



*Institute of Paper Science  
and Technology*

**ANNUAL RESEARCH REVIEW**

**PROCESS SIMULATION AND CONTROL**

March 23-24, 1992



*Atlanta, Georgia*

# INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

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**INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY**

**Atlanta, Georgia**

**ANNUAL RESEARCH REVIEW**

**PROCESS SIMULATION AND CONTROL**

**MARCH 23-24, 1992**



March 13, 1992

TO: MEMBERS OF THE PROCESS SIMULATION AND CONTROL PROJECT  
ADVISORY COMMITTEE

Attached for your review are the Status Reports for the projects to be discussed at the Process Simulation and Control Project Advisory Committee meeting scheduled for March 23, 1992 in Atlanta.

We look forward to seeing you on March 23. Best regards.

Sincerely yours,

Gary Jones, Group Leader  
Process Simulation and Control Group

Attachment

GJ/sj

*Institute of Paper Science and Technology, Inc.*

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## TABLE OF CONTENTS

		<u>Page</u>
Project 3471	Systems Analysis	1
Project 3725	Water Reuse	15

SESSION 2

PROCESS SIMULATION AND CONTROL  
PROJECT ADVISORY COMMITTEE MEETING

March 23, 1992  
Wyndham Hotel  
Atlanta, GA

AGENDA

1:00	Welcome, Introduction	Richard Ellis
1:15	Project 3725 Water Reuse	Gary Jones
2:30	Coffee Break	
2:45	Project 3741 Systems Analysis	Gary Jones
3:30	Student Discussions	
4:00	General Discussions	
5:00	Adjournment	

March 24, 1992

9:00 - 12 noon	Committee Discussions	Richard Ellis
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MAPPS SUPPORT

STATUS REPORT

FOR

PROJECT 3471

TO THE

PROCESS SIMULATION AND CONTROL

PROJECT ADVISORY COMMITTEE

March 23, 1992



**Project Title:** Systems Analysis  
**Project Code:** MAPPS  
**Project Number:** 3471  
**Division:** Engineering and Paper Materials  
**Project Staff:** Gary Jones, Rajen Doshi  
**Budget (FY 92-93):** \$50,000

**OBJECTIVE:**

Continue development of MAPPS in the following areas:

Integration with external programs

Completion of the Performance Attribute system

Addition of features for improved papermaking simulation

**GOALS:**

1. Develop and test the PI-MAPPS interface and the continuous digester application
2. Develop and test the dynamic blocks
3. Add to MAPPS stream components for improved papermaking simulation

**SUMMARY:**

MAPPS development has proceeded rapidly since the last report. The new release of MAPPS (Version 5.0) will contain many new and hopefully useful features. Some of the important improvements are a "streamlined" stream structure, many new components in the stream data base, new multi-phase equilibrium physical property calculations, new suspended solids components and suspended solids handling features, saturated dyed sheet properties and new tried and tested dynamic blocks. New applications include a dynamic continuous digester model running in both a stand-alone and integrated with PI and a new dual line TMP flowsheet model. A dynamic papermachine application is also under development.

In addition a Windows<sup>R</sup> version of MAPPS has been created. This version has some interesting features not available in the normal overlaid version of MAPPS. Also progress has been made in creating a separate dynamic link library of MAPPS modules which can be linked to external programs such as an object oriented expert system, a windows user interface (front end), a CAD package or other programs.

**Introduction**

MAPPS has undergone extensive development over the past several years. Most notable is the addition of the Performance Attribute System to compute fiber characteristics and sheet properties and to more realistically simulate pulping and papermaking processes. In

addition, MAPPS has been integrated with a variety of programs especially real-time data base and control systems such as RPMIS (IBM), Taylor Mod 300, and Oil Systems's PI Data Base.

Elements of the MAPPS library are being translated and incorporated into SACDA's MASSBAL II (steady-state) and III (dynamic) simulation programs. This integration will combine the best and most novel features of MAPPS (process modules and performance attributes) with the user-interface, solution techniques and optimization features of MASSBAL.

Despite this progress there continues to be a need to add features which make MAPPS still more useful. These features include the need for dynamic simulation both as a standalone program and integrated with a real-time data base system for real plant simulation and look-ahead studies. This feature is also essential for dynamic data reconciliation and optimization.

A second important area is the need to predict the impact on the environment, the process, equipment and paper properties of contaminants, trace ions and chlorinated compounds which circulate and buildup in white water systems.

Other important forces driving MAPPS development are the needs of users especially at the mill level. This factor has shifted the emphasis of most simulation programs to the user-interface at the expense of process simulation details. One approach to this problem is to integrate the simulation program directly with the DCS or mill-wide information system. This approach solves a number of problems associated with the use of the simulation program but does not deal with the individual user wanting to solve a specific problem which he must solve in the short term.

