 22, 1971.

94. Jutila, E. and O. Panstar, and P. Uronen, "Computer Control of a Recovery Boiler," Pulp Pap. Mag. Can., 79 (4): 1978.

95. Kallenfors, R., "How Black Liquor is Concentrated for Direct Firing in Swedish Mills," Pulp and Paper, 49 (12):p144 (1975).

96. Karjalainan, P.O., et al., "Chloride Buildup in Kraft Liquor Systems," Pulp. Pap. Mag. Can. 73 (12):95 (1972).

97. Kerr, A.J., "The Kinetics of Kraft Pulping - Progress in The Development of a Mathematical Model," Appita, 24 (3):180-7 (1970).

98. Kinzner, K., "Investigations in the Causticizing of Green Liquors," Proceedings of the Symposium on Recovery of Pulping Chemicals, International Union of Pure and Applied Chemistry, Pulp, Paper, and Board Section, 279-302, Helsinki, Finland (1968).

99. Klasou, P., "Malodorous Substances in Sulfate," Paper Trade J., 79:30 (1924).

100. Kobe, K.A. and J.A. Wilkinson,"Effect of Sulphur Compounds in the Causticizing Equilibrium," I. and E.C., 45 (2):307 (A53).

101. Kuehl, J.F., and C.E. Silverblatt, and C.F. Cornell, "Simplified Recausticizing System," TAPPI, 49 (11):53A (1966).

102. Libby, C.E., "Pulp and Paper Science and Technology, Vol. 1," McGraw-Hill, New York (1962).

103. Lindberg, S., "How Uddeholm Destroys Air and Water Pollutants at the Skoghall Works," Pulp Pap. Mag. Can., 69 (7):125 (1968).

104. Lowendahl, L. and O. Samuelson, "Carbohydrate Stabilization During Kraft Cooking with Addition of Authraquinone," Svensk Pap., 17:549-551 (Nov. 1977).

105. Lundquist, S.O., "Mathematical Model of a Continuous Digester," SCAN Research Report, Number 72, Stockholm (1975).

106. Lyons, D.N. and W.W. Eckenfelder, Jr., "Optimizing A Kraft Mill Water Reuse System," Chem. Eng. Prog. Symp. Ser. 67:381 (1971).

107. Macdonald, G.L.W., "Bleach Plant Washing Studies," Pulp Pap. Mag. Can., 73 (3):56-8 (1972).

108. Martin, G.E., "The Hydrolysis of Sodium Sulphide in Mixtures with Sodium Hydroxide," TAPPI, 33 (2):84 (1950).

109. Misra, N.D. and B.S. Reddy, "Economics of High Calcium Lime in Paper Industry," Indian P and P, 22 (4):253 (1967).

110. Morgan, J.P. and D.F. Sheraton and F.E. Murray, "The Effect of Operating Variables on Strong Black Liquor Oxidation," Pulp Pap. Mag. Can., 71 (6):T120 (1970).

111. Morgan, J.P. and F.E. Murray, "Mass Transfer and Chemical Reaction Rate Considerations in High Efficiency Black Liquor Oxidation Designs," TAPPI, 54 (9):1500 (1970).

112.Motard, R.L., and M. Shacham, and E.M. Rosen, "Steady State Chemical Process Simulation," AICHE J., 21 (3):417 (1975).

113.Murray, F.E., "The Kinetics of Oxidation of Kraft Weak Black Liquor," TAPPI, 42 (9):761-767 (1959).

114.Murray, F.E. and H.B. Rayner, "Emission of Hydrogen Sulfide from Kraft Black Liquor During Direct-Contact Evaporation," TAPPI, 48 (10):588-593 (1965).

115.McCubbin, N., "Air Pollution Control in the Swedish Pulp Industry," Pulp Pap. Mag. Can., 75 (7):96 (1974).

116.McKean, W.T., and B.E. Hrutfiord, and K.V. Sarkanen, "Kinetic Analysis of Odor Formation in the Kraft Pulping Process," TAPPI, 48 (12):699 (1965).

117.McKean, W.T., and B.F. Hrutfiord, and K.V. Sarkanen, and L. Price, and I.B. Douglass, "Effect of Kraft Pulping Conditions on the Formation of Methyl Mercaptan and Dimethyl Sulfide," TAPPI, 50 (8):400 (1967).

118.Neretnieks, I., "A Mathematical Model for Continuous Countercurrent Adsorption," Svensk Papperstid., 77 (11):407-11 (1974).

119.Neretnieks, I., "Note on Some Washing Results with a Kamyr Hi-Heat Washer," Svensk. Papperstid., 77 (13):486-90 (1974).

120.Niggli, P., "Equilibrium Between TiO_2 and CO_2, as well as SO_2 and CO_2 in Alkali-Lime and Alkali-Aluminate Melts," Z. Anov, u. allg. Chem., 98, 281 (1916).

121.Nisenfeld, A.E. and D.L. Hogle, "Dynamic Feedforward Control of Multi-effect Evaporators," Instrument Tech., 17 (2):49 (1970).

122.Norden, H.V., Kemian Teollisous, 22 (6):430 (1965).

123.Olm, L. and G. Tistad, "Control of Batch Kraft Cooking," SCAN Research Report No. 51 (1973).

124.Pettersson, B., "Production Control of a Complex Integrated Pulp and Paper Mill," TAPPI, 52 (11):2155 (1969).

125.Pozo, V.G., "Operation of Black Liquor Oxidation Tower," Assoc. Mex. Tec. Ind. Celulosa Papel, 5 (4):290-5 (1965).

126.Proano, E.C. and L.L. Edwards, "Minimum Cost Design of Strong Black Liquor Oxidation Systems," TAPPI, 60 (7):132-6 (1977).

127.Rapson, W.H., "The R4 Process for ClO_2 Manufacture," Pulp Pap. Mag. Can., 75 (10):53 (1974).

128.Rapson, W.H., "Digestion and Bleaching of Wood Pulp Followed by Recovery of Chemicals and Countercurrent Flow of Wash Water," U.S. Pat. 3,698,995: Oct. 17, 1972.

129.Rapson, W.H. and D.W. Reeve, "The Effluent-Free Bleached Kraft Pulp Mill," TAPPI, 56 (9):112 (1973).

130.Reeve, D.W. and W.H. Rapson, "The Effluent-Free Bleached Kraft Pulp Mill," Pulp Pap. Mag. Can., 74 (1):87 (1973).

131.Robinson, W.I. et al., "Computer Control of a Multi-stage Bleach Plant," Pulp Pap. Mag. Can., 75 (4):73 (1974).

132.Rodgers, J.H. and A.A. Roche, and J.E. Tasman, "A Systems Approach to Process Control," Pulp Pap. Mag. Can., 75 (9):T322 (1974).

133.Rodgers, J.H., and A.A. Roche, and D.A. Reside, and S.C. Vespa, "Economic Analysis of Complex Kraft Mill Operations: Pulp and Paper Research Institute of Canada, PPR 178, Jan. 1977.

134.Rosen, A., "Adsorption in Pulp," TAPPI, 58 (9):156 (1975).

135.Rothrock, C.W., Jr., "The Effect of Certain Variables on the Causticizing Process," TAPPI, 41 (6):241A (1958).

136.Rydholm, S.A., "Pulping Processes," John Wiley and Sons, New York (1965).

137.Rydholm, S.A., "The Application of Modern Pulping Chemistry to the Design of Processes and Machinery," Pulp Pap. Mag. Can., 68 (1):T2-T15 (1967).

138.Rydin, S., "Washing of Pulp: Part 1-V," Swedish Forest Products Research Laboratory, Stockholm, Sweden (1975).

139.Rydin, S., "The Kinetics of the Causticizing Reaction," Svensk. Papperstid., 81 (2):43-8 (1978).

140.Sarkanen, K.V., and B.F. Hruitford, and L.N. Johanson, and H.S. Gardner, "Kraft Odor," TAPPI, 53 (5):766 (1970).

141.Sass, A.,"Simulation of the Heat-Transfer Phenomena in a Rotary Kiln," I & EC Proc. Des. & Dev., 6 (4):532-5 (1967).

142.Satterfield, C.N. and F. Feakes, "Kinetics of the Thermal Decomposition of Calcium Carbonate," AIChE J., 5 (1):115-122 (1959).

143.Scott, D.H. et al., "A Systems Approach to Batch Control," Instrument Tech., 17 (8):50 (1970).

144.Serafin, J. and A. Jameson, "Oxygen Bleaching at Husum, Sweden," Pulp Pap. Mag. Can., 73 (10):81-4 (1972).

145. Shamson, A.S. et al., "Operative Control of the Effectiveness of Pulp Washing," Bumazh. Prom., (3):18-19 (1969).

146. Shih, T.T.C., and B.F. Hrutfiord, and K.V. Sarkanen, and L.N. Johanson, "H_2S Vapor-Liquid Equilibrium in Aqueous Systems as a Function of Temperature and pH," TAPPI, 50 (12):630 (1967).

147. Shih, T.T.C., and B.F. Hrutfiord, and K.V. Sarkanen, and L.N. Johanson, "Methyl Mercaptan Vapor-Liquid Equilibrium in Aqueous Systems as a Function of Temperature and pH," TAPPI, 50 (12):634 (1967).

148. Sillen, L.G. and T. Andersson, Svensk. Papperstid., 55:622 (1952).

149. Sinitsyn, A.I. and B.I. Frid, "Automatic Relief in the Cooking Zone of a Continuous Digester," Bumazh. Prom., (8):14-16 (1966).

150. Smith, C.C., "Mathematical Modelling, Simulation and Control of the Operation of a Kamyr Continuous Digester for the Kraft Process," Ph.D. Thesis, Purdue University, 1974.

151. Subrahmanyau, T. and K. Kivendra, "Fluo Solids Lime and Its Behavior in the Causticizing Unit," Indian P & P, 21 (11):699 (1967).

152. Sylwan, O., "Theory and Practice in Causticizing Green Liquor," Paper Trade J., 143 (2):42 (1959).

153. Tachibana, S. and G. Rowlandson, "Kamyr Continuous Diffuser Washing of Brown Stock at Crestbrook Pulp & Paper Ltd.," Pulp Pap. Mag. Can., 70 (3):59-62 (1969).

154. Tallmadge, G. and E. Gutfinger, "Withdrawal and Drainage Rates of Liquid Films," I & EC, 59 (11):19-34 (1967).

155. Tasman, J.E., "The Kraft Pulping Behavior of Canadian Wood Species," Pulp and Paper Research Institute of Canada, Report PPR/182, June 1977.

156. Teder, A. and D. Tormund, "The Equilibrium Between Hydrogen Sulphide and Sulfide Ion in Kraft Pulping," Svensk Pap., 16:607-9 (1973).

157. Thoen, G.N. and G.G. DeHaas, and R.G. Tallent, and A.S. Davis, "Effect of Combustion Variables on the Release of Odorous Compounds from a Kraft Recovery Furnace," TAPPI, 51, 8, 329-333, (August 1968).

158. Thoen, G.N. and G.G. DeHaas, and R.R. Austin, "Continuous Measurement of Sulphur Compounds and Their Relationship to Operating Kraft Mill Black Liquor Furnaces," TAPPI, 52 (8):1485 (1969).

159. Thoen, G.N. and G.G. DeHaas, "Kraft Recovery Furnace Smelt Bed Measurement System," TAPPI Conference Papers-Alkafine Pulping and Testing 1976, Dallas, Sept. 13-15, 1976, p.228-33.

160.Tinnis, V., "An Optimum Production Control System," Pulp Pap. Mag. Can., 75 (7):84 (1974).

161.Tirado, A. and V. Gonzalez, "Ten Years Experience in Odor Control at the Loreto y Pena Pobre Kraft Mill," TAPPI, 52 (5):853 (1969).

162.Tomiak, A., "Theoretical Recoveries in Filter Cake Reslurrying and Washing," AIChE J., 19 (1):76-84 (1973).

163.Tomiak, A. and M.A. Lanzon, "A Note on Classification of Pulp Washing Literature References," Svensk. Papperstid., 15, 475-6 (Oct. 1977).

164.Treiber, S.S., "An Analysis of the Lovholmen Mill," Internal Report, Swedish Forest Products Research Laboratory, Stockholm, 1978.

165.Treiber, S.S., "Analysis of the Effect of Sulphur in Fuel Oil on Lime Availability," Internal Report, ASSI. Lovholmen, Pitea, Sweden, 1978.

166.Tsuchiya, G. and L.N. Johanson, "Prediction of Generation and Release of Odorous Gases from Kraft Pulp Mills," TAPPI, 55 (5):777 (1972).

167.Twitchell, J.P. and Edwards, L.L., "Kraft Mill Material Balance Calculations for Brown Stock Washing, Screening, and Oxygen Bleaching," TAPPI, 57, 9 (1974).

168.Uronen, P., H. Aurasmaa and K. Leiviska, "Static and Dynamic Modelling of a Lime Circulation Loop," Papper och Tra, 58 (11):775-780 (1976).

169.Venkatesh, V., A. Kirkman, and F. Mera, "Computer-aided Process Analysis and Economics for Pulp and Paper Mills," TAPPI, 61 (3):87-91 (1978).

170.Vroom, K.E., "The 'H' Factor: A Means of Expressing Cooking Times and Temperatures as a Single Variable," Pulp & Pap. Mag. Can., 58 (3):228-31 (1957).

171.V'yukov, I.E. et al., "Experimental Study of Continuous Washing of Sulphate Pulp," Bumazh. Prom. (6):12-14 (1967).

172.V'yukov, I.E. and V.G. Pivorarov, "Interrelation of Lime Recovery Process Parameters on Rotary Kilns," Tr. Vses. N.I.I. Tsellyul.-Bum. Prom. 52:152-73 (1967).

173.V'yukov, I.E. and V.G. Pivorarov, "Lime Recovery Process Mathematical Model and Synthesis of Automatic Control System," PRP2 Autom. (IFAC Conf. Brussels), Paper 5.3: May (1971).

174.V'yukov, I.E. et al., "Computerization of Continuous 'Kamyr' Sulfate Pulp Process Control," PRP2 Autom. (IFAC Conf. Brussels) Paper No. 5.1: 6 p. (May 1971).

175.Wallin, G. and S. Noreus, "Computer Control of Batch Digesters," Svensk

Papperstid., 76 (9):329 (1973).

176.Walther, J.E. and H.R. Amberg, "The Role of the Direct Contact Evaporator in Controlling Kraft Recovery Furnace Emissions," Pulp Pap. Mag. Can., 72 (10):65 (1971).

177.Wells, C.H., "Industrial Process Applications of Modern Control Theory," Instrument Tech. 18 (4):43 (1971).

178.Wetherhorn, D., "The Calculation of Evaporator Heat Balances from Operating Data," TAPPI, 47 (2):168A (1964).

179.Wiberg, R., "Green Liquor Clarification," TAPPI, 43 (3):172A-3A (1960).

180.Wilder, H.D. and S.T. Hau, "A Comparison of the Kinetics of the Neutral Sulfite and Kraft Pulping Processes," TAPPI, 45 (1):1 (1962).

181.Wilder, H.D. and E.J. Daleski, "Kraft Pulping Kinetics 1. Literature Review and Research Program," TAPPI, 47 (5):270 (1964).

182.Wilder, H.D. and E.J. Daleski, "Delignification Rate Studies. Part II. of a Series on Kraft Pulping Kinetics," TAPPI, 48 (5):293 (1965).

183.Wright, R.H., "Kinetics of the Oxidation of Sulphate Black Liquor," TAPPI, 35 (6):276-280 (1952).

APPENDICES

Appendix A

Appended in Volume II

APPENDIX B

Data for Tuning and Validation of the Steady-State Simulation

Table B-1 lists the operating data at four different operating conditions: before black liquor oxidation (BLO), after BLO, after blow heat recovery (BHR) and after the trial. The values are averaged from the operating logs, shift reports and periodic chemical test reports. The data in each group are based on a nominal production rate of 1400 tons of air dry pulp (TADP) per day where an air dry ton is defined to have a 10% moisture content. Each datum is the average of data ranging from hourly values over a typical one week period to daily averages over an eight month period. In the case of the former, a typical week is defined as a week of steady operation with no unit breakdowns and excludes periods prior and subsequent to a scheduled mill shut down. All flow rates and operating temperatures were determined from such samples. Stream compositions,unit reaction efficiencies, chemical make-up steam production and steam usage are averages of data over six to eight months in each of the periods.

Items denoted by an asterisk are the dependent variables of the steady-state simulation and are therefore the parameters of evaluation of the simulation predictions. It should also be noted that only the white liquor stream composition is measured. The compositions of all other streams are generally not measured aside from the solids concentration.

Table B-2 lists the chemical loss data. It can be seen that the only measurement available in all four periods is the titratable brown stock washer chemical loss. It should be pointed out that this variable represents only the loss of residual NaOH, Na_2S, Na_2CO_3 and Na_2SO_4. The measurement technique does not account for NaOH and Na_2S consumed in the delignification reaction. Since approximately 90% of the initial NaOH and 30% of the initial Na_2S are consumed, this represents a sizable discrepancy from the true losses. The chemical loss is reported as equivalent Na_2SO_4 which is consistent with the mill practice of adding only Na_2SO_4 as sodium make-up prior to 1975.

The dregs washer losses were measured on five different days prior to 1974. The sampling procedure was to allow the dregs dump tank to fill after first being empty. Four samples of the contents were withdrawn and analyzed allowing calculation of the losses. The sampling time in each case was two hours. The maximum and minimum values were ±50% of the mean. The sodium content was determined by a colored indicator titration and since the dregs contain a high concentration of unsettled particles, the analytical method is somewhat in doubt.

The particulate loss measurements were carried out by a consulting firm to show that the mill was complying with the standards of the U.S. Environmental Protection Agency. The cross-section of each duct was divided in 28 segments of equal size and a probe was moved to the center of each segment for sampling purposes. The sampling time was three minutes and samples were withdrawn by withdrawing flue gas with a vacuum pump through filters. After the full cross-section was sampled, the filters were weighed and the particulate flow calculated from the weight difference and time average flow rate. This procedure was carried out once for each duct and so no information on variability of data is available.

The emissions measurements for the 1976 period were carried out by a

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pulp production for the period June 1976 to September 1977. This period encompassed the periods defined as before and after the trial. The data are drawn directly from the mill purchase and sales records.