To solve this common type of problem requires a simple flexible, robust simulation package which is "easy to use" and yet is able to handle a wide variety of problems. To handle this requirement a menu interface has been added to MAPPS - the Lahey version of MAPPS. Other improvements in this direction are described in the body of the report.

### **New MAPPS Stream Structure**

A second approach to achieving a number of the objectives of the project is to simplify the MAPPS stream structure. The current version of MAPPS (MAPPS 4.0) has ten predefined stream types: water, gaseous, pulping, recovery, bleaching, paper, waste, fuel, energy and information. There were many reasons for using these predefined types particularly the advantage of having a minimum number of components in each stream type in any given flowsheet application.

However, in order to simulate an integrated mill containing pulping, bleaching and papermaking (refining, screening and forming), it was necessary to convert from one stream

type to another. There was also the problem of dual representation of pulp fibers. In pulping and bleaching fibers were represented as cellulose and lignin components while in paper streams fibers were represented as chips, fibers, shives, fines and chips.

The performance attribute stream, which is the same for all stream types, and contained both composition and fiber shape characteristics, formed the bridge between these two different component representations thus making it possible to efficiently convert from one stream type to another.

Another problem with the multiple stream types was that it was not always certain whether a module would work if a stream was modified to include additional components. Also the waste stream type (7) had water as the only default component. This not only "wasted" a stream type but created the impression that the MAPPS modules could use this stream type to simulate water treatment operations when in fact it was not used in the system.

To solve these problems and to simplify and enhance the stream structure, a new stream system was developed. In the new system all the stream types 3 through 7, i.e. pulping, recovery, bleaching, paper and waste, have been collapsed into a single pulp stream type (3). In the new system there will be 6 stream types instead of 10. Stream types 8 through 10 have been renumbered from 4 through 6. All the modules in the system have been rewritten internally to handle the simplified stream structure.

In addition, all the modules have been written to handle components in a more general fashion using a series of indices defined in block data and passed in common. This allows the user to redefine the stream components without changing the way the modules work. The new pulping stream definition combines the fibers from the paper stream with the chemical components of the pulping, bleaching and recovery streams to eliminate overlap and ambiguities. It also includes many more new components including a wide variety of suspended solids and bound metallic ion components and trace components. The components cellulose or carbohydrate and lignin have been eliminated. However, components such as dissolved carbohydrate, dissolved lignin, chlorolignin, etc. were retained.

The new system eliminates the need to convert from one stream type to another in order to simulate an integrated mill system. However, there is one new requirement of the system --- that performance attributes **must** be used for all simulations. In the previous version (MAPPS 4.0) it was possible, although not desirable, to run simulations without using PAT variables. Now, in order to bridge between fibers and carbohydrate and lignin components within fibers it is necessary to always use performance attributes. The reasons for this are that pulping and bleaching kinetics are based on lignin, cellulose and hemicellulose contents in the fibers. This information is contained only in the PAT stream.

Because the WOOD01 block could not initialize performance attributes at the same time it initialized the pulping stream, this module has been eliminated from the library. The WOOD02 block which initializes PATs as well as stream component flows should be used

to initialize streams. The WOOD02 block has been simplified to initialize just one stream type (pulp) instead of two (pulp and paper) in the earlier version.

Other than this change, all the existing MAPPS modules work in exactly the same way from a user's standpoint.

### **Improved Handling of Non-fibrous Suspended Solids**

The 4.0 version of MAPPS contained several performance attributes to simulate the effects of suspended solids on paper properties. For example, the relative bonded area and sheet strength decreased in proportion to the solids loading in the sheet. The absorption and scattering of the suspended solids changed the overall levels of scattering and absorption in the filled sheet thus influencing sheet brightness and opacity. The shape attribute influenced the degree to which solids loading adversely affected strength. The particle size attribute was useful in influencing the separation of the solids.

All the information on the suspended solids attributes was contained in the PAT variables for that stream. Thus the PAT variables were the average values of the characteristics of the individual suspended solids. This system could not differentiate between different suspended solids and tended to average the effects of various solids. Also it did not allow for selective separation of suspended components in screening, cleaning and particularly forming operations. The new expanded stream definition system was designed to overcome these limitations.

The new system includes a suspended solids data base containing data on 30 new suspended solids components which have been added to the default stream (pulp) definition. The data base defines six characteristics: specific gravity, average diameter, standard deviation of the size distribution, scattering coefficient, absorption coefficient, and specific surface area for each suspended solid component. Operations such as forming and cleaning which tend to separate suspended solids based on different characteristics of the solids (e.g. specific gravity, surface area or size) result in different splits for each solid component.

### **Solids Separations in the Hydrocyclone**

To work with this new set of properties, the separation block, HYFRAC, which simulates screening, cleaning or thickening now has new features to handle various types of suspended solids. In the cleaning or hydrocyclone mode, the model now takes the dimensions of the cyclone and computes the separations of the suspended solids based on a first principles model (Bradley 1958) which determines the separations based on both specific gravity and drag or surface area characteristics of each solid. Thus the various solids are selectively separated in the cyclone.

The pressure drop across the cyclone is given by

$$\Delta P = \rho \left( \frac{V_i^2}{2g_c} \right) \frac{\alpha^2}{N} \left[ \left( \frac{D_c}{D_o} \right)^{2n} - 1 \right] \quad (1)$$

where  $\Delta P$  is the pressure drop,  $\rho$  is the liquid phase density,  $V_i$  is the average velocity of the slurry entering the cyclone,  $\alpha$  is a parameter with a default value of 0.45,

The reject separation efficiency is given by

$$\epsilon_r = 1 - e^{-\left( \frac{D_p}{D_{50}} - 0.115 \right)^2} \quad (2)$$

where  $D_p$  is the particle diameter,  $D_{50}$  is the diameter for 50% separation efficiency given by

$$D_{50} = 2.7 \xi_2 \sqrt{\xi_1} \quad (3)$$

where

$$\xi_1 = \frac{\xi_0}{\rho_p - \rho_l} \quad (4)$$

and  $\rho$  refers to density and subscripts p and l refer to particle and liquid or slurry phase. The remaining terms are defined as

$$\xi_0 = \tan\left(\frac{\theta}{2}\right) \frac{\mu_l (1 - RF)}{D_c Q} \quad (5)$$

where RF is the total reject flow split,  $\theta$  is the angle of the cyclone, Q is the volumetric flow rate through the cyclone which is the total volumetric flow rate fed to the cyclone system divided by the number of cyclones in the bank,  $\mu_l$  is the liquid phase viscosity. The other term is given by

$$\xi_2 = \left( \frac{2.3 D_o}{D_c} \right)^N \frac{D_i^2}{\alpha} \quad (6)$$

$D_o$ ,  $D_i$  and  $D_c$  are the diameters of the outlet, inlet and large end of the cyclone respectively. The default values of each of these is provided.  $\alpha$  is the ratio of the cylinder to inlet velocity with a default value of 0.45.  $N$  is the power of the dependence of the cylinder velocity on the cylinder radius which has a default value of 0.8. The inlet velocity is obtained by dividing  $Q$  by the area of the inlet.

For the screen the reject fraction for each particle is given by the same function of diameter used for the fiber separation. This is

$$\epsilon_r = RF + \frac{1}{2} (1 - RF) \left( 1 - \frac{1}{e} \right) \left( 1 + \tanh(p_1(D_s - p_2 + 15 D_s (RF D_s)^{1/2})) \right) \quad (7)$$

When MAPPS is booted up, the suspended solids data base is read and the properties of all the suspended solids are stored in arrays for use with physical property models. When properties of a sheet are required, the contributions of each suspended solid is available from the arrays.

### Adsorbed Trace Metal Ions

Trace metal ions are also handled in the new system. When trace metals such as calcium, sodium, aluminum, cesium, barium etc. are adsorbed onto pulp fibers, they will be carried throughout the papermaking system on the fibers and tend to be separated selectively depending on the characteristics of the fiber furnish. The total amount of each adsorbed metal is passed as a separate component in the pulp stream. When the stream encounters a separation system such as a cleaner or a forming block which separates fibers selectively, the trace metals are distributed to the various fiber fractions, i.e. fines, fiber 1 through 9, based on the relative surface area of each fiber. Then the fractionation of each trace metal ion is based on the fractionation of each fiber component.

In mixing steps the process is straightforward and each adsorbed trace metal is mixed based on a weight average of the contents of the inlet streams. In each equilibrium stage, trace metal absorption is recomputed based on local composition and trace metals are redistributed between the fiber and the liquid phase.

The distribution of trace metals and other absorbable species is determined in a new equilibrium block which is described in the report on project 3725 (Water Reuse).

### **Performance Attributes**

The PAT stream structure and modeling philosophy have not changed. However, several additions and enhancements have been made. The PAT stream now contains 31 variables. The PAT stream can be broken down into three main parts based on the types of components in the stream: fibers, suspended solids and other components such as dyes.

The PATs are as follows:

fiber composition PATs: yield, kappa, hemicellulose and fiber absorption coefficient, and **carboxylate content**;

shape attributes: length, standard deviation of length, fiber width, standard deviation of width, distribution type and CSF;

physical properties: fiber tensile, fiber elastic modulus, cell wall thickness, fiber stiffness factor, specific bond strength;

network attributes, top and bottom sheet contact factors, average bonding factor, formation factor, MD and CD stretch, average fiber orientation factor;

suspended solids attributes: average diameter, **standard deviation of diameter**, **average light absorption coefficient**, **average scattering coefficient**, shape factor and **specific gravity**;

dye loadings: red dye, blue dye and yellow dye.