Table B-4 lists the results of an experiment designed to test the rotary drum, brown stock washer loss relationship. The fresh wash water feed rate was changed from the normal 240 gpm while maintaining constant pulp feed rate. The system was allowed 2 hours for equilibration before samples of pulp were taken from the 3rd stage. The time constant of the washer is approximately one hour. The timing of the experiment was constrained by operational requirements and the need to complete all sampling in one eight hour shift. A sample was taken from three positions on the drum, one from each edge and one from the center, to overcome the effect of matte non-uniformity. The loss analysis was made by testing the conductivity of squeezings from the samples. This conductivity had previously been correlated with a titration of free inorganics in brown stock squeezings and is the standard test procedure in the mill. The consistency was calculated by washing and drying a known weight of wet sample and then weighing the oven dry sample.

Table B-5 lists the results of an experiment to determine the effect of pressure in the vapor side of the 6th effect on steam economy. The vacuum in the 6th effect was controlled by adjusting the flow rate of cooling water to the vapor condenser. Inlet and outlet stream concentrations were measured by the evaporator operator using hydrometers. Control of stream flow was left to the discretion of the operator and was not an independent variable of the experiment. The system was allowed 2.5 hours to equilibrate after each change of 6th effect vacuum. The system time constant is approximately 1.5 hours but the timing of this experiment was once again constrained by operational requirements and the need to complete the experiment in one eight hour shift.

Table B-6 lists the analyses of input and output streams from a slaking and causticizing unit and a rotary lime kiln. The system was subjected to large uncontrolled upsets, during the five day period, caused by emergency shut downs and start-ups of one of the recovery furnaces. Samples were collected once each day. The sampling time was eight to twelve hours after an upset. The green and white liquor analysis was used to test the causticizing model of Carrol (31) and Hughey et al. (89). The time constant of the green liquor storage system is approximately 6 hours and so the greeen liquor samples were taken before the equilibrium was attained; however, the information of interest is the effect of green liquor composition on final white liquor composition. Since the time constant of the slaking and causticizing system is much less (1.5 hours) than the green liquor storage system the changing green liquor composition after eight to twelve hours will not seriously effect the results.

The lime kiln data was used to develop a calcining model. The lime mud analysis for December 2 indicates mud of a very different composition than other samples. On this day a breakdown of the mud filter necessitated the pumping of mud from the primary mud washer directly into the kiln resulting in a lower mud solids content and higher Na_2O and CaO carryover. The kiln temperatures were measured four times daily. The gas temperature to the flue (i.e. back temperature) was measured with a thermocouple and the temperature of hot lime exiting the kiln (i.e. front temperature) was measured with an optical pyrometer focused on the lime one foot from the kiln edge.

Douglass and Price (44) carried out experimental cooks of various wood species and measured the emission of CH_3SH, $(CH_3)_2S$ and $(CH_3)_2S_2$. The experiments involved cooking 1 gm. of oven dry wood in a 7 ml. digester with a synthetic cooking liquor. The experiments were carried out at two different sulphidities and the data for the time and temperature range appropriate to industrial conditions are tabulated in Table B-7. The total of the three pollutants is reported as equivalent pounds of sulphur per oven dry ton of wood. Pine data is taken as the model for softwoods and Birch data is taken as the model for hardwoods.

Table B-8 presents a reformulation of the calcining data of Hughey et al. (89). Using samples of mud from two Kraft mills Hughey calcined the samples in a muffle furnace at different temperature. The data in Table B-7 has been recalculated as mole % and was used to develop a simple kinetic model of calcining.

Table B-9 lists the analyses of grab samples collected during the 1977 trial, of unclarified green liquor from the smelt dissolving tanks, white liquor from the causticizers, white liquor from storage and black liquor to the oxidation system.

Table B-10 lists the storage volumes measured daily during the trial. The volumes listed have been converted into equivalent volume of white liquor of active alkali concentration 6 lbm Na_2O/ft^3.

Table B-11 lists the upsets, during the trial, that caused inventory modification through sporadic water addition and bed burn downs and estimates of the volume changes caused by the events.

Figure B-1 presents a typical daily cooking schedule for a batch digester. These temperature time profiles were used to calculate the H-factor for a batch cook.

B-1 General Operating Data

	Units	1974 Before BLO	1975 After BLO	1976 After BHR Before Trial	1977 After Trial
General:					
Batch pine digester prod.*	TADP/DAY	797	803	803	803
Continuous hardwood prod.*	TADP/DAY	572	595	628	628
Salt cake make-up *	lbm/TADP	73	58	44	30
Caustic make-up*	lbm/TADP	00	4	16	21
Lime make-up*	lbm/TADP	20	35	32	26
Kiln fuel*	BTU/TADP	3.5×10^6	2.8×10^6	2.7×10^6	2.8×10^6
White liquor sulphidity	%	21	29	29	24
White liquor composition					
Total titratable alkali*	$lbmNa_2O/ft^3$	7.0	7.0	7.0	7.0
Active alkali	$lbmNa_2O/ft^3$	6.1	6.0	6.0	6.0
Sulfide	$lbmNa_2O/ft^3$	1.3	1.7	1.7	1.4
Batch (Pine) digesters					
No. of digesters		12	12	12	12
Top cook Temp	°F	338	338	338	338
Total cycle time	min	225	235	235	235
Blow and fill time	min	40	40	40	40
Active alkali on wood	$\frac{lbmNa_2O}{lb\ wood}$	0.16	0.1625	0.1625	0.16
Total liquor volume	ft^3/batch	1800	1800	1800	1800
Total wood charge (wet)	Tons/batch	48.5	48.5	48.5	48.5
Wood moisture*	%	50	50	50	50
Nominal yield *	%	44	44	44	44
Brown stock $KMnO_4$ No.*		19	19	19	19
Blow line consistency	$\frac{lbm\ pulp}{lbm\ slush}$	0.11	0.11	0.11	0.11
Steam usage*	BTU/TADP$\times10^6$	2.1	2.1	2.1	2.1
Continuous digester					
Wood species		GUM	GUM	GUM	GUM
Chip meter feed rate	RPM	15.5	16.0	17	17
Wood moisture	%	52	52	52	52
Upper heater temp.	°F	308	314	309	309
Lower heater temp.	°F	317	324	320	319
Active alkali on wood	$\frac{lbm\ Na_2O}{lbm\ ODW}$ %	16.5	16.25	16.35	16.0
White liquor flow rate	U.S.GPM	319	325	344	337
Nominal yield	%	45	45	45	45

* Data used for simulation evaluation

B-1 General Operating Data (continued)

	Units	1974 Before BLO	1975 After BLO	1976 After BHR Before Trial	1977 After Trial
Continuous digester (cont)					
Brown stock $KMnO_4$ No.*		11.5	11	11	11
Steam usage *	10 xBTU/TADP	1.4	1.4	1.4	1.4
Blow line consistency*	$\frac{\text{lbm pulp}}{\text{lbm slurry}}$	0.11	0.11	0.11	0.11
Brown stock washers					
No. of lines		5	5	5	5
Wash water flow rate	USGAL/TADP	1900	1900	1900	1900
Wash water temperature	°F	180	180	180	180
Nominal pulp consistency	$\frac{\text{lbm pulp}}{\text{lbm slush}}$	0.15	0.15	0.15	0.15
Nominal weak liquor conc.*	wt.% solids	16.5	16.5	16.5	16.5
Multi-effect evaporators					
No. of evaporators		4	4	4	4
Total feed rate*	US GPM	1200	1200	1200	1200
Nominal outlet conc.	wt. % solids	43	43	43	43
Steam pressure	psig[a]	50	50	50	50
steam flow rate*	lbm/hr	$160x10^3$	$160x10^3$	$160x10^3$	$160x10^3$
Steam economy	$\frac{\text{lbmcondensate}}{\text{lbm steam}}$	4.5	4.5	4.5	4.5
6th effect vacuum	in. Hg	27	27	27	27
Black liquor oxidation					
Efficiency	%	--	95	99.9	99.9
No. of towers operating		--	1	2	2
Air flow	SCFM[b]	--	6200	12400	12400
Outlet liquor conc.*	wt. % solids	--	45	46.5	46.5
Liquor feed rate*	U.S. GPM	--	800	800	800
Recovery Furnaces					
No. of furnaces		4	4	4	4
Liquor feed rate *	10 lbm/hr	310	310	310	310

* Data used for simulation evaluation

[a] 1 psig = 0.333 N/m

[b] 1 SCFM=471.9 m^3/sec

B-1 General Operating Data (continued)

	Units	1974 Before BLO	1975 After BLO	1976 After BHR Before Trial	1977 After Trial
Recovery furnaces (cont.)					
Liquor concentration	wt. % solids	61	61	61	61
Liquor feed templ	F	205	205	210	210
Air feed	10^6 lbm/hr	1.19	1.19	1.19	1.19
Air distribution, 1:2:3	%	50:32:18	50:32:18	50:32:18	50:32:18
Steam production*	10^6 BTU/hr	560	520	520	538
Steam pressure	psig	550	550	550	550
Reduction efficiency*	%	95	94.5	93.1	93.5
Smelt temperature	*F	N.A.+	1750	1750	1750
Flue gas temp.	*F	600	600	N.A.	N.A.
Causticizers					
No. operated		3	3	3	3
Green liquor feed rate*	ft^3/min	130	140	140	135
Caustic conversion effic.*	%	85	84	84	84.6
Slaker temp.	°F	190	190	190	190
Lime kilns					
Mud feed to filter*	U.S. GPM	234	214	214	224
Mud consistency to filter	%	37	39	39	39
Mud consistency to kiln	%	55	55	55	55
Lime exit temperature	°F	2350	2250	2250	2250
Flue gas temperature	°F	600	550	550	550
Lime availability*	%	89	87	87	87.5
Excess CaO in mud in*	%(dry)	1.5	2	2.5	2.0
Na_2O in mud	%	0.7	1	1.5	1.5
Blow heat recovery: Efficiency	%	--	--	54	54

* Data used for simulation evaluation
\+ N.A. Denotes data not available

B-2 Chemical Loss Data

		1974 Before BLO	1975 After BLO	1976 After BHR Before Trial	1977 After Trial
Titratable brown stock Washer Losses	$\frac{lbmNa_2SO_4}{TADP}$	24	25	26	26
Dregs washer losses: sodium losses	$\frac{lbmNa_2SO_4}{TADP}$	1.4	--	--	--
calcium losses	$\frac{lbmCaCO_3}{TADP}$	2.6	--	--	--
Particulate losses (EPA report): recovery furnaces	lbm/TADP	--	5.6	--	--
lime kilns	lbm/TADP	--	1.9	--	--
Malodorous emissions:					
Continuous digester & turpentine vent	$lbmH_2S/TADP$	--	0.2	2.3	--
Batch digesters	$lbmH_2S/TADP$	--	1.0	3.7	--
Multi-effect evaporators	$lbmH_2S/TADP$	--	1.8	1.3	--
Recovery furnaces	$lbmH_2S/TADP$	1.0	--	2.4	--
Direct contact evaporators	$lbmH_2S/TADP$	7.0	--	1.5	--
Lime kilns	$lbmH_2S/TADP$	--	--	0.5	--

B-3 Raw Material Usage and Pulp Production Before and After Trial

	Total wet chips cooked Tons/month	Total Pulp Produced TADP/month	Salt-cake Make-up lbm/month	Caustic Make-up lbm/month	Lime Make-up lbm/month
June '76	147222	38645	1646721	618300	1185517
July '76	154926	40236	2149183	516400	1243018
August '76	143350	39030	1211936	560700	1038873
Sept. '76	122648	31115	2191289	539200	1243994
Oct. '76	181013	47117	1597518	657500	1275199
Nov. '76	150250	39987	1999100	805300	985120
Dec. '76	139855	36220	1188012	647100	1823345
Jan. '77	153647	39004	2583345	732700	1564596
Feb. '77	153515	39165	1387707	414800	1503532
Mar. '77	145863	37084	978091	783500	1128094
Apr. '77	182141	47466	1395972	1293000	918578
May '77	151138	38509	773002	741900	859742
June '77	146340	37318	740372	681100	724927
July '77	154626	40246	2157738	953400	1387801
Aug. '77	152357	39375	456659	759500	1190603
Sept. '77	128697	33114	1616787	602700	912140

B-4 Brown Stock Washer Experiment

Wash Water Feed Rate	USGPM	210	240	300
Pulp Feed Rate	TADP/DAY	200	200	200
Pulp slurry feed rate	USGPM	320	320	320
Blow line pulp consistency	$\frac{\text{lbm pulp}}{\text{lbm slurry}}$	0.11	0.11	0.11
Wash water temp.	°F	145	160	148
1st stage filtrate S.G.		1.08	1.08	1.08
3rd stage pulp consistency	$\frac{\text{lbm pulp}}{\text{lbm matte}}$	0.175	0.153	0.147
3rd stage titratable loss	$\frac{\text{lbm Na}_2\text{O}}{\text{TADP}}$	14.9	17.3	16.2
Drum rotation speed	RPM	2.3	2.3	2.3

B-5 Multi-Effect Evaporator Experiment

6TH Effect Vacuum	in Hg	25	26	27
Weak liquor flow rate	10^3xlbm/hr	220	220	220
Steam feed (50 psig)	10^3xlbm/hr	34.5	34	33
Weak liquor temp.	°F	181	181	188
Strong liquor temp.	F	218	218	218
Weak liquor conc.	wt. % solids	15.6	15.3	15.1
Strong liquor conc.	wt. % solids	43.7	44.5	45.4
Steam economy	$\frac{\text{lbm vapor}}{\text{lbm steam}}$	4.1	4.25	4.45

Table B-6 White Liquor Preparation Loop Experiment (1975)

		Dec. 1	Dec. 2	Dec. 3	Dec. 4	Dec. 5
SLAKING AND CAUSTICIZING						
White Liquor -	Total Na_2O $(\#/Ft^3)$	6.6	7.1	7.4	7.3	7.3
	Active Na_2O $(\#/Ft^3)$	6.1	5.6	5.4	4.5	6.0
	Sulfide Na_2O $(\#/Ft^3)$	1.6	1.7	1.7	1.8	1.9
	% Activity	92.4	78.9	73.0	61.6	82.2
	% Sulfidity	26.2	30.4	31.5	40.0	29.5
	Chlorides	.16	.18	.18	.18	.18
	Caustic Conversion %	93.0	74.7	67.0	50.8	78.9
Green Liquor -	Total Na_2O $(\#/Ft^3)$	6.6	7.2	7.4	7.3	7.3
	Active Na_2O $(\#/Ft^3)$	2.5	3.4	2.9	2.9	2.8
	Sulfides Na_2O $(\#/Ft^3)$	1.6	1.7	1.8	1.9	1.8
	% Reduction	92.0	90.9	90/9	92.7	92.8
	Unconverted Na_2SO_4	.33	.40	.41	.33	.32
KILN						
Lime Mud -	% Na_2O	1.3	4.9	0.9	1.3	0.8
	% Unconsumed CaO	3.3	12.5	3.4	2.9	1.6
	% Solids	54.8	47.4	56.0	53.6	56.6
Reburned Lime -	% Available CaO	83.0	78.8	86.2	87.2	89.0
	% Conversion CaCO	88.0	71.6	91.5	94.6	89.6
% Solids Scrubber		1.53	.62	.88	3.33	.42
Gas Analysis - -	% CO_2	-	13.5	23.6	21.3	22.8
	% O_2	-	5.6	0.6	0.1	1.0
	% CO	-	0.5	0.4	2.8	0.8
Front Temperature (°F)		2110	2190	2400	2250	2310
Back Temperature (°F)		550	510	610	560	600
Oil Flow (gpm)		6.0	5.75	6.0	6.0	6.0
Mud Flow (gpm)		90	50	82	85	85
Mud Density (% solids)		37	41.7	41	39.2	38.8

B-7 Digester Emission: Softwood and Hardwood (Douglass & Price)

		PINE		BIRCH	
White Liquor Sulphidity(%)		14.7	30.5	14.7	30.5
Cooking Time Min	Cook Temp. °F	TRS Emissions lbm S / Ton Wood	lbm S / Ton OPW	lbm S / Ton OPW	lbm S / Ton OPW
120	320	0.235	0.644	0.659	1.13
	338	0.570	1.09	1.25	2.28
	356	1.46	2.08	1.88	2.87
180	320	0.458	0.996	1.15	1.58
	338	0.838	1.49	1.58	2.41
	356	1.50	3.24	2.31	3.03
240	320	0.753	1.26	1.18	1.88
	338	1.15	2.05	1.99	2.54
	356	1.99	3.36	3.00	4.18

B-8 Calcining Data of Hughey et al (96)

	Remaining CaCO (mole %)	
Calcining Temp F	Calcining Time 1 hr	2 hr
1652	81.9	74.7
1742	63.0	41.7
1832	25.9	8.9
1922	15.9	9.5
2420	13.1	6.5
2520	18.3	17.5

Table B-9 Liquor Compositions During Trial

	Unclarified Grn. Liquor			Surge Tank White Liquor			Digester White Liquor			260 218 287 Unoxidized Black Liquor
DATE	TA	AA	Sul	TA	AA	Sul	TA	AA	Sul	Sul
2-21	7.3	2.5	1.4	7.0	5.9	1.4	7.2	6.1	1.4	1.30
2-22	7.8	2.6	1.5	7.2	6.4	1.3	7.1	6.1	1.3	1.18
2-23	7.0	2.8	1.36	7.0	6.2	1.30	7.1	6.2	1.30	1.11
2-24	6.80	2.30	1.30	7.05	5.90	1.34	7.30	5.95	1.36	1.11
2-25	7.35	2.40	1.46	7.05	6.05	1.38	7.15	6.15	1.38	1.22
2-26	7.07	2.40	1.44	7.30	6.05	1.44	7.30	6.05	1.44	1.25
2-27	7.05	2.40	1.42	6.95	6.15	1.36	7.05	5.95	1.36	1.25
2-28	6.85	2.35	1.34	7.00	6.00	1.38	7.03	6.08	1.39	1.09
3-1	7.05	3.35	1.42	7.05	6.20	1.49	7.05	6.10	1.44	1.27
3-2	7.15	2.50	1.44	7.15	5.95	1.42	7.20	6.00	1.46	1.27
3-3	7.15	2.55	1.47	7.00	5.95	1.46	7.10	6.05	1.46	1.33
3-4	7.35	2.40	1.51	7.06	6.06	1.46	7.06	6.06	1.46	1.35
3-5	7.55	2.95	1.51	7.30	6.25	1.46	7.25	6.24	1.49	N.A.
3-6	7.10	2.60	1.46	7.15	6.15	1.42	7.15	6.20	1.44	N.A.
3-7	6.95	2.65	1.49	7.00	6.25	1.42	7.00	6.25	1.42	1.25
3-8	6.65	2.52	1.42	7.00	6.12	1.46	7.05	6.05	1.46	1.15
3-9	7.45	2.75	1.59	7.20	6.25	1.49	7.28	6.18	1.47	1.31
3-10	7.45	2.85	1.49	7.30	6.22	1.49	7.32	6.32	1.51	1.38
3-11	6.90	2.35	1.42	6.83	5.65	1.42	7.02	5.76	1.42	1.30

Table B-10 Liquor Inventory @ W.L.