The highlighted words indicated new or modified variables in the PAT stream.

The new PATs are carboxylate concentration, CD stretch, suspended solids specific gravity and optical properties (absorption and scattering coefficients) and the three dye loadings for the primary color dyes. In addition, the PAT data base contains the reflectance data for each of the three primary dyes over the visible range at 16 wavelengths. The new features of dyed sheets will be discussed in a later section.

### **Adsorption, Retention and Wet End Chemistry Effects**

The addition of the carboxylate concentration is essential in calculating surface adsorption as part of the electrolytic equilibrium calculations. Long term, the carboxylate concentration can be related to lab data and linked to retention and wet end chemistry effects on the papermachine and as well as to pulping and bleaching chemistry. This variable will hopefully tie together many diverse aspects of pulping, bleaching and papermaking.

### **Dimensional Stability**

The CD stretch was added to calculate dimensional stability and curl. In addition to MD and CD restraint (stretch or shrinkage), the variation in fiber orientation through the thickness of the sheet will be used to determine curl or dimensional stability. The average fiber orientation PAT is not sufficient. These properties will be added to the property system once an empirical PAT model for fiber orientation distribution is determined.

### **Saturated Dyed Sheets and Color Matching**

Dye loading attributes (as a weight fraction of the fiber components) were added to determine the color of a dyed sheet. MAPPS 4.0 contained a property model to determine Tappi brightness and opacity at 457 and 572 nm for lightly dyed fine papers. The extended optical property calculation module (OPTPRP) now determines the CIE  $L^*a^*b$  values and the reflectance at 16 wavelengths over the visible range for the entire range of dye loadings from light (oz./ton) to saturated (lbs/ton). This model was developed from experimental data and validated on the Western Michigan University papermachine for several types of papers as well as handsheets and machine papers produced over a wide range of dye loadings with both individual dyes and mixtures of cationic dyes.

Dye mixing is simulated by means of a DYEMIX block which determines the material balance and changes the dye loading PAT values. In this way it is possible to mix several dyes in sequence or all at once. It is also possible to control color  $L^*a^*b$  of the final sheet by setting up a control loop which compares the predicted  $L^*A^*B$  with the set point and adjusts the three primary dyes until the set point is achieved.

Agreement between model predictions and measurements were judged by comparing the reflectance curves over the 400 to 700 nm wavelength range and by comparing the root mean square (RMS) error of the  $L^*a^*b$  values. The latter represents the measure of the way the eye perceives color. The RMS error is a direct quantitative measure of the error in predicting the visual effect. The model predictions were in excellent agreement for individual dyes over wide ranges of loading. However, the error was higher although generally acceptable for mixtures of dyes at higher loadings. This work was done as a graduate project at WMU and we expect to submit several papers for publication from this work.

### **Process Dynamics**

Dynamic process modules described in a previous project report are a new feature of MAPPS simulation. At the time these were in an early stage of development. Since that time the stirred tank (CSTANK), the process dead time (DELAY) and the dynamic controller (DCONTL) blocks have been extensively tested, debugged and enhanced as part of a continuous digester model application. Also a new PID controller module (PID) has been added which controls a process output by manipulating a single process input using a



full PID control algorithm. A signal generator block will also be developed to generate a sinusoid, ramp or random signal to the process or to vary a stream variable in a specified way. The DCONTL block is placed at the beginning and end of the flowsheet to control the looping through the calculations and to increment time and control the stopping and starting of the simulation. The system running on a VAX is capable of running orders of magnitude faster than real time thus making it possible to predict hours in advance the effects of changes in the process.

### **New Applications**

The continuous digester application makes extensive use of tanks and delays on pulp and liquor flows. In addition, both blocks handle PAT variables as well as mass and energy variables. This dynamic version of MAPPS is currently running on the VAX both in the normal MAPPS modes and in a stand alone mode as part of IPST's PI database system. In both modes, the system can be made to run much faster than real time thus allowing the model to predict the result of current conditions. A set of scenarios is being developed to demonstrate the system.

In the PI integration mode, MAPPS receives inputs from the process via the PI data base tag values. These inputs, which are continuously changing, result in continuously varying outputs from MAPPS which can be displayed or plotted. In addition, it is possible to run MAPPS faster than real time for a given set of PI input conditions and determine the future conditions. Thus it will be possible to predict an off-spec product condition enabling the operator to respond and minimize the problem.

The predicted kappa number agrees with the mill data. The model and PI tag data are now at a stage where they can be installed at the mill site and tested against actual mill data with live process inputs such as chip flows, blow flows, digester level, kappa number, and liquor flows.

### **Linerboard**

The dynamic blocks are also being added to the linerboard model to convert it into a dynamic papermachine model. The intent is to port this model to the PI system and then to the client mill to provide on-line predictions of liner compressive properties. Ultimately, the compressive properties could be optimized by adding a dynamic optimization feature to MAPPS. The linerboard model is a detailed flowsheet of the Georgia Pacific Monticello PM No. 2 including calculations of each single ply forming and the two ply forming, dewatering, calendering, white water recycle, and multi-ply sheet property development. This model was developed as a student project and is currently being converted from a steady state to a dynamic form on a second student project.

### **Thermomechanical Pulping Model**

A flowsheet model of the Bowater Catawba mill thermomechanical pulping lines is also nearly complete. Good agreement between MAPPS predictions and Bowater data of fiber length distributions and CSF at various locations has been obtained. Predictions of handsheet properties are also reasonably good. This model, which is being developed as a student MS degree project, will be used as a "pilot plant" to simulate the sensitivity of CSF and handsheet properties to 10 key independent variables. Using a fractional factorial design, 50 case studies have been run using the MAPPS REPEAT or case study block. The simulated data will then be correlated in SAS to rate the sensitivities of the handsheet properties to process variables. These correlations can then be used as a first step in reducing variations in pulp quality in the process. Long range, a system will need to be put in place at the mill to dynamically reconcile and optimize the process inputs to reduce variability in pulp quality.

Figures 1 and 2 represent the overview MAPPS flowsheets for the lightweight coated and newsprint lines respectively.

### **Ring Crush Optimization**

An application is under development to determine the conditions which would optimize compressive strength of corrugating medium. The corrugating medium model developed as a case study to validate the PAT models in MAPPS (see project report 3471 no. 3 validation of a corrugating medium papermachine model) will be used as the benchmark case. Long term, the techniques and information obtained from this study will be used with the linerboard model to optimize ring crush on line at the mill site.