Date 1977	White and Green	Weak	45%	55%	BLO	Blow Tanks	Total
11/2	86700	21712	34320	26302	52000	7939	228973
12/2	84500	20152	32630	25848	53182	9239	225551
13/2	80100	19719	36530	26227	53773	8651	225000
14/2	81900	19719	34580	26605	54363	5711	225664
15/2	74400	21322	38805	26831	54364	8496	224218
16/2	72700	23445	38025	26605	53772	8466	223014
17/2	85500	19502	34450	28872	51609	7652	227386
18/2	83700	20369	39975	25320	41009	4271	214644
19/2	75700	26176	35555	22977	40181	6949	207539
20/2	84500	18111	34450	25698	37227	8821	208808
21/2	95800	20455	29575	23959	40773	7777	223980
22/2	93800	21582	35100	25320	42545	5633	223980
23/2	72500	21060	42705	27814	40773	5014	209866
24/2	81400	21190	32500	28267	40182	4550	208089
25/2	21100	22100	36335	30233	39827	4279	203873
26/2	65700	20410	31850	30384	39000	6423	193766
27/2	66600	20453	30225	30837	38409	8992	195516
28/2	73400	24960	33150	30308	39000	9549	200818
1/3	59600	25480	36270	33936	39000	9193	203478
2/3	62900	24960	37635	29174	40182	7073	201924
3/3	71100	17507	35425	29477	39000	6345	198854
4/3	77100	17030	36075	26302	37818	7908	202234
5/3	71600	18157	34450	28721	37818	6771	197517
6/3	71000	23834	30810	29250	39000	5339	199233
7/3	78700	16640	28665	26983	40182	7119	198288
8/3	86800	16380	33345	24186	38409	7583	206704
9/3	69100	25740	33540	23279	38409	7227	197295
10/3	63900	19240	32370	29326	38409	7645	190890
11/3	82300	16380	28470	30988	39148	4380	201637

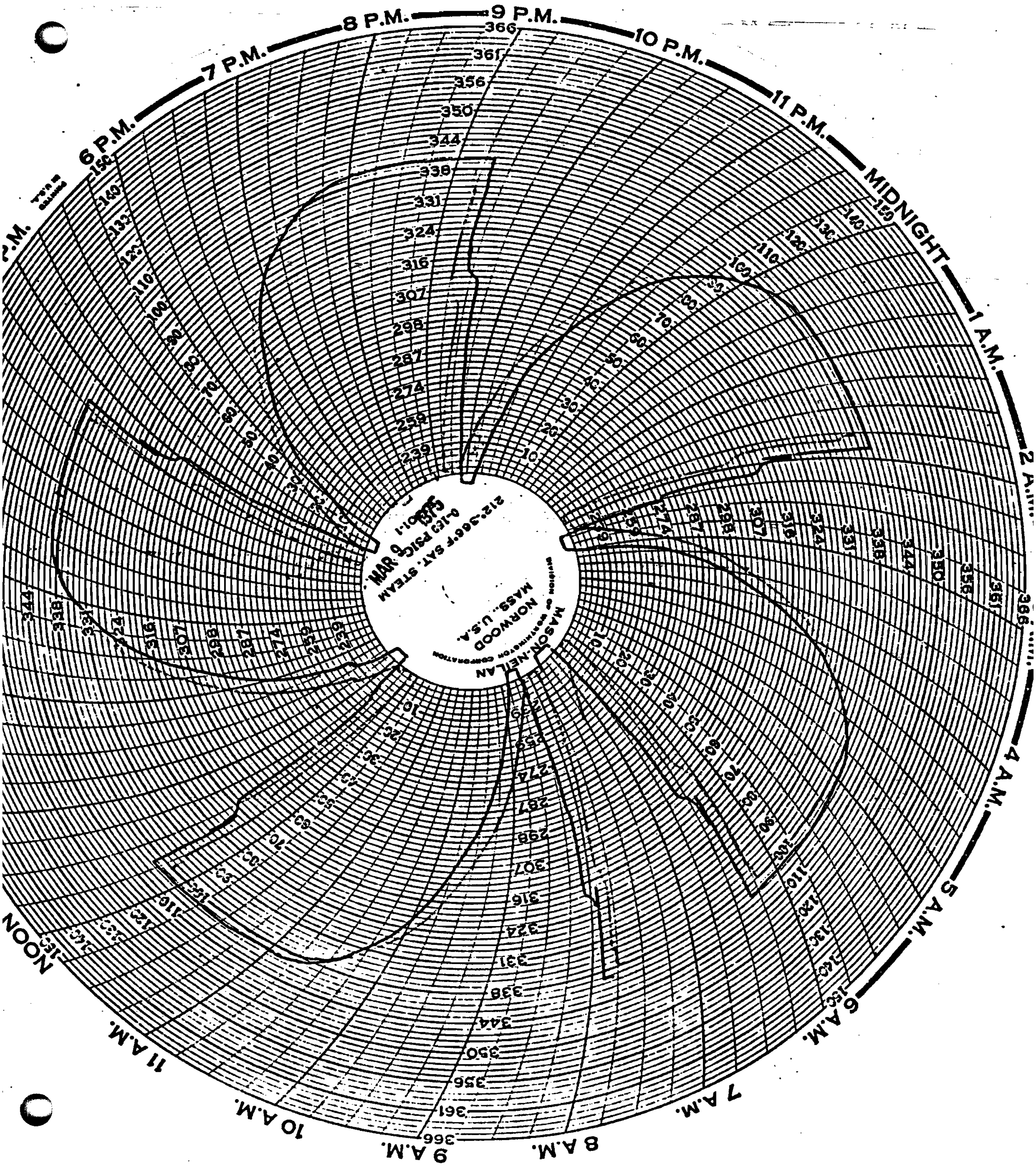
Table B-11 Effect of Temporary Inventory Modifying Events of Observed Volume of Liquor

Date 1977	(ft^3) Observed Volume Shifted to Baseline of 200000	Temporary Volume, Temporary Volume	(ft^3) Temporary Volume Correction	(ft^3) Corrected Volume
11/2	200000	weak liquor in #6-Dp tank	o0	200000
12/2	197000	#4 recovery out 2 hrs w.l. in #6-Dp	-15000	182000
13/2	196500	w.l. in #6-Dp	-5000	191500
14/2	197000	#4 recovery out 10 hrs, 55% liq in #5-Dp, w.l. in #6-Dp	-20000	177000
15/2	195000	w.l. in #3, 4, 5 and 6-Dps w.l. in #6-Dp	-25000	170000
16/2	194000	w.l. in #6-Dp	-5000	189000
17/2	198000	w.l. in #6-Dp	-5000	193000
18/2	185000	#5 recovery out 1 hr, 55% liq in #5-Dp, w.l. in #6-Dp, #6 recovery out 6 hrs, 55% in #4-Dp, w.l. in #5-Dp	-35000	150000
19/2	179000	55% in #4-Dp, w.l. in #5-Dp	-10000	169000
20/2	180000	#3 evap. set out 8 hrs, #3 recovery out 5 hrs, 55% in #4-Dp, w.l. in #5,6-Dp, w.l. in #4, 6-Dp	-45000	135000
21/2	189000	#2 evap set out 8 hrs	-10000	179000
22/2	195000	#1 evapoout 23 hrs., #6 recovery	-50000	145000
22/2	195000	#1 evap out 23 hrs, #6 recovery out 16 hrs, #5 recovery out 6 hrs, 55% in #3, 5-Dp, w.l. #4, 6-Dp	-50000	145000
23/2	181000	#6 Recovery set 2.5 hrs #1 evap out 5 hrs	-20000	171000
24/2	179000	w.l. in #6-Dp, w.l. in #6-Dp	-10000	169000
25/2	175000		0	175000

Table B-11 (cont)

Date 1977	(ft^3) Observed Volume Shifted to Baseline of 200000	Temporary Volume, Modifying Events	(ft^3) Temporary Volume Correction	(ft^3) Corrected Volume
26/2	165000	#1, 2 evaps out 8 hrs, w.l. in #6-Dp	-25000	140000
27/2	172000	w.l. in #6-Dp	-5000	152000
28/2	172000	#4 recovery out 11 hrs, 55% in #4, 5-Dp, w.l. in #6-Dp	-25000	147000
1/3	175000	55% in #5-Dp, w.l. in #6-Dp	-10000	165000
2/3	173000	55% in #5-Dp, w.l. in #6-Dp	-10000	163000
3/3	170000	#1 evap out 8 hrs, 55% in #3, 5-Dp, w.l. in #4, 6-Dp	-30000	140000
4/3	173000	#2 evap out 8 hrs, w.l. in #6-Dp	-15000	158000
5/3	169000	w.l. in #6-Dp	-5000	164000
6/3	170000	#2 evap out 5 hrs, w.l. in #6-Dp	-15000	155000
7/3	170000	55% in #4, 5-Dp, w.l. in #6-Dp	-15000	155000
8/3	177500	#1 evap out 8 hrs, #4 recovery out 5 hrs, 55% in #4-Dp, w.l. in #5, 6-Dp	-35000	142500
9/3	168000	w.l. in #6-Dp	-5000	163000
10/3	162000	#2 evap out 16 hrs, w.l. in #6-Dp	-15000	147--0
11/3	172500	#1 evapoout 8 hrs, #4 recovery out 5 hrs, 55% in #4-Dp, w.l. in #5, 6-Dp	35000	137500

Figure B-1: Batch Digester Cooking Profiles



Appendix C

Development and Tuning of the Simulation Causality

Appendix C

Development and Tuning of the Simulation Causality

In this section, the procedures for the development and tuning of the predictive equations are presented. In the case of causality taken directly from the literature, only the tuning procedure will be shown. The data used to tune the causality is generally taken from Appendix B which is a compendium of mill measurments; however, in many cases, there is no measured data available. In these cases, the input flows used to tune the causality have been calculated by a previuos module. For example, in section C-5, the inputs to the washer model are the calculated outputs from the flow tanks and digesters. Thus, given the measured inputs to the digester module that module was tuned and the calculated output from that module was used as the input to tune the washer causality. Where measured data was available, the Table in Appendix B from which numbers have been taken is cited.

C-1 Pulp Yield Equation

As shown in Chapter 5 the yield of pulp is predicted by a relationship due to Hatton (79,80,81).

$$Y = a - b \log (H) EA^{n}$$

Hatton provides the coefficients for the equation for twelve species of wood. For the test mill, Hatton's coefficients for Pine fit the Pine cooks and the coefficients for Trembling Aspen fit the Gum cooks.

Pine: $a=92.6$, $b=5.88$, $n=0.35$

Gum: $a=73.6$, $b=1.37$, $n=0.76$

In the case where none of the species listed by Hatton fit the species of interest, a set of experiments should be carried out to determine the values of the coefficients. A temporary measure can be to use the known values of the coefficients, b, and n, for a species having similar fiber and density characteristics and adjust the constant, a, to match to the desired yield.

C-2 Yield-Kappa Relationship

The Kappa number is an empirical measure of the residual lignin bonded to pulp. The Kappa number is linearly related to yield when the lignin residual is greater than approximately 3%. Yield measurements require accurate knowledge of the mass of dry wood originally pulped as well as accurate measurement of the final product. The Kappa number can be determined by a relatively simple chemical test of the final product and so is normally the only direct measurement of yield made in a pulp mill. Hatton provides the coefficients for twelve species for the equation

$$Y = a + bK$$

where for

Pine: $a=38.9$, $b=0.195$

Gum: $a=42.8$, $b-0.155$

Most mills use this approach and the coefficients of the equation are readily available. Figure C-1 shows a plot of yield vs. kappa data, from the test mill, for Pine. Hatton's coefficients match the mill's own relationship exactly. As can be seen fromtthe plot, the realtionship would be incressing non-linear at Kappa numbers below the set point of 26.

C-3 Chemical Consumed in Cooling

The relationships predicting the residual active chemical has been developed from a single data point (143,p.603). In a Pine cook at 30%, white liquor sulphidity 0.283 lbm effective alkali was consumed per lbm of dissolved organics. Converting into actual mass of NaOH and Na_2S relationships are

$$NaOH_{residual} = NaOH_{initial} - 0.2413(1-Y)$$

$$Na_2S_{residual} = Na_2S_{initial} - 0.0417(1-Y)$$

where <u>Y</u> is the fractional pulp yield. The calculation of the coefficients is

$$\begin{aligned} NaOH_{consumed} &= 0.283(1-0.5S) \\ &= 0.283(1-0.5(0.3)) \\ &= 0.2413 \text{ lbm/lbm dissolved organics} \end{aligned}$$

$$\begin{aligned} Na_2S_{consumed} &= 0.283-0.2413 \\ &= 0.0417 \text{ lbm/lbm dissolved organics} \end{aligned}$$

When the equation if applied to a particular stream of black liquor, the term (1-Y) is equal to the soluable organic flow in that stream.

C-4 H_2S Emission from Digesters

An equation to predict the emission of sulphurous gas hab been fit to the data in Table B-7, p.B.15 using Pine as a model for softwoods and Birch as a model for hardwoods. The equation takes the form

$$TRS = a+bS+cT+d\theta$$

where TRS is the sulphur lost in lbm S/Ton Wood, S is the white liquor sulphidity (wt. fraction), T is the top cooking temperature in °F and θ is the cooking time in minutes. The coefficients of the fit are

softwood: a= -10.376, b=3.275, c=0.02858, d=0.006708
hardwood: a= -4.446, b=6.473, c=0.01325, d=0.002248

These coefficients were tuned to a single measured (point (see Table B-1, p.B.8) by multiplying through by a constant and subsequent adjustment so as to fit the equations' response to white liquor sulphidity (see chapter 8). This procedure results in the coefficients

softwood= a= -23.473, b=25.948, c=0.04759, d=0.01116
hardwood: a= -9.563, b=20.792, c=0.018232, d=0.003091

An alternate form of this equation has been proposed in Chapter 8 to more accurately take into account the temperature-time dependency of the emission reaction.

$$TRS = a+bS+cH$$

where H is the Vroom (177) H-factor. The eoeffiicents are

softwood: a= -23.473, b=25.948, c=5.645
hardwood: a= -9.563, b=20.792, c=1.301

The coefficients a and b are unchanged and the coefficient c has been adjusted so that TRS at the known point (Table B-1) is the same by either equation.

C-5 Brown Stock Washer Loss

A test of the washer loss causality was carried out on a three stage washer. Three different amounts of wash water were showered on a constant flow of pulp at a constant inlet consistency. The measurements are shown in Table B-4, p.B.13. The washer loss equation is

$$F = \frac{W_{pulp}}{W_{TOT}} / \eta$$

where F is the fraction of the chemical entering that will be lost with pulp, W_{pulp} is the mass flow of liquid leaving with pulp, W_{TOT} is the mass flow of total liquid entering the washer system and η is the washing efficiency. Since the pulp inlet flow conditions do not change a plot of Total loss versus W_{pulp}/W_{TOT} serves as a validation of the linear causality.

A pulp flow of 200 Tons/Day at a consistency of 11% gives 67.4 Tons/hr of liquid entering with pulp. Adding this amount to the wash water flow rates gives W_{TOT} for each condition. Dividing the pulp flow by the outlet pulp consistency and subtracting the pulp flow gives W_{pulp} for each condition. These calculations have been performed and the results are tabulated in Table C-1. The losses versus the ratio of (W_{pulp}/W_{TOT}) are plotted in Figure C-2. A straight line has been fit to the three points. It can be seen that the best fit through the points would not pass through the origin indicating that a higher order relationship might give better results. Unfortunately, the points are too clustered and too few to make such a fit despite the fact that the wash water flow rate was changed by almost 50% of the smallest value.

The causal equation is tuned to the loss measurement by using either measured inlet and outlet conditions, when available, or the simulation output itself. For example, tuning the single loss equation to the total washing system:

measured losses = 26 lbm Na_2O/TADP

from the simulation, input to the washer

Total water in with pulp = 339.8 Tons/hr

total pulp flow = 59.5 Tons/hr (air dry)

Total chemical flow in = 24.35 Tons Na_2O/hr

Wash water = 475 Tons/hr

Outlet pulp consistency = 0.15

Then

$$W_{pulp} = (59.5/0.15-59.5)0.9$$
$$= 303.5 \text{ Tons/hr}$$

where 1 Ton of air dry pulp = 0.9 Tons of pulp

$$W_{TOT} = 339.8 + 475$$
$$= 814.8 \text{ Tons/hr}$$

$$\text{Total Chemical Lost} = 26(59.5)/2000.$$
$$= 0.77 \text{ Tons } Na_2O\text{/hr}$$

$$F = 0.77/24.35 = 0.031$$

$$W_{pulp}/W_{TOT} = 0.37$$

and $$\eta = \frac{0.37}{0.031} = 11.7$$

Clearly, the modules prior to the washers must be tuned if the inlet conditions are to be taken from the simulation.

The outlet flow of liquor from the tuned digester modules would serve as an initial estimate of inlet conditions to all subsequent modules and thus would serve for a rough tuning pass through the entire simulation.