Figure 1

## BOWATER NEWSPRINT TMP LINES

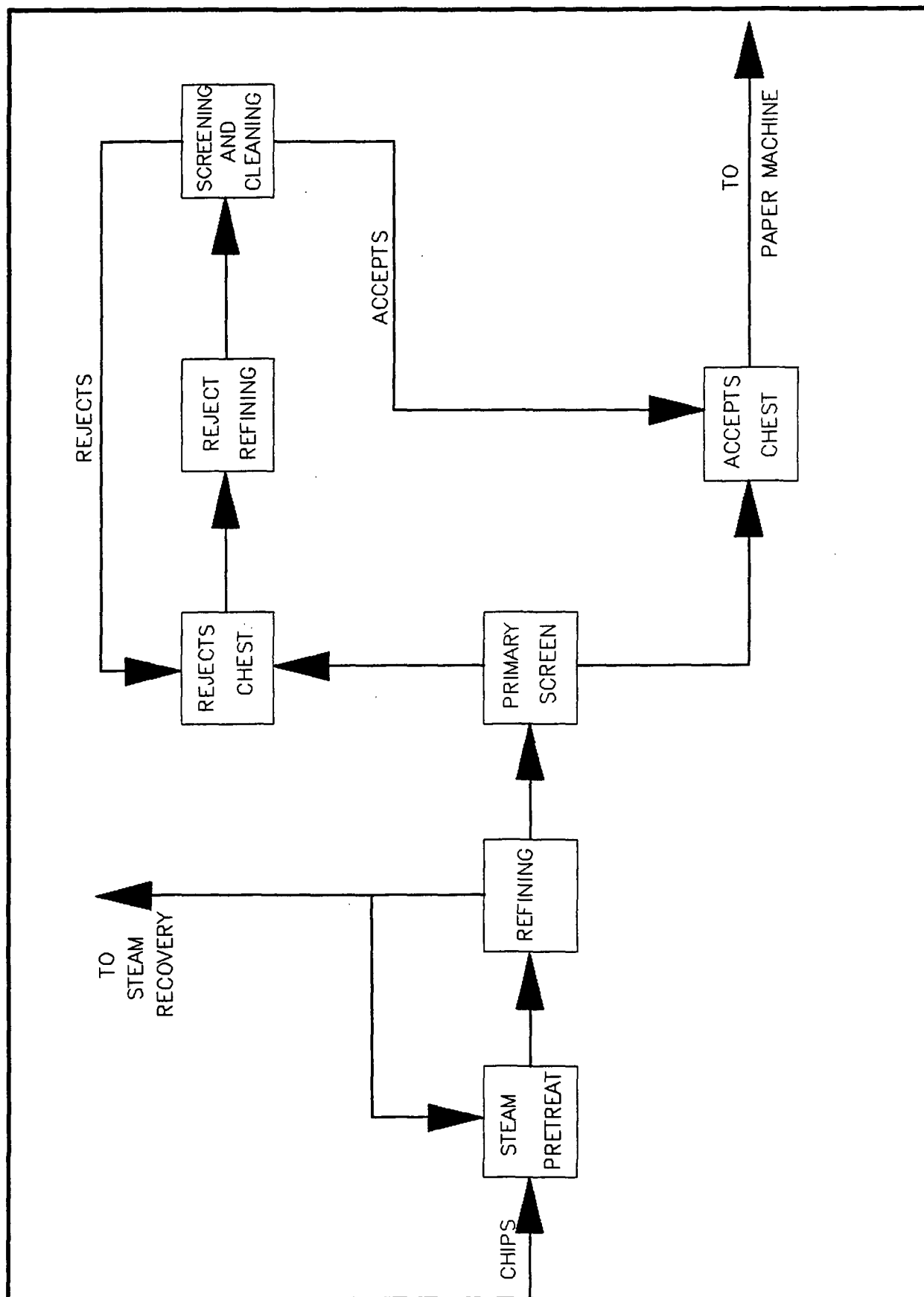
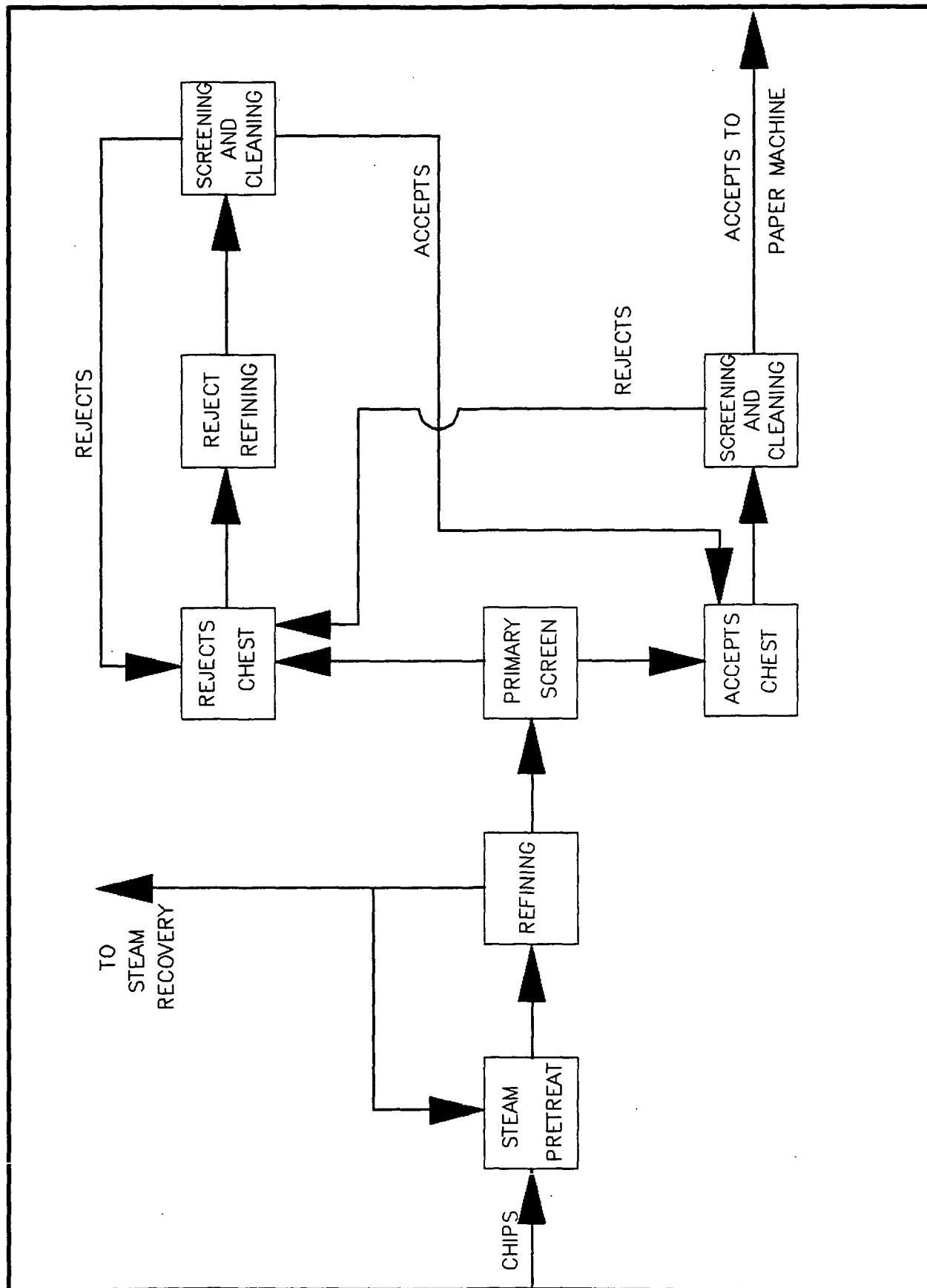


Figure 2

## BOWATER LWC TMP LINES



MAPPS SUPPORT

STATUS REPORT

FOR

PROJECT 3725

TO THE

PROCESS SIMULATION AND CONTROL

PROJECT ADVISORY COMMITTEE

March 23, 1992

**Project Title:** WATER REUSE  
**Project Staff:** Gary Jones  
**Budget (FY 92-92):** \$75,000  
**Reporting Period:** July 91 - July 92  
**Division:** Engineering and Paper Materials  
**Project Code:** MAPPS  
**Project No.:** 3725

#### **OBJECTIVE:**

Develop the capability for detailed modeling of aqueous chemistry effects in pulp and paper processes using MAPPS.