C-6 Evaporator Steam Economy

The steam economy is defined as the mass of water evaporated from the liquor feed per unit mass of steam used. A sample calculation is provided based on the data in Table B-5, p.B.13. Taking the case where the vacuum in the 6th Effect is 27 in. Hg.

$$\text{Liquor Solids in} = \text{Liquor flow} \times \text{Solids Conc.}$$
$$= 220 \times 10^3 (0.151)$$
$$= 33.2 \times 10^3 \text{ lbm/hr}$$

$$\text{Water in} = (220-33.2) \times 10^3$$
$$= 186.8 \times 10^3$$

$$\text{Water Out} = \frac{\text{solids in}}{\text{conc out}} (1-\text{conc. out})$$
$$= \frac{33.2\text{x}10^3}{0.454} (1-0.454)$$
$$= 39.95\text{x}10^3 \text{ lbm/hr}$$

$$\text{Steam economy}, E_c = \frac{\text{water in-out}}{\text{steam used}}$$
$$= \frac{186.8\text{x}10^3 - 39.95\text{x}10^3}{33\text{x}10^3}$$

$$= 4.45$$

Based on the data in Table B-5, an equation relating E_c to the vacuum in the 6th or final effect (with respect to vapor flow) was been developed.

$$E_c = a+bP$$

where P is the vacuum in inches of Hg. For the evaporator analyzed a=4.3 and b=0.2. The relationship is not general as a number of other factors will affect steam economy. However, the model is self-tuning and the user needs only to supply a known steam economy, E_c^1 at a known vacuum, P'. The equation that will be solved given these values is;

$$E_c = (E_c'-0.2P') + 0.2P$$

The steam economy is applied to the equation predicting steam requirement by evaporator set as shown in equation 5-25.

C-7 Evaporator H_2S Emission

As in the case of the brown stock washer losses, the H_2S emission may be tuned to the measured loss by using either measured input data or the simulation statement of the inlet conditions. The relationship is

$$TRS = a\left[\frac{0.5Na_2S}{NaOH+0.5Na_2S}\right]_{active}$$

where TRS is in lbm sulphur/Ton of lignin in black liquor, a is the coefficient to be tuned and the chemical flows are the active residuals in Tons Na_2O/hr. From Table B-2, p.B.11

$$\text{Emission of } H_2S = 1.3 \text{ lbm } H_2S/\text{TADP}$$

$$= 1.3 \times 59.5 \text{ TADP/hr}$$

$$= 77.4 \text{ lbm } H_2S/\text{hr}$$

$$= 72.8 \text{ lbm sulphur/hr}$$

From the simulation statement of the inlet conditions

Lignin Flow = 64.5 Tons/hr

TRS = 1.13 lbm sulphur/Ton Lignin

Total NaOH = 13.75 Tons Na_2O/hr

Total Na_2S = 5.18 Tons Na_2O/hr

Now, calculating the active residual NaOH and Na_2S from the equations in section C-3

$$NaOH_{active} = 1.69 \text{ Tons } Na_2O/\text{hr}$$

$$Na_2S_{active} = 3.05 \text{ Tons } Na_2O/\text{hr}$$

$$\frac{0.5Na_2S}{NaOH+0.5Na\ S}\text{ active} = 0.45$$

and

$$a = \frac{1.13}{0.45} = 2.51$$

C-8 <u>H_2S Emission from Direct Contact Evaporator</u>

The emission of H_2S is predicted by the equations

$$C_e = K_1 \left[\frac{Na_2S}{NaOH}\right]_{active}$$

$$C_o = C_e - \frac{(C_e - C_i)}{K_2}$$

where K_1 and K_2 are the adjustable coefficients. Two data points are required for tuning. Again using the simulation statement of input condition:

For the 1974 operating point with no black liquor oxidation

H_2S emitted = 614.3 lbm/hr

Total gas flow out(dry) = 747.4 Tons/hr

$$Co = 0.858 \text{ lbm } H_2S/\text{Ton gas}$$

H_2S in = 79.9 lbm/hr

Total gas flow in(dry)= 717.06 Tons/hr

$$C_i = 0.111 \text{ lbm } H_2S/\text{Ton gas}$$

and applying the equations in section C-3 to the inlet liquor flow

$NaOH_{active}$ = 2.653 Tons Na_2O/hr

Na_2S_{active} =1.603 Tons Na_2O/hr

Similarly for the 1975 operating ponnt

Co = 0.143 lbm H_2S/Ton gas

Ci = 0.118 lbm H_2S/Ton gas

$NaOH_{active}$ = 1.783 Tons Na_2O/hr

Na_2S_{active} = 0.158 Tons Na_2O/hr

Substituting into the equations for the two conditions

$$0.858 = K_1 \frac{1.603}{2.643} - \frac{K_1 \frac{1.603}{2.643} - 0.111}{K_2}$$

$$0.143 = K_1 \frac{0.158}{1.673} - \frac{K_1 \frac{0.158}{1.673} - 0.118}{K_2}$$

and solving

$$K_1 = 1.54$$

$$K_2 = 10.797$$

C-9 Recovery Furnace Reduction Efficiency

An equation has been fit to the curves in Figure C-3 (57) showing the relationship between reduction efficiency, R_D, smelt bed temperature, T, and primary zone oxygen deficiency, Δ. The equation fit to the region $1500^\circ F \leq T \leq 2061^\circ F$ and $-11\% \leq \Delta \leq -1\%$ is

$$R_D = a_3 + \sqrt{4a_2(a_4 - \Delta - a_1 T)}/2a_2$$

where $a_1=0.022$, $a_2=354$, $a_3=0.791$, $a_4=33.45$. The equation is applicable in the range $0.781 \leq R_D \leq 0.99$.

The relationship is tuned through the equation defining the oxygen deficiency, Δ.

$$\Delta = \frac{R-1}{a_5+R-1} \times 0.21 \times 100$$

where a_5 is a parameter, usually equal to one, and

$$R = \frac{O_2 \text{ available to burn all organics}}{O_2 \text{ required to burn all organics}}$$

The O_2 available is defined as that entering through the primary air ports. In that case, the parameter $a_5=1$; however, depending on the shape and height of the bed not all the primary air may take part in burning organics in the bed or alternately. Some of the secondary air may penetrate the bed. The equations have been applied to six recovery furnaces in three mills and the fit has been satisfactory with $a_5=1$. In a case where the fit is unsatisfactory, the tuning procedure is as follows:

Given $R_D = 0.91$

$T = 1700^{\circ}F$

O_2 available= 5 Tons/hr

O_2 required = 6 Tons/hr

substituting T and R_D into the first equation and solving for

$$= -(R_D-a_3)^2 a_2-a_4+a_1 T$$

$$= -(0.91-.791)^2(354)-33.45+0.022(1700)$$

$$= -1.06\%$$

Rearranging the second equation and solving for a_5,

$$a_5 = \frac{R-1}{\Delta} \times 21+1-R$$

$$= \frac{5/6-1}{-1.06} (21)+1-5/6$$

$$= 3.46$$

In this case, secondary air is also penetrating the bed.

C-10 Furnace H_2S Emission

H_2S emission is predicted by a relationship due to Blosser (22)

$$\text{TRS} = 1.67 \times 10^{-4} - 0.26 \times 10^{-4} \frac{\text{Primary Air}}{\text{Black Liquor Solids}}$$

where TRS is in lbm H_2S/Ton flue gas. The procedure for tuning is to multiply both coefficients by a constant to match the measured value of TRS at known air and black liquor solids flow rates.

C-11 Furnace Particulate Loss

Na_2SO_4 and Na_2CO_3 are emitted as particulates.

$$Na_2SO_{4_{out}} = a_1 (Na_2S+Na_2SO_4)_{in\ liquor}$$
$$Na_2CO_{3_{out}} = a_2 (NaOH+Na_2CO_3)_{in\ liquor}$$

all as Na_2O

$$Na_2SO_{4_{out}} = 1050 \text{ lbm } Na_2O/hr$$
$$Na_2S_{in} = 4332 \text{ lbm } Na_2O/hr$$
$$Na_2SO_{4_{in}} = 8370 \text{ lbm } Na_2O/hr$$
$$a_1 = \frac{1050}{(4332+8370)} = 0.083$$

$$Na_2CO_{3_{out}} = 312 \text{ lbm } Na_2O/hr$$
$$NaOH_{in} = 26300 \text{ lbm } Na_2O/hr$$
$$Na_2CO_{3_{in}} = 4980 \text{ lbm } Na_2O/hr$$
$$a_2 = \frac{312}{(26300+4980)} = 0.01$$

An alternate set of equations has been proposed where the losses are a function of the active residual chemical. All the Na_2SO_4 and Na_2CO_3 reported in a simulation stream vector is free chemical but only some of the NaOH and Na_2S reported is actual free residual.

$$Na_2SO_{4_{out}} = b_1(Na_2S+Na_2SO_4)_{active\ in}$$

$$Na_2CO_{3_{out}} = b_2(NaOH+Na_2CO_3)_{active\ in}$$

The mass flow of organics in the black liquor is

$$\text{Lignin} = 61.17 \text{ Tons/hr}$$

and then using the equations in section C-3

$$NaOH_{active} = 3400 \text{ lbm } Na_2O/hr$$

$$Na_2S_{active} = 283 \text{ lbm } Na_2O/hr$$

$$b_1 = \frac{1050}{(283+8370)} = 0.121$$

$$b_2 = \frac{312}{(3400+4980)} = 0.037$$

As before, the inlet conditions can be determined experimentally or be taken from the simulation's statement of the inlet conditions.

C-12 Dregs Losses

The dregs losses are proportional to the total flow

$$x_{i_{out}} = ax_{i_{in}}$$

where i=NaOH, Na_2S, Na_2SO_4,Na_2CO_3, and CaO all sodium compounds expressed as Na_2O.

$$\text{Total } Na_2O_{loss} = 40 \text{ lbm/hr}$$

$$\text{Total } Na_2O_{in} = 82800 \text{ lbm/hr}$$

$$a = \frac{40}{82800} = 4.6 \times 10^{-4}$$

All $CaCO_3$ entering with weak wash is lost.

C-13 Causticization Efficiency

The causticization efficiency, η, is not a true efficiency. It is a measure of the degree of conversion of Na_2CO_3 to NaOH is defined as

$$\eta = \frac{NaOH}{NaOH+Na_2CO_3} \times 100$$

all expressed as Na_2O and measured in the product, white liquor. The causticization efficiency is predicted by an equation due to Hughey et al (96) and modified by Carrol (31).

$$= 95 - (0.048TTA^2+0.196TTA+0.638S+1.594A)$$

where $TTA = (NaOH+Na_2S+Na_2CO_3)\text{lbm } Na_2O/ft^3$

$s = Na_2S \text{ lbm } Na_2O/ft^3$

$A = Na_2SO_4 \text{ lbm } Na_2O/ft^3$

in the green liquor entering the slaker. This equation has been satisfactory in two pulp mills;however, tuning would normally involve adjustment of the constant only.

Given the following average operating data:

white liquor composition;

$TTA = 7.0 \text{ lbm } Na_2O/ft^3$

$\text{Active Alkali} = 6.0 \text{ lbm } Na_2O/ft^3 \ (NaOH+Na_2S)$

$Na_2S = 1.5 \text{ lbm } Na_2O/ft^3$

$Na_2SO_4 = 0.3 \text{ lbm } Na_2O/ft^3$

$$\eta = \frac{6.0-1.5}{7.0-1.5} \times 100 = 86.5\%$$

green liquor composition;

$$\text{TTA} = 7.2 \text{ lbm } Na_2O/ft^3$$

$$\text{Active alkali} = 2.5 \text{ lbm } Na_2O/ft^3$$

$$Na_2S = 1.5 \text{ lbm } Na_2O/ft^3$$

$$Na_2SO_4 = 0.3 \text{ lbm } Na_2O/ft^3$$

$$86.5 = \text{const} - (0.048(7.2)^2+0.196(7.2)$$

$$+0.638(1.5)+1.594(0.3))$$

$$\text{const}= 91.9\%$$

The constant is the maximum causticizing efficiency for the specific system flow conditions.

C-14 Slaker Inerts Purge

The slaker rakes reject a fraction of the inert flowing into the slaker.

$$\text{Inert}_{\text{out}} = a \text{ Inert}_{\text{in}}$$

Given

$$\text{Inert}_{\text{in}} = 5.0 \text{ Tons/hr}$$

$$\text{Inert}_{\text{out}} = 500 \text{ lbm/hr}$$

$$a = \frac{0.250}{5} = 0.05$$

C-15 Mud Washing $CaCO_3$ Carryover

The $CaCO_3$ lost to the weak wash is passed to the smelt dissolving tank and then is purged in the dregs washing system. Thus the $CaCO_3$ carryover is an important part of the calcium balance in the system.

$$CaCO_{3_{\text{lost}}} = a \; CaCO_{3_{\text{in}}}$$

$$CaCO_{3_{in}} = 22.3 \text{ Tons/hr from clarifiers}$$

$$CaCO_{3_{out}} = 1.3 \text{ Tons/hr in dregs}$$

$$a = \frac{1.3}{22.3} = 0.058$$

C-16 Lime Kiln Particulate Loss

The particulate loss is a specified fraction of the total solids flowing into the kiln.

$$Total_{loss} = a\ Total_{in}$$

or $$Component_{loss} = a\ Component_{in}$$

where the fraction a is applied to each component, if known, or the total flow of solids.

From Table B-2, p.B.11 the kiln particulate loss is 1.9 lbm/TADP.

Total Mud in = 40.3 Tons/hr

Consistency = 55%

Total solids = 40.3 (0.55) = 22.2 Tons/hr

Total pulp produced = 59.5 TADP/hr (see section C-5)

particulate loss = 59.5 (1.9) = 113 lbm/hr

$$a = \frac{113}{22.2(2000)} = 0.00255$$

The fraction is then applied to each of the chemical components.

C-17 Kiln Sodium Loss by Reaction

The loss of sodium by the reaction

$$2NaOH + CaO + CO_2 = Na_2Ca(CO_3)_2$$

is predicted by a relationship derived from the data of Hughey et al. (96).

$$Na_2O_{lost} = 0.5\ (Na_2O_{in} - 1)\ \text{Total Solids}/100$$

That is above an inlet concentration of 1% as Na_2O one half of the sodium compounds entering react to form the inert $Na_2Ca(CO_3)_2$.

$$\begin{aligned} Na_2O_{in} &= 2\% \\ \text{Total solids} &= 22.2\ \text{Tons/hr} \\ Na_2O_{lost} &= 0.5(2-1)22.2/100 \\ &= 0.111\ \text{Tons/hr} \\ &= 0.143\ \text{Tons NaOH/hr} \end{aligned}$$

The amount of CaO lost and inert formed is determined stoichiometrically from the reaction above.

C-18 Kiln Reaction to Produce CaO

The conversion of $CaCO_3$ to CaO has been modelled as a first order reaction

$$CaCO_3 \longrightarrow CaO + CO_2$$

with an Arrhenius rate constant at temperatures below 2400°F and as a reversible reaction

$$CaCO_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CaO + CO_2$$

at temperature above 2400°F.

The integrated rate equation for the first reaction, $T \leq 2400°F$, is

$$k\theta = \ln\left[\frac{C_{CaCO_{3_o}}}{C_{CaCO_3}}\right] \qquad (C.18.1)$$

where θ is time in hour and

$$k = Ae^{-E/RT} \qquad (C.18.2)$$

The data of Hughey et al. is presented in Table B-8, p. B.16 and is plotted in Figure C-4 for temperatures less than 2400 F. The rate constant, k, is calculated from equation C.18.1 and is plotted semi-logarithmically against, 1/T, in Figure C-5. The fit to the points yields the coefficients of equation C.18.2

$$A = e^{23.81} \text{ 1/hr} \qquad (C.18.3)$$

$$\frac{E}{R} = 54075 \ ^{o}R$$

Now, for $T \geq 2400^{o}F$ the integrated rate expression is

$$(k_1+k_2) = \ln\left[\frac{C_{CaCO_{3o}} - C_{CaCO_{3e}}}{C_{CaCO_3} - C_{CaCO_{3e}}}\right] \qquad (C.16.4)$$

Again from Table B-8, taking the data for $T=3012^{o}F$ and assume that the point after 2 hours is the equilibrium value

$$C_{CaCO_{3o}} = 1$$

$$C_{CaCO_{3e}} = 0.175$$

$$C_{CaCO_3} = 0.183$$

at T=2520°F, $k_1+k_2=\ln\dfrac{1-0.175}{0.183-0.175} = 4.64$

and at T=2400°F, $k_1+k_2= \ln\dfrac{1-0.065}{0.131-0.065} = 2.651$

At T=2400°F k_2 is very small and is set to

$$k_2 = 0.1$$

$$k_1 = 2.551$$

and from Figure C-4

$$\text{at } T = 2280^\circ F$$

$$k_1 = 1$$

Solving equation C.18.2 for k_1 at 2280°F and 2400°F

$$A_1 = e^{4.356} \text{ 1/hr}$$

$$\frac{E_1}{R} = 19640 \quad {}^\circ R \tag{C.18.5}$$

Now from C.18.5

$$k = 2.924 \quad \text{when } T=2520^\circ F$$

$$k_2 = 1.71 \quad \text{when } T=2520^\circ F$$

and as previously stated

$$k_2 = 0.1 \quad \text{when } T=2400^\circ F$$

Again, solving equation C.18.2 for k_2

$$A_2 = e^{53.97}$$

$$\frac{E_2}{R} = 319600 \; \frac{1}{{}^{o}R}$$

Now, as for the Vroom H-factor define a value, Q, which is the relative reaction rate for the calcining reaction

$$T \leq 2400^{o}F \qquad Q = \int e^{(A-E/RT)}dt \qquad (C.18.7)$$

$$T > 2400^{o}F \qquad Q = \int e^{(A_1-E_1/RT)} - e^{(A_2-E_2/RT)} \; dt$$

The molar conversion of $CaCO_3$ to CaO is then predicted by the equation

$$\text{conv} = 1 - \frac{aTA^{n}}{\log Q} \qquad (C.18.8)$$

$TA > 1, \; n=n$

$TA \leq 1, \; n=0$

where TA is the percent total alkali in dry mud entering the kiln.

For the experimental kiln data shown in Table B-6, p.B.14 the kiln temperature profiles for the five conditions were estimated from the end temperatures by assuming a characteristic profile (97) and are plotted in Figure C-6. The kiln residence time was measured as 2 hrs. The Q-factors were calculated and using the percent conversion and TA for each condition in Table B-6 the value (1-conv) log Q is plotted semi-logarithmically against TA in Figure C-7. The fit yields the relationship

$$\text{conv} = 1-0.08923\ (\text{TA})^{0.1325}/\log Q \qquad \text{(C.18.9)}$$

The lime availability is then

$$\text{Availability} = \frac{\text{Conv}(\text{CaCO}_3)_{\text{in}}\text{MW}_{\text{CaO}}+\text{CaO}_{\text{in}}}{\text{Total flow out}} \qquad \text{(C.18.10)}$$

C-19 Blow Heat Recovery Efficiency

It has been postulated that some of the sulphur from the digester gases that are burned in the kilns form $CaSO_4$ and subsequently reacts to form Na_2SO_4 in the slakers when the lime is added to the green liquor

$$CaSO_4 + Na_2CO_3 \qquad Na_2SO_4 + CaCO_3$$

Analysis of lime and mud from the kilns gave very indeterminate results; however, a material balance about the slaking and causticizing system allows an estimate of the sulphur recovery efficiency. Values denoted by an asterisk are measurements.

Flow of liquor through slakers

$$Q = 5880\ \text{ft}^3/\text{hr}^*$$

$$Na_2SO_4 = 3.9^*\ \text{gm}/\ = 0.24\ \text{lbm/ft}^3$$

$$Na_2SO_4 = 6.35^*\text{gm}/\ = 0.40\ \text{lbm/ft}^3$$

$$\begin{aligned} Na_2SO_4 &= 5880(0.4-0.24) \\ &= 899\ \text{lbm/hr} \\ &= 203\ \text{lbm sulfur/hr} \end{aligned}$$

Flow of sulphurous gas to kilns, NCG

NCG = 303* lbm sulfur/hr

$$\% \text{ S Recovery} = \frac{203}{303} \times 100 = 67\%$$

Table C-1 Washer Loss Experiment

		1	2	3
W_{pulp}	(Tons/hr)	39.3	46.1	48.4
W_{TOT}	(Tons/hr)	120.0	127.5	142.5
Loss	$\frac{\text{lbmNa}_2\text{O}}{\text{TADP}}$	14.9	17.3	16.2

FIGURE C-1:

PINE YIELD VS. KAPPA CORRELATION

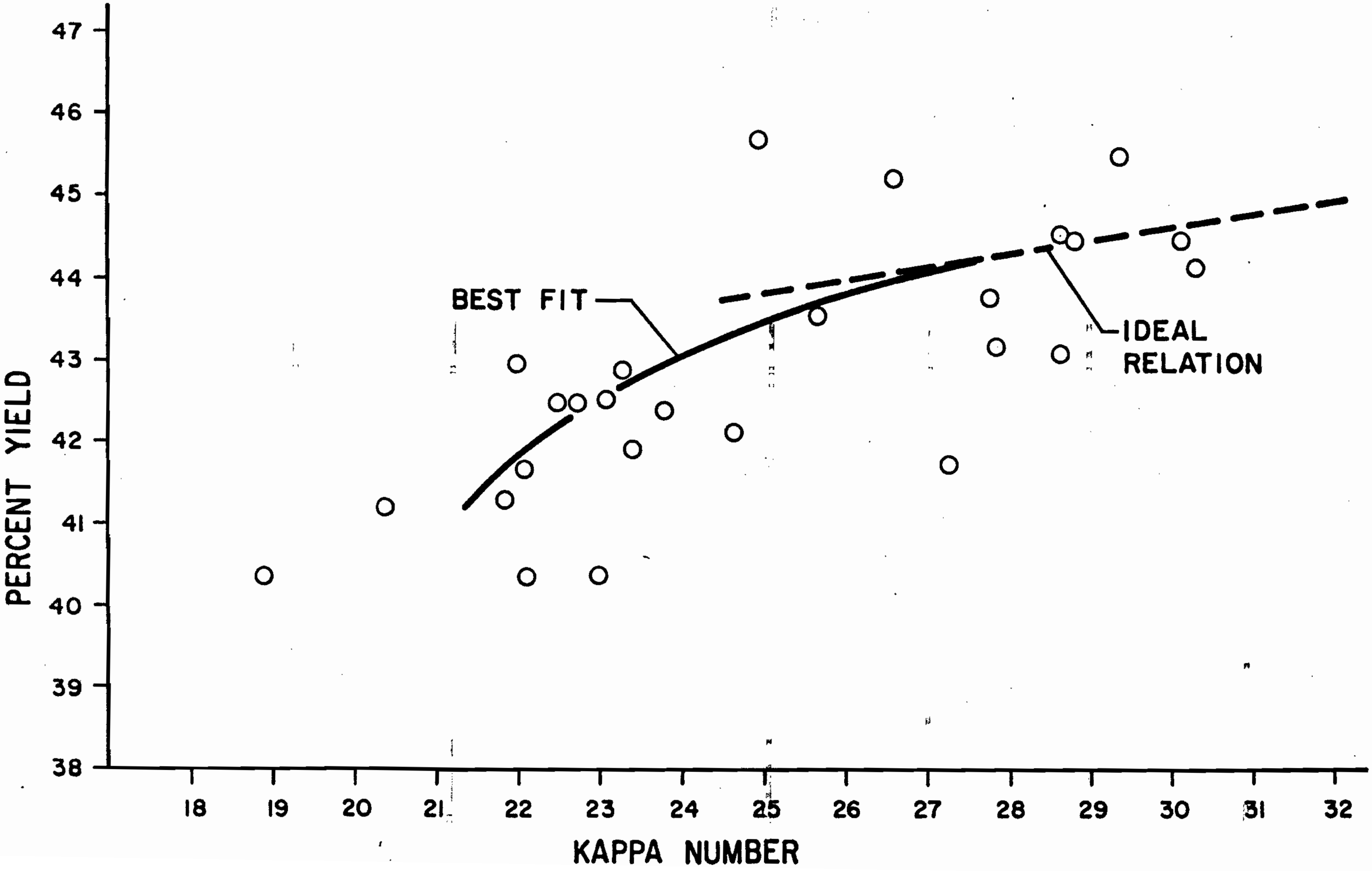


FIGURE C-2:

BROWN STOCK WASHER LOSS RELATIONSHIP

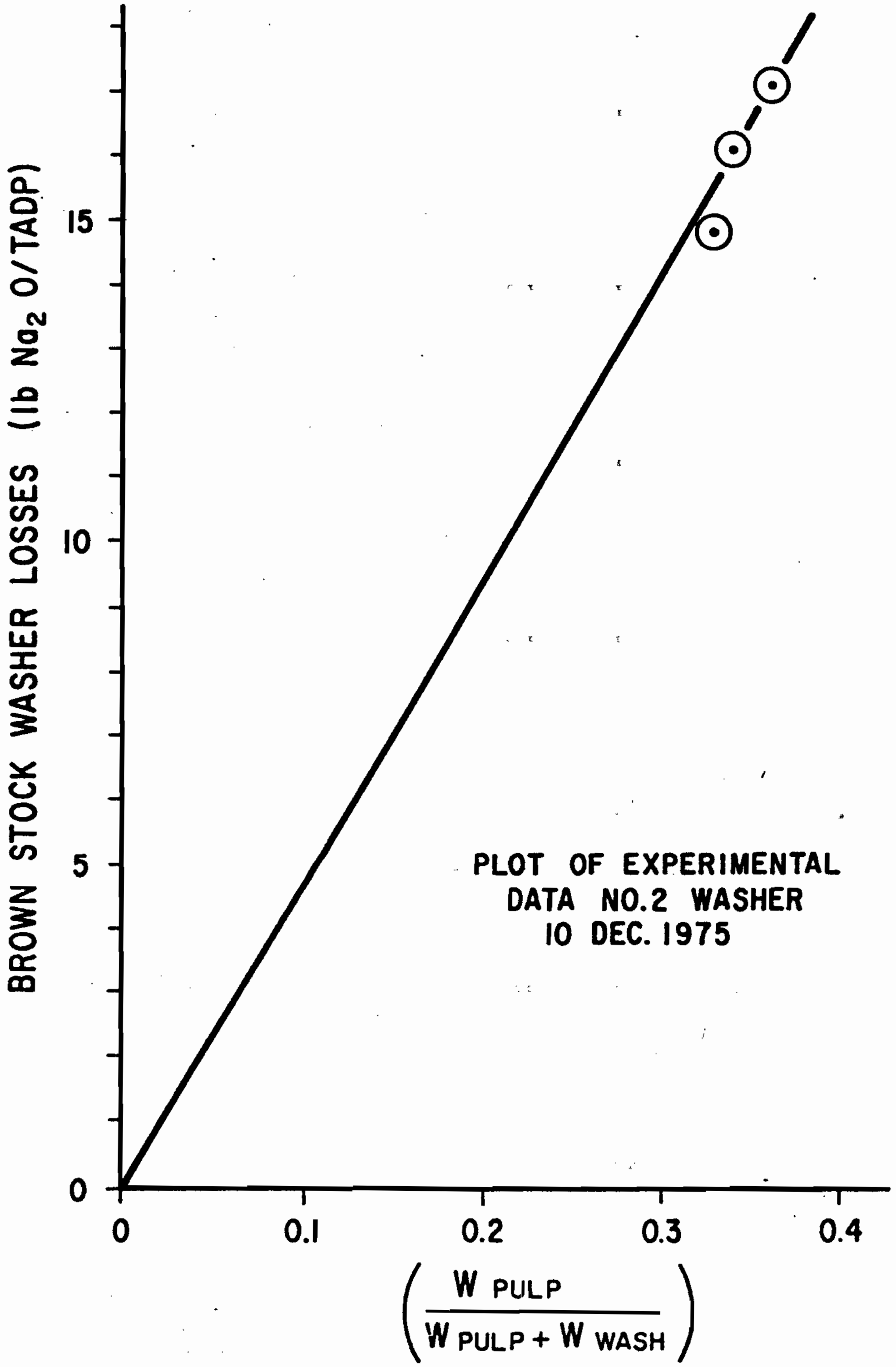


FIGURE C-3:

REDUCTION EFFICIENCY VS. PRIMARY OXYGEN DEFICIENCY AND TEMP (57)

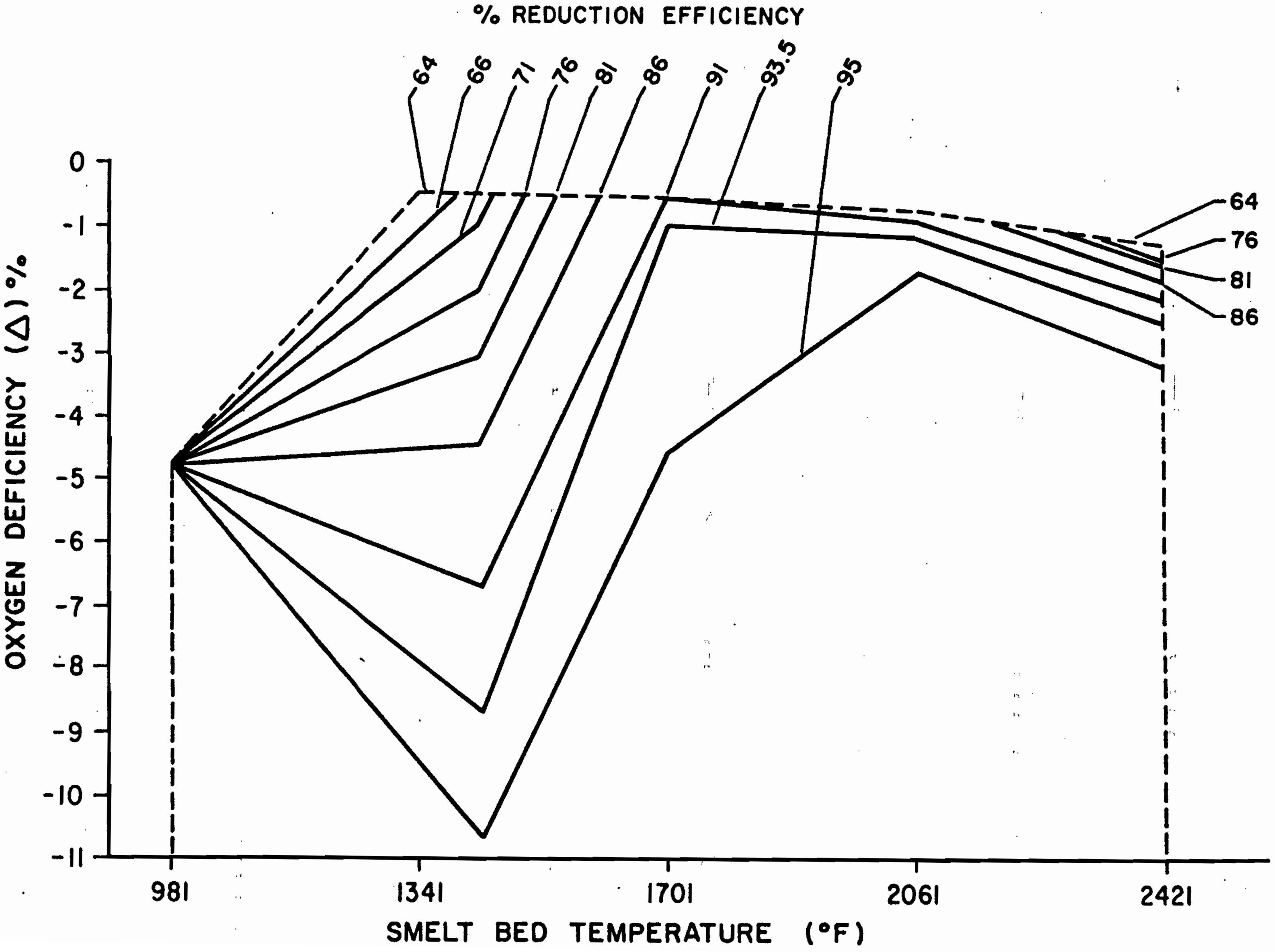


FIGURE C-4:

CONVERSION OF $CaCO_3$ TO CaO

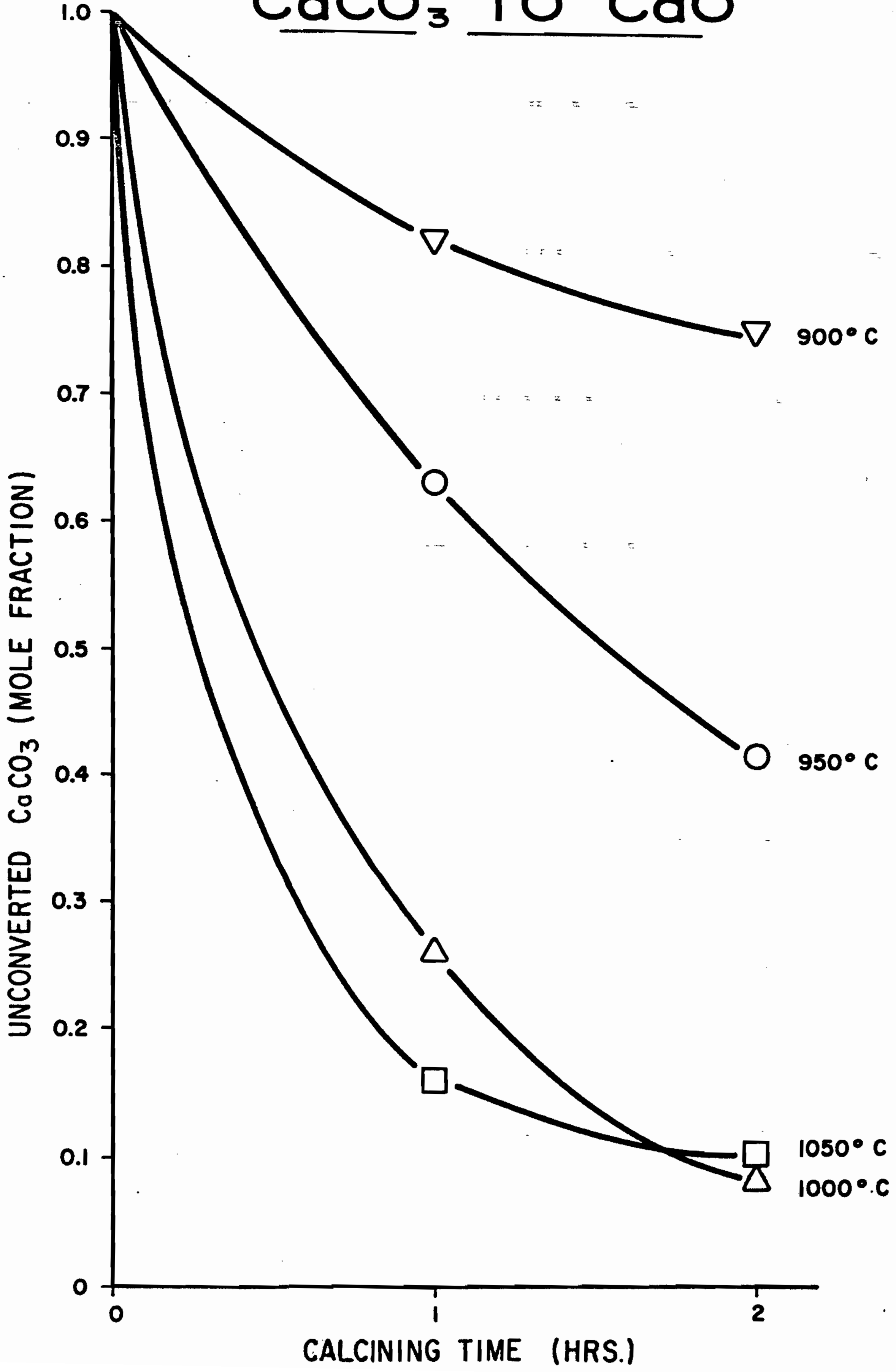


FIGURE C-5:

DETERMINATION OF ARRHENIUS COEFFICIENTS

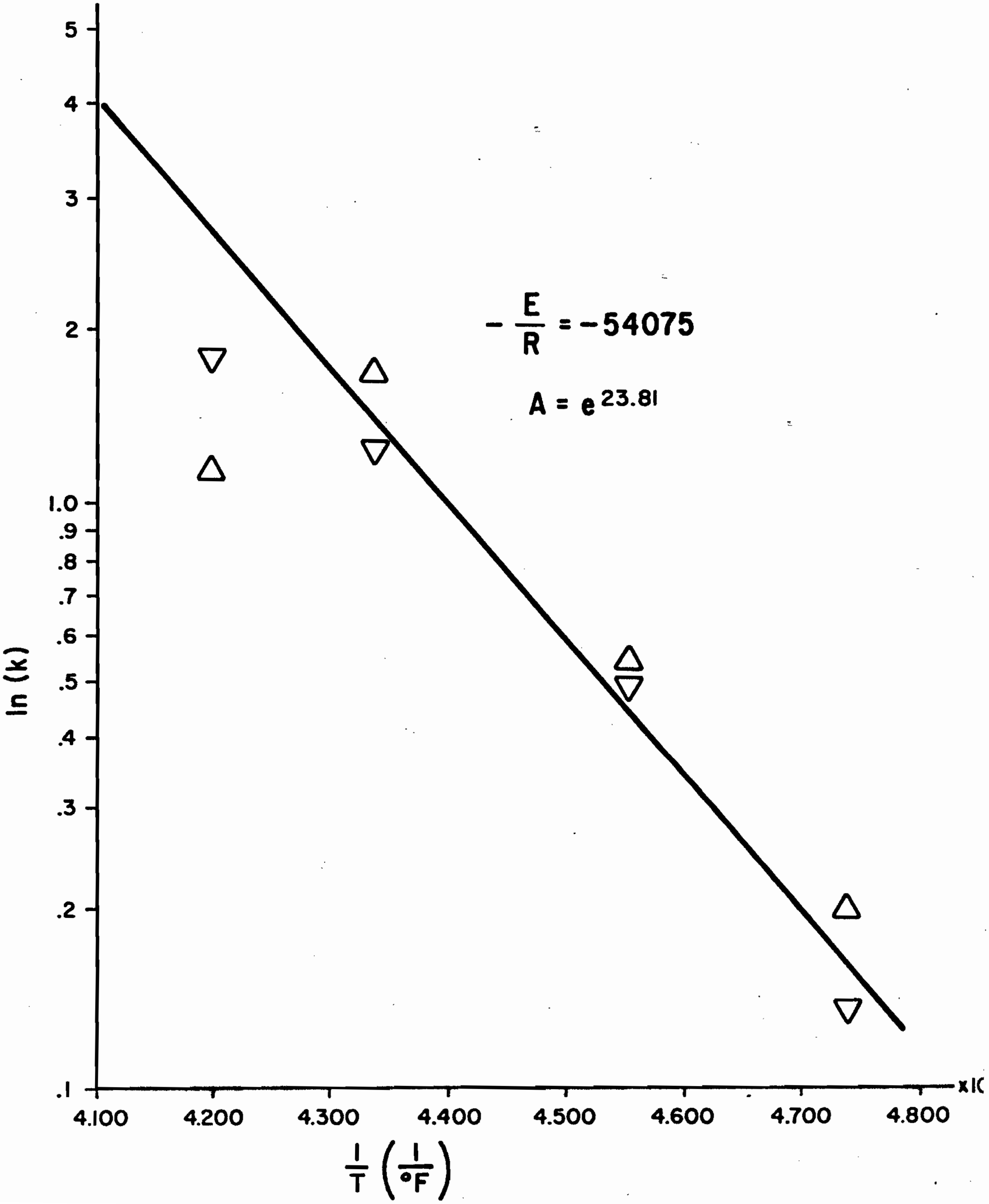


FIGURE C-6:

TEMPERATURE PROFILES FOR Q-FACTOR DETERMINATION

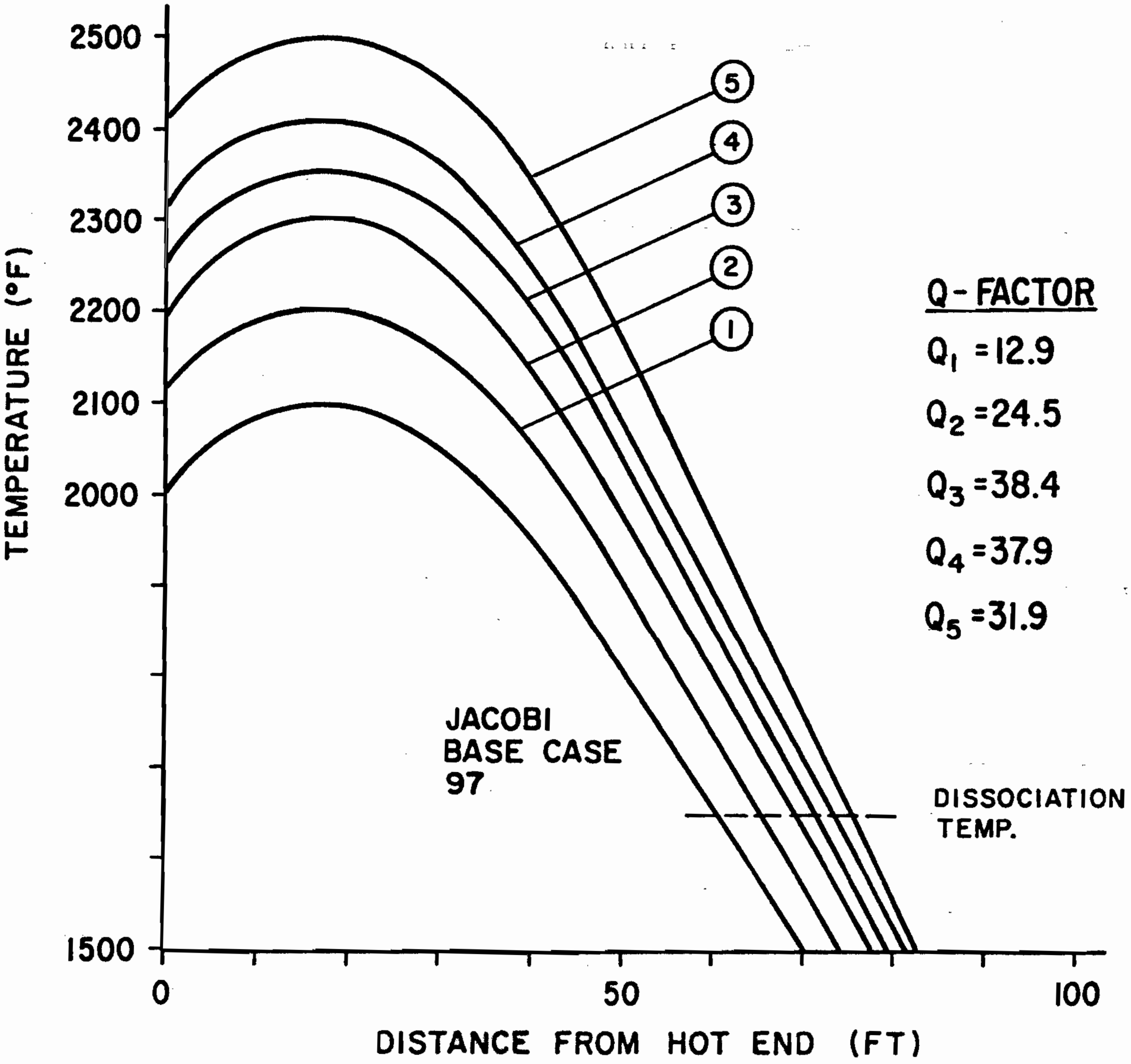
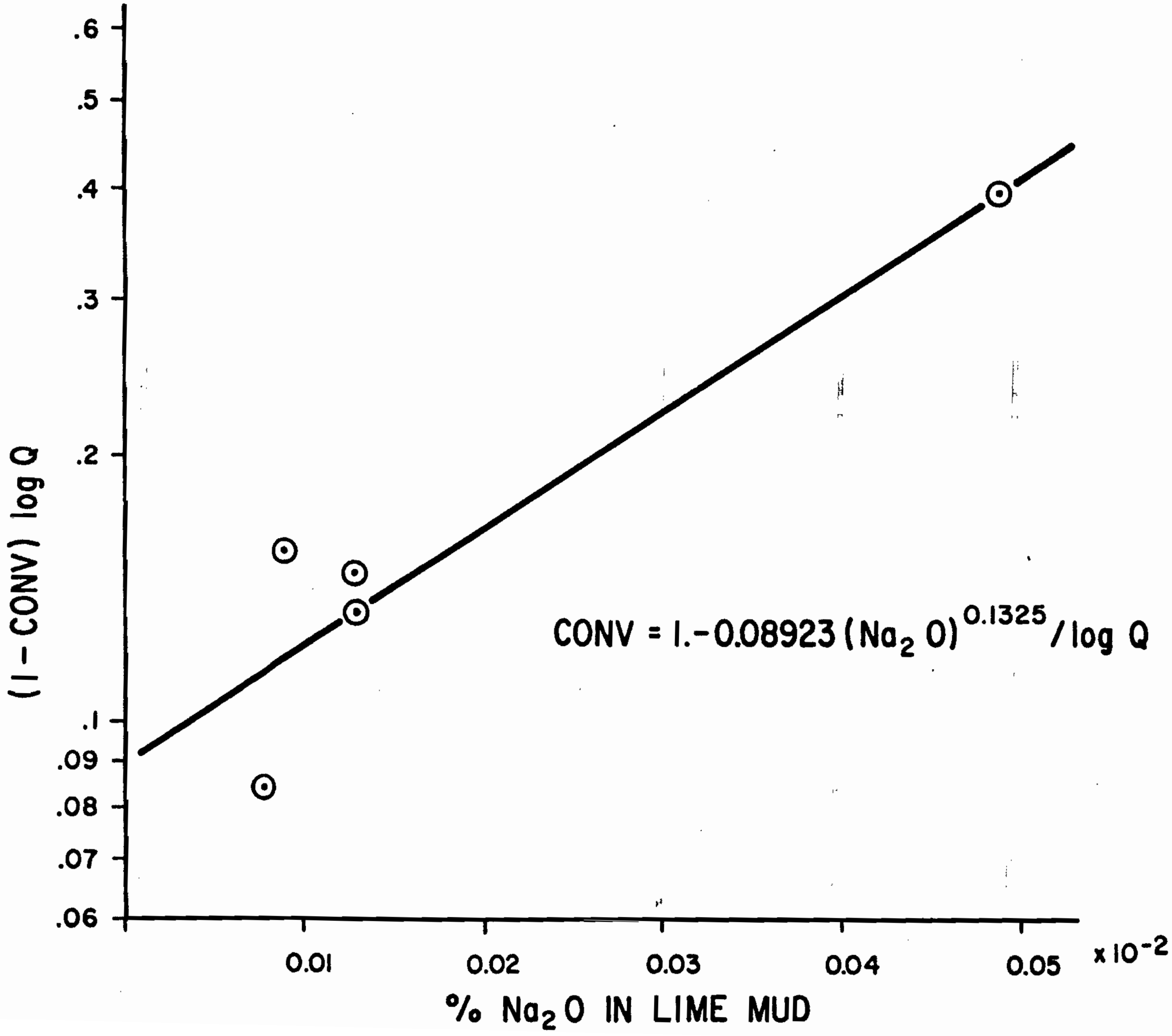


FIGURE C-7:

CALCINING CORRELATION



$$CONV = 1.-0.08923\,(Na_2O)^{0.1325}/\log Q$$

Appendix D

Dynamic Model Listing

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C               DYNAMIC MODEL OF KRAFT MILL


C               DYNAMIC MODEL OF KRAFT MILL
C
C
C *******************************************************************
C
C               INITIALIZE VARIBLES AND READ DATA FOR PROBLEM
C
C *******************************************************************
C
C               THREE HOLDING AREAS: 1)WHITE STORAGE
C                                    2)BLACK LIQUOR STORAGE
C                                    3)BLO SYSTEM (INCL. 45% TANKS)
C                       * ALL LIQUOR STORED PRESUMED STRONG, THUS WEAK
C                         BLACK LIQUOR VOLUME INCLUDED IN BLACK LIQUOR
C                         AS STRONG LIQUOR VOLUMETRICALLY.
C
      COMMON/BLK1/H,LP
      COMMON LR
      COMMON DEBUG,DAYS,CNTRL,PRNTYP,TIM,KPRNT,AAC,RD,EC,CAUSMX,XK2,XK
      COMMON XMNAMX,TARG,P,VSET,XKP,CONTIM,Q1,Q2,Q3,Q4,Q5,XNASO4,XNAOH
      COMMON XMS,XMNA,UMAKE,NMAKE,FLOLIQ,NFLOW,FLOS1,NLOS1,FLOS2,NLOS2
      COMMON DVOL,NVOL,T,NCNTRL,IPRNT,NO,ITIM,I,A1,A2,B1,B2,C1,C2,D1,D
      COMMON PRNT,XLS,XLNA,NCONTI,FLS,FLNA,VTEST
      DIMENSION CS(5),CNA(5),A(20),B(20),DV(3),V(3),XV(3)
      DIMENSION TIME1(100),TIME2(100),TIME3(100),TIME4(100),TIME5(100)
      DIMENSION SALT(100),CAUST(100),,FLOW(100,4),VOL(100,4)
      DIMENSION COEF(100,4),COEF2(100,4),CSS(3,5),CNAS(3,5)
      DIMENSION U(500),X(500),Y(500),Z(500),W(500)
      EQUIVALENCE (U(1),TIME1(1)),(U(101),SALT(1)),(U(201),CAUST(1))
      EQUIVALENCE (X(1),TIME2(1)),(X(101),FLOW(1)),(Y(1),TIME3(1))
      EQUIVALENCE (Y(101),COEF(1)),(Z(1),TIME4(1)),(Z(101),COEF2(1))
      EQUIVALENCE(W(1),TIME5(1)),(W(101),VOL(1))
      EQUIVALENCE(V(1),VTEST)
      LR=5
      LP=6
      DO 1 I=1,500
      U(I)=0.
      X(I)=0.
      Y(I)=0.
      Z(I)=0.
      W(I)=0.
    1 CONTINUE
C             READ TITLE CARDS (FIRST TWO IN DATA DECK, LEAVE BLANK IF
C                                  NO SECOND CARD DESIRED.)
 5000 READ(LR,2000)(A(I),I=1,20),(B(I),I=1,20)
      IF(A(1).EQ.A(2)) GO TO 5001
C             PRINT CONTROL FOR DEBUGGING DATA SET
C             SET TO ONE OF PRINTOUT OF INPUT DESIRED
      READ(LR,2001) DEBUG
C             DAYS OF STUDY, TIME (HRS) WHEN OPTIMAL STRATEGY TO BE CA
```

```
C           DYNAMIC MODEL OF KRAFT MILL

      READ(LR,2001) DAYS,CNTRL
      IF(DEBUG.EQ.1.) WRITE(LP,4001) DAYS,CNTRL
C            FORMAT, PRINT INTERVAL (HRS.), MAKE-UP CHANGE INTERVAL (H
      READ(LR,2001) PRNTYP,PRNT,TIM
      IF(DEBUG.EQ.1.) WRITE(LP,4001) PRNTYP,PRNT,TIM
      KPRNT=PRNTYP+.001
C            SET PHYSICAL PARAMETERS
      READ(LR,2001) AAC,RD,EC,CAUSMX,XK2,XK3
      IF(DEBUG.EQ.1.) WRITE(LP,4001) AAC,RD,EC,CAUSMX,XK2,XK3
      XMNAMX=CAUSMX*382./1.29
C            SET INTEGRATION STEP SIZE & TARGET SULFIDITY
      READ(LR,2001) H,TARG
C            COMPUTED TO MAINTAIN INVENTORY LEVELS, IF THIS IS
C            SATISFACTORY SET P TO ONE: VSET IS THE TARGET INVENTORY
C            XKP IS PROPORTIONAL GAIN FOR CONTROL
C            CONTIM IS TIME UP TO WHICH XKP IS APPLICABLE
      READ(LR,2001) P,VSET,XKP,CONTIM
      IF(DEBUG.EQ.1.) WRITE(LP,4001) H,TARG,P,VSET,XKP,CONTIM
C            INITIALIZE STREAM CONCENTRATIONS
      READ(LR,2001) (CS(I),CNA(I),I=1,5)
      IF(DEBUG.EQ.1.) WRITE(LP,4001) (CS(I),CNA(I),I=1,5)
C            INITIALIZE ALL FLOW RATES
      READ(LR,2001) Q1,Q2,Q3,Q4,Q5
      IF(DEBUG.EQ.1.) WRITE(LP,4001) Q1,Q2,Q3,Q4,Q5
C            INITIALIZE INVENTORYS
      READ(LR,2001) (V(I),I=1,3)
      IF(DEBUG.EQ.1.) WRITE(LP,4001)(V(I),I=1,3)
C            INITIALIZE MAKE-UPS AS LB/HR & USGPM RESPECTIVELY
      READ(LR,2001) XNASO4,XNAOH
      IF(DEBUG.EQ.1.) WRITE(LP,4001) XNASO4,XNAOH
      XMS=XNASO4/2.29
      XMNA=XNAOH*382./1.29
C            NUMBER OF HISTORICAL CHANGES IN MAKE-UP
C            * SET TO ZERO IF STRATEGY WILL BE COMPUTED BY MODEL
C              WITH NO HISTORICAL ENTRYS
      READ(LR,2001) UMAKE
      IF(DEBUG.EQ.1.) WRITE(LP,4001) UMAKE
      IF(UMAKE) 50,50,49
   49 NMAKE=UMAKE+.001
C            TIME HISTORY OF MAKE-UP CHANGES
C            TIME1(J) IS TIME (HR) UP TO BUT NOT INCLUDING WHICH
C            THE STRATEGY WAS APPLICABLE
      DO 200 J=1,NMAKE
      READ(LR,2001) TIME1(J),SALT(J),CAUST(J)
      IF(DEBUG.EQ.1.) WRITE(LP,4001) TIME1(J),SALT(J),CAUST(J)
  200 CONTINUE
C            TIME HISTORY OF STREAM FLOWS
C            TIME2(J) IS TIME (HRS) UP TO WHICH ( NOT INCL.) THE
C            STRATEGY WAS APPLICABLE
C
```