#### **GOAL:**

Add models to MAPPS to compute detailed aqueous electrolyte equilibrium including phase changes. The system must be capable of predicting distribution of trace ions and determining the disposition of pulp and papermaking additives affected by pH.

#### **SUMMARY:**

An equilibrium calculation module and property utility programs have been developed and added to MAPPS. The new module determines the local equilibrium and redistributes the entering components into the outgoing stream to reflect the equilibrium conditions. The module also computes the local pH, ionic strength and carboxylate concentration on the pulp as well as the distribution of trace cations on the pulp fibers. The module is currently being tested on a papermachine application. The new module called EQUIL01 utilizes the larger stream structure in the version of MAPPS currently under development. This new stream structure includes 15072 components in the default pulp stream.

Considerable time and effort was saved by using existing public code, data and documentation for EQUIL01 and the basic property models. These public domain programs and the fundamental theory used in EQUIL01 are described in detail in the Discussion. Considerable effort was expended to integrate the stand-alone programs into the MAPPS framework. No single code accounted for adsorption onto pulp fibers as well as aqueous equilibrium. This required combining elements of two programs into EQUIL01. Also the models for adsorption onto inorganic solids had to be adapted for adsorption onto pulp fibers. Equilibrium constants for absorption of trace metal ions onto pulp fibers are currently assumed. These data must be determined in the future to accurately simulate adsorption phenomenon.

The predictions from EQUIL01 for several test cases agrees with the calculations of the stand-alone programs. However, the internal calculations are not yet correctly translated into the MAPPS outlet stream due to a problem in detecting precipitates formed and translating these into MAPPS components. This defect should be corrected in the very near future.

## INTRODUCTION

Closure of mill white water systems inevitably leads to an increase in ionic and nonionic components in the white water which can adversely affect pulp and paper properties, retention, drainage and corrosivity of the white water. Typical sources of trace metal ions or cations include ground water and other outside water sources as well as opacifiers and fillers such as calcium carbonate and alum and retention aids and strengthening agents such as cationic starches. The ionic concentrations depend not only on equilibrium within the liquid phase but also on the equilibrium between the liquid phase, precipitated solid phases, the gas phase and the fiber phase. Fibers act as ion exchange media in a water-swollen state. The hydroxyl ends of the carboxylate groups readily give up a hydronium ion to metal ions or to cationic starches.

Presently MAPPS has the capability of predicting pulp and paper process material and energy flows using pre-defined streams which have been structured to include most of the components of interest in pulp and papermaking. For instance, a paper stream contains water, fibers, fines, shives and suspended solids; a pulping stream contains water, cellulose, lignin, several kinds of extractives, dissolved cellulose and lignin, and the chemical ionic species associated with pulping; and a bleaching stream contains water, cellulose, lignin, dissolved lignin and cellulose and the chemical ions associated with bleaching. Presently, however, the interactions of many of the ionic species are not properly accounted for and realistic modeling of aqueous chemistry is not possible.

Because of this shortcoming, MAPPS process models cannot consider environmental chemistry, trace metal ion distribution, and the other aqueous chemistry process effects which, in turn, affect process corrosivity, pulp brightness, brightness reversion, paper machine retention, paper and pulp properties, etc. The development of the capability of modeling such effects using MAPPS will be very beneficial to the pulp and paper industry.

## REVIEW OF PAST PROJECT ACTIVITY

This project was opened as a new activity in the E&PM division in 1991. As a result there is no past activity to report.

## DISCUSSION OF 1991 RESULTS

Chemical equilibrium calculations have been carried out for many years and equilibrium constants for the reactions of importance in pulp and paper have been determined (Westall 1986, Allison 1991). Gaps in the data appear to exist for equilibrium between cations and pulp surface carboxylate groups. However, ion exchange experiments have determined relative activities of trace metals such as Na, Ca, Al, Mg etc. (Ohlsson 1975,). Korhonen et al. determined the effects of pH and ionic strength on the activities of specific ions using ion specific electrodes. The effects of chemical equilibrium conditions on fiber swelling have also been qualitatively measured. The numerous effects of system contaminants in highly closed white water systems have been extensively studied (Springer et. al.) The chemistry of alum salts and their effect on papermaking has been a major field of study for many years (Arnson 1982). The use of zeta potential to determine retention effects in papermaking is also widely discussed (Gerischer 1981). The presence of trace chlorinated components (Ota 1973) is also a field of very active study and is of considerable interest in this project.