```
C             DYNAMIC MODEL OF KRAFT MILL

C        N.B. Q1, THE FLOW OF FRESH WHITE LIQUOR FROM THE CAUSTICIZERS
C             IS ALWAYS COMPUTED BY THE MODEL UNDER AUTOMATIC DENSITY
C             CONTROL
C
C             IF NO FLOW RATE CHANGES ARE MADE THE SINGLE ENTRY NECESAR
C             ARE THE FLOWS AT TIME=DAYS*24.+1
   50 READ(LR,2001) FLOLIQ
      IF(DEBUG.EQ.1.) WRITE(LP,4001) FLOLIQ
      NFLOW=FLOLIQ+.001
      READ(LR,2001) (TIME2(J),(FLOW(J,I),I=1,4),J=1,NFLOW)
      IF(DEBUG-1.) 210,250,210
  250 WRITE(LP,4001)(TIME2(J),(FLOW(J,I),I=1,4),J=1,NFLOW)
C             TIME HISTORY OF LOSS COEFFICIENTS @ RECOVERY FURNACES,
C             D,C. EVAP, W.L. PREPARATION LOOP
  210 READ(LR,2001) FLOS1
      IF(DEBUG.EQ.1.) WRITE(LP,4001) FLOS1
      NLOS1=FLOS1+.001
      READ(LR,2001) (TIME3(J),(COEF(J,I),I=1,4),J=1,NLOS1)
      IF(DEBUG.EQ.1.) WRITE(LP,4001)(TIME3(J),(COEF(J,I),I=1,4),J=1,
     1NLOS1)
C             TIME HISTORY OF LOSS COEFFICIENTS @ DIGESTERS, BROWN
C             STOCK WASHERS, EVAPORATORS.
      READ(LR,2001) FLOS2
      IF(DEBUG.EQ.1.) WRITE(LP,4001) FLOS2
      NLOS2=FLOS2+.001
      READ(LR,2001) (TIME4(J),(COEF2(J,I),I=1,4),J=1,NLOS2)
      IF(DEBUG.EQ.1.) WRITE(LP,4001)(TIME4(J),(COEF2(J,I),I=1,4),
     1J=1,NLOS2)
C             TIME HISTORY OF INVENTORY CHANGES
C               THIS TABLE IS USED WHEN VOLUMES OF LIQUOR ARE TAKEN
C               OF LINE ( I.E. BLO OUTAGE) REMOVING THAT INVENTORY
C               FROM THE SYSTEM FOR A TIME
C
C*********** ONLY ONE INVENTORY CHANGE MAY OCCUR AT A TIME   ********
C
C             IF NO SUCH CHANGES HAVE OCCURRED,DVOL, IS SET TO ZERO.
C
C             IF SUCH A CHANGE HAS  OCCURED, VOL(2-4,J) CONTAINS
C             THE INVENTORY CHANGE (NEG. IF LOSS & POS. IF GAIN)
C             IN THE APPROPRIATE STORAGE AREA( I=2 IF WHITE LIQUOR, V(
C                                              I=3 IF BLACK LIQUOR V(2
C                                              I=4 IF BLO V(3)
C
C             VOL(1,J) CONTAINS THE STREAM NUMBER (1,...5) OF THE STRE
C             LEAVING THE UNIT WHERE THE INVENTORY CHANGE OCCURS
C             * VOL(1,J) IS NEG. FOR INVENTORY LOSS
C             * VOL(1,J) IS POS. FOR INVENTORY GAIN
C
C             THE COMPOSITION OF THE LIQUOR INVOLVED IN THE TEMPORARY
C             INVENTORY LOSS WILL BE STORED IN CSS & CNAS FOR LATER
```

```
C              DYNAMIC MODEL OF KRAFT MILL

C              ADDITION WHEN THAT INVENTORY COMES BACK INTO SERVICE
C
      READ(LR, 2001) DVOL
      IF(DEBUG. EQ. 1. ) WRITE(LP, 4001) DVOL
      IF(DVOL) 60, 60, 59
   59 NVOL=DVOL+. 001
      READ(LR, 2001)(TIME5(J), (VOL(J, I), I=1, 4), J=1, NVOL)
      IF(DEBUG. EQ. 1. ) WRITE(LP, 4001)(TIME5(J), (VOL(J, I), I=1, 4), J=1, NV
   60 CALL DYN(TIME1, TIME2, TIME3, TIME4, TIME5, SALT, CAUST,
     1FLOW, VOL, CS, CNA, A, B, DV, V, XV, COEF, COEF2, CSS, CNAS, U, X, Y, Z, W)
      GO TO 5000
 5001 STOP
 2001 FORMAT(5F12. 0)
 2000 FORMAT(20A4)
 4001 FORMAT(1X, 5(2X, E12. 6))
      END
      SUBROUTINE DYN(TIME1, TIME2, TIME3, TIME4, TIME5, SALT, CAUST,
     1FLOW, VOL, CS, CNA, A, B, DV, V, XV, COEF, COEF2, CSS, CNAS, U, X, Y, Z, W)
C
C *********************************************************************
C
C              SOLVE THE PROBLEM AND PRINT THE RESULTS STEP BY STEP
C
C *********************************************************************
C
      COMMON/BLK1/H, LP
      COMMON LR
      COMMON DEBUG, DAYS, CNTRL, PRNTYP, TIM, KPRNT, AAC, RD, EC, CAUSMX, XK2, X
      COMMON XMNAMX, TARG, P, VSET, XKP, CONTIM, Q1, Q2, Q3, Q4, Q5, XNASO4, XNAO
      COMMON XMS, XMNA, UMAKE, NMAKE, FLOLIQ, NFLOW, FLOS1, NLOS1, FLOS2, NLOS
      COMMON DVOL, NVOL, T, NCNTRL, IPRNT, NO, ITIM, I, A1, A2, B1, B2, C1, C2, D1,
      COMMON PRNT, XLS, XLNA, NCONTI, FLS, FLNA, VTEST
      DIMENSION TIME1(100), TIME2(100), TIME3(100), TIME4(100), TIME5(100
      DIMENSION SALT(100), CAUST(100), FLOW(100, 4), VOL(100, 4)
      DIMENSION CS(5), CNA(5), A(20), B(20), DV(3), V(3), XV(3)
      DIMENSION COEF(100, 4), COEF2(100, 4), CSS(3, 5), CNAS(3, 5)
      DIMENSION U(500), X(500), Y(500), Z(500), W(500)
      DUM=0.
      DO 45 I=1, 3
      DO 45 J=1, 5
      CSS(I, J)=0.
      CNAS(I, J)=0.
   45 CONTINUE
   60 T=-H
C              RECALCULATE CONTROL PARAMETERS IN TERMS OF ITERATION STE
      NCNTRL=(CNTRL+. 00001)/H
      IPRNT=(PRNT+. 00001)/H
      NO=DAYS*(24. +. 0001)/H
      ITIM=(TIM+. 00001)/H
      WRITE(LP, 100)
```

```
      WRITE(LP,2000) (A(I),I=1,20)
      WRITE(LP,2000) (B(I),I=1,20)
      DO 1000 II=1,NO
      I=II-1
      T=T+H
C              FIND CURRENT FLOW RATES
      CALL TABLE(Q2,Q3,Q4,Q5,I,NFLOW,X)
      IF(DEBUG.EQ.1) WRITE(LP,4001) Q2,Q3,Q4,Q5
C              FIND CURRENT LOSS PARAMETERS
      CALL TABLE(A1,A2,B1,B2,I,NLOS1,Y)
      IF(DEBUG.EQ.1) WRITE(LP,4001) A1,A2,B1,B2
      CALL TABLE(C1,C2,D1,D2,I,NLOS2,Z)
      IF(DEBUG.EQ.1) WRITE(LP,4001) C1,C2,D1,D2
C              PROPORTIONAL LOSSES AT DIG. WASHERS,EVAPS
C                   SULFUR BEARING CHEMICAL LOSS FACTOR
      XLS=C1*CS(2)+C2
C              NON-SULFUR BEARING CHEMICAL LOSS FACTOR
      XLNA=D1*CNA(2)+D2
C              IS THE STRATEGY TO BE OPTIMAL OR HISTORICAL ?
    7 IF(I.GE.NCNTRL) GO TO 8
C              SET CHEMICAL MAKE-UP
      CALL TABLE(XNASO4,XNAOH,DUM,DUM,I,NMAKE,U)
      IF(DEBUG.EQ.1.) WRITE(LP,4001) XNASO4,XNAOH
      XMS=XNASO4/2.29
      XMNA=XNAOH*382./1.29
C              CALCULATE PROPORTIONAL LOSS PARAMETERS AT FURNACES ETC.
C                   SULFUR BEARING CHEMICAL LOSS FACTOR
      FLS=A1*(CS(5)+XMS/Q5)+A2
C              NON SULFUR BEARING CHEMICAL LOSS FACTOR
      FLNA=B1*CNA(5)+B2
      GO TO 9
C              IS IT TIME TO MAKE A MAKE-UP CHANGE ?
C              CALCULATE OPTIMAL MAKE-UP STRATEGY
    8 IF(MOD(I,ITIM)) 9,11,9
   11 NCONTI=(CONTIM+.0001)/H
C              IS INVENTORY TO BE CHANGED?
      IF(I.GE.NCONTI) P=1.
      CALL SODA(XMS,XMNA,CS(5),CNA(5),Q5,FLS,FLNA,TARG,AAC,Q2,XMNAMX,F
     1EC,CS(1),CNA(1),CS(2),CNA(2),VSET,VTEST,A1,A2,B1,B2,I,P,XKP)
      XNASO4=XMS*2.29
      XNAOH=XMNA*1.29/382.
C              FRESH WHITE LIQUOR FLOW RATE
    9 Q1=(EC*(CNA(5)*Q5*(1.+FLNA))+RD*(CS(5)*Q5+XMS)*(1.+FLS))/AAC
C              FRESH WHITE LIQUOR COMPOSITION
C              SULFUR BEARING CHEMICAL
      CS(1)=(CS(5)*Q5+XMS)*(1.+FLS)/Q1
C              NON-SULFUR BEARING CHEMICAL
      CNA(1)=CNA(5)*Q5*(1.+FLNA)/Q1
C              POTENTIAL SULFIDITY OF B.L. TO FURNACES
      BBLS=RD*CS(5)/(EC*CNA(5)+RD*CS(5))*100.
```

```
C               DYNAMIC MODEL OF KRAFT MILL


C               POTENTIAL SULFIDITY OF B.L.  TO B.L.O.  SYSTEM
      BLS=RD*CS(4)/(EC*CNA(4)+RD*CS(4))*100.
C               SULFIDITY OF FRESH WHITE LIQUOR ( CAN BE CONSIDERED
C                                                UNCLARIFIED GREEN LIQUOR)
      GLS=RD*CS(1)/(EC*CNA(1)+RD*CS(1))*100.
C               SULFIDITY OF W.L.  FROM STORAGE TO DIGESTERS
      WLS=RD*CS(2)/(EC*CNA(2)+CS(2)*RD)*100.
C               HAS THERE BEEN AND INVENTORY OUTAGE AT ANY TIME ?
      IF(NVOL) 14,14,20
C               CHECK HISTORY OF INVENTORY OUTAGES
   20 CALL TABLE2(DV,STREAM,I,NVOL,NPOINT,NJ,W)
      IF(DEBUG.EQ.1.) WRITE(LP,4001) (DV(K),K=1,3)
      IF(NPOINT.EQ.0) GO TO 14
      NS=ABS(STREAM)+.001
      NTIM=TIME5(NPOINT)/H+.001
      IF(I-NTIM) 14,10,14
   10 IF(STREAM) 12,14,13
C               IF AN INVENTORY OUTAGE HAS OCCURRED STORE COMPOSITIONS
   12 CSS(NJ,NS)=CS(NS)
      CNAS(NJ,NS)=CNA(NS)
C               MODIFY INVENTORY
      V(NJ)=V(NJ)+DV(NJ)
      GO TO 14
C               IF A PAST OUTAGE HAS COME ON LINE AVERAGE THE COMPOSITION
C               OF THE ON-LINE AND OFF-LINE STREAMS
   13 CS(NS)=(CSS(NJ,NS)*ABS(DV(NJ))+CS(NS)*V(NJ))/(V(NJ)+DV(NJ))
      CNA(NS)=(CNAS(NJ,NS)*ABS(DV(NJ))+CNA(NS)*V(NJ))/(V(NJ)+DV(NJ))
C               MODIFY INVENTORY
      V(NJ)=V(NJ)+DV(NJ)
   14 IF(MOD(I,IPRNT)) 5,1,5
    1 IF(KPRNT-2) 2,3,4
    2 WRITE(LP,102) XNASO4,XNAOH
      WRITE(LP,101)T,(CS(IP),CNA(IP),IP=1,5),GLS,V(1),WLS,V(2),BLS,V(3
     1BBLS,Q1,Q2,Q3,Q4,Q5
      GO TO 5
    3 IF(I.EQ.0) WRITE(LP,3003)
      WRITE(LP,3001) T,CS(2),CNA(2),CS(4),CNA(4),V(1),V(2),V(3),XNASO4
     1XNAOH,GLS,WLS,BLS
      GO TO 5
    4 IF(I.EQ.0) WRITE(LP,3004)
      WRITE(LP,3002) T,Q1,Q2,Q3,Q4,Q5,V(1),V(2),V(3),XNASO4,XNAOH
     1,GLS,WLS,BLS
C ***********************************************************************
C
C               SOLVING DIFFERENTIAL EQUATIONS
C
C               INTEGRATE INVENTORY CHANGE
    5 XV(1)=V(1)+H*(Q1-Q2)
      XV(2)=V(2)+H*(Q2/XK2-Q4)
      XV(3)=V(3)+H*(Q4-Q5)
```

```
C             DYNAMIC MODEL OF KRAFT MILL

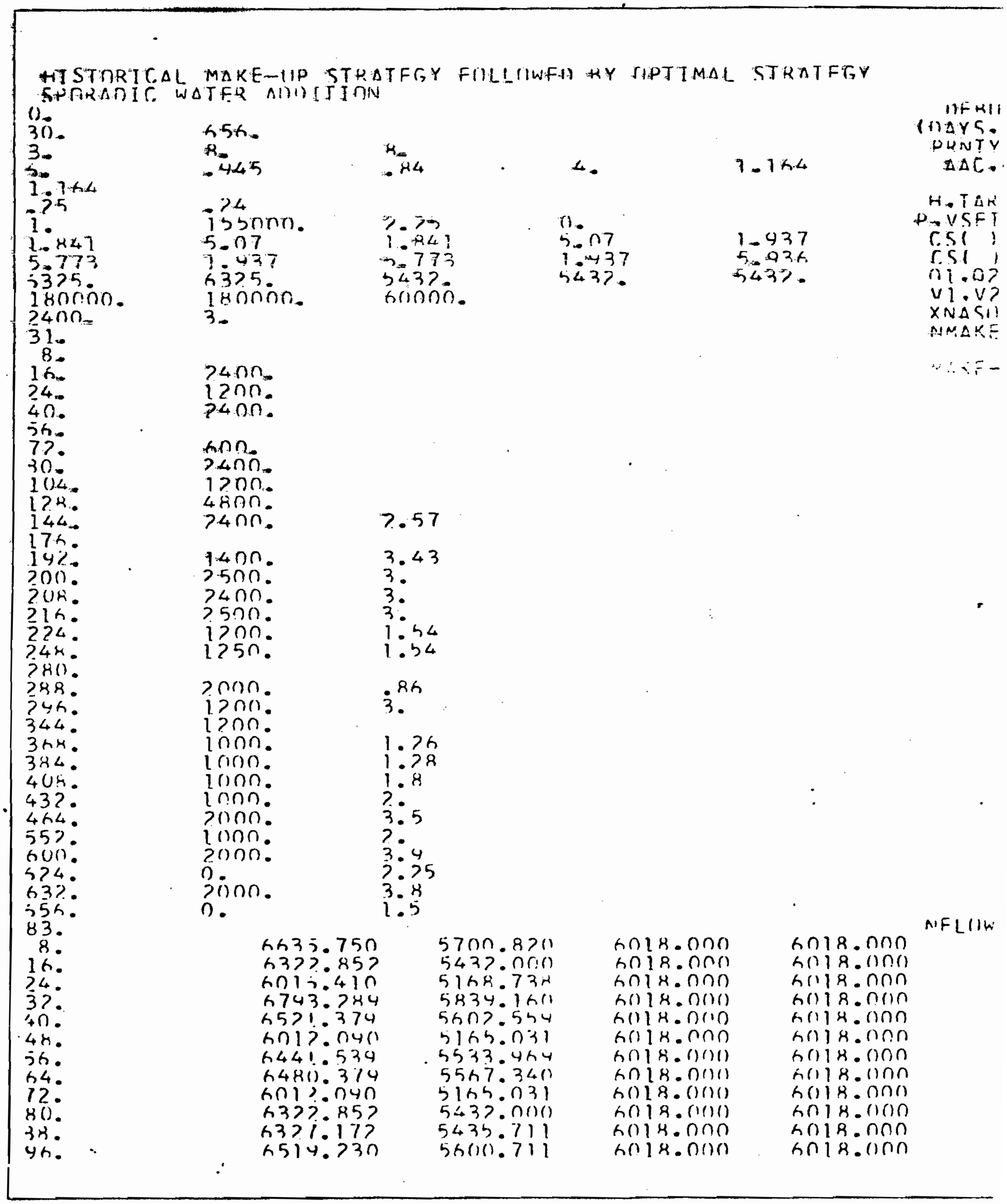
C             BLACK LIQUOR TO B.L.O.
      XC4S=CS(4)+H*Q2/XK2*(CS(2)*XK2*(1.+XLS)-CS(4))/V(2)
      XC4NA=CNA(4)+H*Q2/XK2*(CNA(2)*XK2*(1.+XLNA)-CNA(4))/V(2)
C             BLACK LIQUOR TO FURNACE
      XC5S=CS(5)+H*(CS(4)-CS(5))*Q4/V(3)
      XC5NA=CNA(5)+H*(CNA(4)+XMNA/Q4-CNA(5))*Q4/V(3)
C             WHITE LIQUOR FROM STORAGE
      XC2S=CS(2)+H*(CS(1)-CS(2))*Q1/V(1)
      XC2NA=CNA(2)+H*(CNA(1)-CNA(2))*Q1/V(1)
C
C ******************************************************************************
C
C             RETRIEVE VALUES FROM DUMMY VARIABLES
      V(1)=XV(1)
      V(2)=XV(2)
      V(3)=XV(3)
      CS(5)=XC5S
      CS(4)=XC4S
      CS(2)=XC2S
      CNA(5)=XC5NA
      CNA(4)=XC4NA
      CNA(2)=XC2NA
C             STRONG BLACK LIQUOR TO STORAGE
C               INSTANTANEOUSLY TRANSFERRED FROM DIGESTERS ,WASHERS, ET
      CS(3)=CS(2)*XK2*(1.+XLS)
      CNA(3)=CNA(2)*XK2*(1.+XLNA)
 1000 CONTINUE
      RETURN
  100 FORMAT(1H1)
  101 FORMAT(1X,F5.0,10F5.2,F5.1,F7.0,F5.1,F7.0,F5.1,F7.0,F5.1,5F7.0)
  102 FORMAT(1H0,'SALT CAKE MAKE-UP',F6.1,'LB/HR',10X,'CAUSTIC MAKE-UP
     1F6.1,'USGPM')
 2000 FORMAT(20A4)
 3001 FORMAT(1X,F5.0,5X,4(2X,F6.2),3(2X,F8.0),2X,F7.0,2X,F6.2,3(1X,F5.
     1))
 3002 FORMAT(1X,F5.0,5X,5(2X,F7.0),3(2X,F8.0),2X,F7.0,2X,F6.2,3(2X,F5.
     1))
 3003 FORMAT(1H ,T3,'TIME',T16,'W.L.CONC.',T32,'B.L.CONC.',T47,
     1'W.L.VOL.',T56,'B.L.VOL.',T66,'B.L.O.VOL.',T78,'SALT',T85,
     2'CAUSTIC',T97,'GLS',T104,'WLS',T111,'BLS'//)
 3004 FORMAT(1H0,T1,'TIME',T14,'Q1',T23,'Q2',T32,'Q3',T41,'Q4',T53,'Q5
     1,T60,'W.L.VOL.',T70,'B.L.VOL.',T80,'B.L.O.VOL.',T91,'SALT',
     2T99,'CAUSTIC',T108,'GLS',T115,'WLS',T122,'BLS'//)
 4001 FORMAT(1X,5(2X,E12.6))
      END
      SUBROUTINE SODA(XMS,XMNA,C5S,C5NA,Q5,FLS,FLNA,TARG,AAC,Q2,XMNAMX
     1RD,EC,C1S,C1NA,C2S,C2NA,VSET,VTEST,A1,A2,B1,B2,I,P,XKP)
C
C             COMPUTE SALT-CAKE AND CAUSTIC MAKE-UP
C
```

```
      IF(P.EQ.1.) GO TO 10
      E=(VSET-VTEST)/VSET
      P=1.+XKP*E
   10 EAC=(RD*C2S+EC*C2NA)*P
      XNAOH=EC*C5NA*Q5*(1.+B1*C5NA+B2)
C            SALT CAKE MAKE-UP
      A=A1/Q5
      B=1.+A2+2.*A1*C5S
      C=XNAOH*TARG/((TARG-1.)*RD)+(1.+A2+A1*C5S)*C5S*Q5
      XMS=(-B+SQRT(B*B-4.*A*C))/(2.*A)
C            CALCULATE FRACTIONAL LOSS COEFFICIENT
      FLS=A1*(C5S+XMS/Q5)+A2
C            CAUSTIC MAKE-UP
      XNA2S=RD*C5S*Q5*(1.+FLS)
      XMNA=XMNA+EAC*Q2-XNAOH-XNA2S-RD*XMS*(1.+FLS)
C            CHECK FOR VIOLATION OF CONSTRAINTS
      CALL CONSTR(XMS,XMNA,XMNAMX,EC,RD)
C            RESET FRACTIONAL LOSS COEFFICIENTS
      FLS=A1*(C5S+XMS/Q5)+A2
      FLNA=B1*C5NA+B2
      RETURN
      END
      SUBROUTINE CONSTR(XMS,XMNA,XMNAMX,EC,RD)
C            CHECK MAKE-UP CONSTRAINTS AND CORRECT IF NECESSARY
C
C            0 < XMS
C            0< XMNA < XMNAMX
C
      IF(XMNA-XMNAMX) 200,200,100
  100 XMS=XMS+(XMNA-XMNAMX)/RD
      XMNA=XMNAMX
  200 IF(XMS) 300,400,400
  300 XMNA=XMNA+XMS/EC
      XMS=0.
      IF(XMNA.GT.XMNAMX) XMNA=XMNAMX
  400 IF(XMNA) 800,900,900
  900 IF(XMNA-XMNAMX) 1000,1000,1100
  800 XMS=XMS+XMNA/RD
      XMNA=0.
      IF(XMS.LT.0.) XMS=0.
 1000 RETURN
 1100 XMS=XMS+(XMNA-XMNAMX)/RD
      XMNA=XMNAMX
      RETURN
      END
      SUBROUTINE TABLE(X1,X2,X3,X4,I,N,A)
      COMMON/BLK1/H,LP
      DIMENSION A(500)
C
C            A GENERAL PURPOSE TABLE LOOK-UP FOR HISTORICAL EVENTS
```

```
C                 DYNAMIC MODEL OF KRAFT MILL

C
      TIM=I
      DO 10 J=1,N
      TIME=INT((A(J)+.00001)/H)
      IF(TIM-TIME) 2,10,10
    2 X1=A(J+100)
      X2=A(J+200)
      X3=A(J+300)
      X4=A(J+400)
      RETURN
   10 CONTINUE
      WRITE(LP,1) N
      STOP
    1 FORMAT(///10('*'),'INSUFFICIENT DATA- ADD LAST DAYS CARD',5X,'N
     1,I3,10('*'))
      END
      SUBROUTINE TABLE2(DV,STREAM,I,N,NPOINT,NJOINT,A)
      COMMON/BLK1/H,LP
      DIMENSION DV(3),A(500)
C
C               SPECIAL PURPOSE TABLE LOOK-UP IN CASE OF INVENTORY OUTAGE
C
      DO 10 J=1,N
      ITIM=A(J)/H+.0001
      IF(I-ITIM) 10,2,10
    2 DO 3 KK=1,3
      K=(KK+1)*100+J
      DV(KK)=A(K)
      IF(DV(KK)) 4,3,4
    4 NJOINT=KK
      KKK=100+J
      STREAM=A(KKK)
      NPOINT=J
    3 CONTINUE
      RETURN
   10 CONTINUE
      DO 5 K=1,3
      DV(K)=0.
    5 CONTINUE
      NPOINT=0.
      STREAM=0.
      RETURN
      END
```

Table D-1 Sample Data Set



```
HISTORICAL MAKE-UP STRATEGY FOLLOWED BY OPTIMAL STRATEGY
SPORADIC WATER ADDITION
0.                                                                           DEBU
30.          656.                                                            (DAYS.
3.           8.           8.                                                 PRNTY
5.           .445         .84          4.           1.164                    AAC.
1.164
.25          .24                                                             H.TAR
1.           155000.      2.25         0.                                    P.VSET
1.841        5.07         1.841        5.07         1.937                    CS( )
5.773        1.937        5.773        1.937        5.936                    CS( )
6325.        6325.        5432.        5432.        5432.                    Q1.Q2
180000.      180000.      60000.                                             V1.V2
2400.        3.                                                              XNASO
31.                                                                          NMAKE
 8.
16.          2400.                                                           MAKE-
24.          1200.
40.          2400.
56.
72.          600.
80.          2400.
104.         1200.
128.         4800.
144.         2400.        2.57
176.
192.         1400.        3.43
200.         2500.        3.
208.         2400.        3.
216.         2500.        3.
224.         1200.        1.54
248.         1250.        1.54
280.
288.         2000.        .86
296.         1200.        3.
344.         1200.
368.         1000.        1.26
384.         1000.        1.28
408.         1000.        1.8
432.         1000.        2.
464.         2000.        3.5
552.         1000.        2.
600.         2000.        3.9
624.         0.           2.25
632.         2000.        3.8
656.         0.           1.5
83.                                                                          NFLOW
 8.              6635.750     5700.820     6018.000     6018.000
16.              6322.852     5432.000     6018.000     6018.000
24.              6015.410     5168.738     6018.000     6018.000
32.              6743.284     5839.160     6018.000     6018.000
40.              6521.379     5602.554     6018.000     6018.000
48.              6012.090     5165.031     6018.000     6018.000
56.              6441.539     5533.464     6018.000     6018.000
64.              6480.379     5567.340     6018.000     6018.000
72.              6012.090     5165.031     6018.000     6018.000
80.              6322.852     5432.000     6018.000     6018.000
88.              6327.172     5435.711     6018.000     6018.000
96.              6519.230     5600.711     6018.000     6018.000
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104.          6053.102    5200.262    6018.000    6018.000
112.          6327.172    5435.711    6018.000    6018.000
120.          6637.910    5702.672    6018.000    6018.000
128.          6482.539    5569.191    6018.000    6018.000
136.          6327.172    5435.711    6018.000    6018.000
144.          6327.172    5435.711    6018.000    6018.000
152.          6482.539    5569.191    6018.000    6018.000
160.          6482.539    5569.191    6018.000    6018.000
168.          6171.801    5302.230    6018.000    6018.000
176.          6637.910    5702.672    6018.000    6018.000
184.          5471.449    4699.699    6018.000    6018.000
192.          6637.910    5702.672    6018.000    6018.000
200.          6327.172    5435.711    6018.000    6018.000
208.          6171.801    5302.230    6018.000    6018.000
216.          6637.910    5702.672    6018.000    6018.000
224.          5705.672    4901.781    6018.000    6018.000
232.          5975.422    5133.520    5692.000    5692.000
240.          5934.410    5098.289    5692.000    5692.000
248.          5705.672    4901.781    5692.000    5692.000
256.          6327.172    5435.711    5692.000    5692.000
264.          6016.410    5168.738    6018.000    6018.000
272.          6171.801    5302.230    6018.000    6018.000
280.          4833.852    4152.789    6018.000    6018.000
288.          4402.262    3782.010    6018.000    6018.000
296.          6402.500    5500.430    5951.000    5951.000
304.          6249.051    5368.602    5951.000    5951.000
312.          6249.051    5368.602    5951.000    5951.000
320.          6240.520    5361.270    5951.000    5951.000
328.          6018.859    5170.840    5951.000    5951.000
336.          6632.680    5698.180    5951.000    5951.000
344.          6555.961    5632.289    5951.000    5951.000
352.          6169.699    5300.430    5951.000    5951.000
360.          6244.789    5364.941    5467.000    5467.000
368.          6244.789    5364.941    5467.000    5467.000
376.          6169.699    5300.430    5951.000    5951.000
384.          5660.801    4863.230    5951.000    5951.000
392.          6249.051    5368.602    5951.000    5951.000
400.          6555.961    5632.270    5951.000    5951.000
408.          6112.641    5251.410    5951.000    5951.000
416.          6393.980    5493.109    5951.000    5951.000
424.          6555.961    5632.270    5951.000    5951.000
432.          6168.059    5299.020    5951.000    5951.000
440.          6555.961    5632.270    5951.000    5951.000
448.          6555.961    5632.270    5951.000    5951.000
456.          5754.578    4943.801    5951.000    5951.000
464.          5549.980    4768.020    5951.000    5951.000
472.          6555.961    5632.270    5951.000    5951.000
480.          6027.391    5178.172    5414.000    5414.000
488.          4845.641    4163.781    5736.000    5736.000
496.          5515.879    4738.730    5951.000    5951.000
504.          6249.051    5368.602    5951.000    5951.000
512.          6555.961    5632.270    5951.000    5951.000
520.          6402.500    5500.430    5951.000    5951.000
528.          5942.141    5104.930    5951.000    5951.000
536.          6095.602    5236.770    5951.000    5951.000
544.          6555.961    5632.270    5951.000    5951.000
552.          6095.602    5236.770    5632.000    5632.000
560.          6249.051    5368.602    5951.000    5951.000
568.          6402.500    5500.430    5951.000    5951.000
576.          5942.141    5104.930    5951.000    5951.000
584.          6402.500    5500.430    5951.000    5951.000
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592.                6402.500      5500.430      5951.000      5951.000
600.                6087.070      5229.441      5951.000      5951.000
608.                5442.141      5104.430      5951.000      5951.000
616.                6244.051      5368.602      5951.000      5951.000
624.                6555.461      5632.270      5951.000      5951.000
632.                6043.020      5236.770      5951.000      5951.000
640.                6555.461      5632.270      5951.000      5951.000
648.                6244.051      5368.602      5951.000      5951.000
656.                6240.520      5361.270      5951.000      5951.000
721.                6244.051      5368.602      5951.000      5951.000
                                                                            NLUS1
4.
3.          -.0060754     .026555       .0062414      -.047523          100% B
128.        -.066962      .0075015      -.044425      .32306            0% BLO
152.        -.10072       .14788        -.031946      .20892            65% BL
721.        -.0060764     .026555       .0062414      -.047523          100% B
                                                                        NLOS2
1.
721.        .0017634      -.100616      -.012846      .043069
41.                                                                      NVOL
8.          -5.                                       -20000.
40.         4.                          5000.
64.         4.                          5000.
88.         4.                          10000.
96.         4.                          20000.
112.        4.                          5000.
128.        5.                                        20000.
136.        4.                          5000.
144.        4.                          5000.
168.        4.                          10000.
184.        4.                          10000.
192.        4.                          10000.
216.        4.                          25000.
224.        4.                          10000.
240.        4.                          10000.
264.        4.                          30000.
304.        4.                          10000.
312.        4.                          5000.
328.        4.                          5000.
360.        4.                          25000.
384.        4.                          5000.
408.        4.                          10000.
416.        4.                          5000.
448.        4.                          10000.
456.        4.                          10000.
480.        4.                          20000.
488.        4.                          10000.
520.        4.                          15000.
536.        4.                          5000.
560.        4.                          5000.
568.        4.                          10000.
576.        4.                          5000.
584.        4.                          10000.
600.        4.                          15000.
608.        4.                          10000.
616.        4.                          10000.
640.        4.                          5000.
648.        4.                          15000.
670.        4.                          10000.
678.        4.                          10000.
686.        4.                          5000.
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HISTORICAL MAKE-UP STRATEGY FOLLOWED BY OPTIMAL STRATEGY
SPORADIC WATER ADDITION
IME           Q1        Q2        Q3        Q4            Q5        W.L.VOL.   B.L.VOL.   B.L.O.VOL.


  0.          6812.     6636.     5701.     6018.         6018.     180000.    180000.      60000.
  8.          6912.     6323.     5432.     6018.         6018.     181062.    177462.      40000.
 16.          6818.     6016.     5169.     6018.         6018.     185618.    172774.      40000.
 24.          6869.     6793.     5839.     6018.         6018.     191985.    165980.      40000.
 32.          6867.     6521.     5603.     6018.         6018.     192581.    164524.      40000.
 40.          6744.     6012.     5165.     6018.         6018.     195347.    166200.      40000.
 48.          6649.     6442.     5534.     6018.         6018.     200729.    159376.      40000.
 56.          6675.     6480.     5567.     6018.         6018.     202338.    155502.      40000.
 64.          6693.     6012.     5165.     6018.         6018.     203959.    156896.      40000.
 72.          6707.     6323.     5432.     6018.         6018.     208980.    150072.      40000.
 80.          6655.     6327.     5436.     6018.         6018.     212069.    145384.      40000.
 88.          6686.     6519.     5601.     6018.         6018.     214807.    150724.      40000.
 96.          6513.     6053.     5200.     6018.         6018.     215240.    167384.      40000.
104.          6352.     6327.     5436.     6018.         6018.     217090.    160842.      40000.
112.          6382.     6638.     5703.     6018.         6018.     217288.    161182.      40000.
120.          6410.     6483.     5569.     6018.         6018.     215231.    158658.      40000.
128.          6368.     6327.     5436.     6018.         6018.     215068.    155066.      60000.
136.          6590.     6327.     5436.     6018.         6018.     216941.    155406.      60000.
144.          6436.     6483.     5569.     6018.         6018.     218910.    155746.      60000.
152.          6202.     6483.     5569.     6018.         6018.     218108.    152154.      60000.
160.          6237.     6172.     5302.     6018.         6018.     215949.    148562.      60000.
168.          6311.     6638.     5703.     6018.         6018.     216747.    152834.      60000.
176.          6282.     5470.     4700.     6018.         6018.     213475.    150310.      60000.
184.          6387.     6634.     5703.     6018.         6018.     220365.    149762.      60000.
192.          6369.     6327.     5436.     6018.         6018.     217824.    157238.      60000.
200.          6221.     6172.     5302.     6018.         6018.     217404.    152578.      60000.
208.          6283.     6638.     5703.     6018.         6018.     217938.    146850.      60000.
216.          6311.     5706.     4902.     6018.         6018.     215538.    169326.      60000.
224.          5617.     5975.     5134.     5692.         5692.     218545.    170396.      60000.
232.          5445.     5934.     5098.     5692.         5692.     214774.    165928.      60000.
240.          5503.     5706.     4902.     5692.         5692.     210993.    171178.      60000.
248.          5392.     6327.     5436.     5692.         5692.     209142.    164856.      60000.
256.          5779.     6016.     5169.     6018.         6018.     201875.    162804.      60000.
264.          5923.     6172.     5302.     6018.         6018.     200521.    186010.      60000.
272.          5569.     4834.     4153.     6018.         6018.     196797.    180282.      60000.
280.          5698.     4402.     3782.     6018.         6018.     202518.    165360.      60000.
288.          5704.     6403.     5500.     5951.         5951.     213336.    147472.      60000.
296.          5922.     6249.     5369.     5951.         5951.     208592.    143866.      60000.
304.          6053.     6249.     5369.     5951.         5951.     206464.    149206.      60000.
312.          5987.     6241.     5361.     5951.         5951.     204485.    149546.      60000.
320.          5967.     6019.     5171.     5951.         5951.     202253.    144828.      60000.
328.          6061.     6633.     5698.     5951.         5951.     202163.    143586.      60000.
336.          6081.     6556.     5632.     5951.         5951.     197576.    141562.      60000.
344.          6166.     6170.     5300.     5951.         5951.     194139.    139012.      60000.
352.          5797.     6245.     5365.     5467.         5467.     194663.    133806.      60000.
360.          5893.     6245.     5365.     5467.         5467.     191463.    157988.      60000.
368.          6020.     6170.     5300.     5951.         5951.     186957.    157170.      60000.
376.          5963.     5661.     4863.     5951.         5951.     185388.    151064.      60000.
```

Table D.2 : Simulation Results Of Sample Data Set