The complex chemical equilibrium is of such important in environmental studies that a large data base has been generated for thousands of reactions and chemical species occurring naturally. The chemical equilibrium has been codified in several compute programs including MINEQL and MICROQL by John Westall at Oregon State University and by researchers at EPA, Athens, Ga. (Allison 1991). The equilibrium adsorption between trace metals and pulp fibers have not been brought into this formal framework. However, theoretical models and practical computer programs have been developed using several double layer electrostatic theories (constant capacitance, Gouy-Chapman, basic Stern Model and extended Stern triple-layer models) to determine adsorption onto amphoteric oxide surfaces. These models can determine for example the distribution for  $Al_2O_3$  in 0.1 molar  $NaClO_4$  at pH 7.

Mike Purdue at Georgia Tech and many others have studied the adsorption of ionic species onto carboxylate groups in humic substances to develop a theoretical and practical understanding of the distribution of trace ions in soils and ground water aquatic systems.

First the basic elements of the chemical equilibrium problem not including charged surfaces is described. Then the extension to charged surfaces for a constant capacitance model is described.

## BASIC DEFINITIONS IN CHEMICAL EQUILIBRIUM

The basic building blocks of the system are called MINEQL components referring to the data base and program developed by John Westall. His system consisted of 68 basic components ranging from very common ions such as  $H^+$ ,  $Ca^{++}$  to more unusual ions



such as threonine, isoleucine, nocardamine. The electron is also included as a component in order to handle oxidation-reduction reactions. An example would be reactions between various states of iron.

Complementing this set of MINEQL components are the MINEQL species consisting of thousands of complexes in various phases and types. Each complex is a combination of MINEQL components defined in terms of an equilibrium constant. Two phases of species are defined: soluble and solid species. Soluble species consist of both components and soluble complexes (products of reactions involving components). Solids are species of a fixed activity such as  $\text{CaCO}_3$  (s) or  $\text{CaOH}_2$  (s). Solids may be in two states, dissolved and precipitated. Precipitated solids are those solid phases which are present at a fixed activity.

Five types are defined: type 1 species consist of the MINEQL components since a component is also a species, type 2 consist of soluble complexes such as  $\text{HCO}_3^-$ , type 3 are precipitated solids not allowed to dissolve, type 4 are precipitated solids which are allowed to dissolve if the amount present becomes less than zero, type 5 are dissolved solids which are subject to precipitation if the solubility product is exceeded, and type 6 are species which are not to be considered at all, e.g. dissolved solids which are not subject to precipitation or the electron which does not exist in solution. Thus species not included do not appear in the final list of species but are taken into account in the equilibrium calculations.

#### STATEMENT OF THE BASIC EQUILIBRIUM PROBLEM

The problem of chemical equilibrium in an aqueous system can be described in mathematical terms as the set of equations:

$$C_i = K_i \prod_{j=1}^n X_j^{a_{ij}} \quad (1)$$

for  $i = 1, n$ .

$$Y_j = \prod_{i=1}^m a_{ij} C_i - T_j \quad (2)$$

for  $j = 1, n$  for which the solution is the set  $\{X_{j=1,n}\}$  such that  $\{Y_{j=1,n}\} = 0$  given  $K_i$ ,  $a_{ij}$  and  $T_j$ .  $T_j$  is the total analytical concentration of component  $j$  and  $Y_j$  is the difference

(error) between the imposed total analytical concentration of  $j$ ,  $T_j$ , and the amount of component  $j$  in all of the complexes as computed from the  $X_j$ 's. The solution to the problem is to determine  $X$  such that  $Y$  is zero.

Eq. 1 can be written in logarithmic form,

$$C_i^* = K_i^* + \sum_{j=1}^m a_{ij} X_j^* \quad (3)$$

where

$$\begin{aligned} C_i^* &= \log C_i \\ K_i^* &= \log K_j \\ X_j^* &= \log X_j \end{aligned} \quad (4)$$

In matrix form the linear system of equations becomes,

$$\bar{\bar{C}} = \bar{K} + \bar{\bar{A}} \bar{X} \quad (5)$$

Gas phases are also considered. To include a gas phase at a fixed partial pressure, it is necessary to include the gas as a type 3 species (fixed solid) and to specify its partial pressure. An example using  $\text{CO}_2$  (g) is as follows:

$$\begin{aligned} [H^+]^2 [CO_3^{-2}] K &= [CO_2(g)] = P_{CO_2} \\ \log K &= 18.0 \end{aligned} \quad (6)$$

Since every solid phase has an activity of one, the expression is rearranged to

$$[H^+] [CO_3^{-2}] \left[ \frac{K}{P_{CO_2}} \right] = 1 \quad (7)$$

and the effective constant for the phase at a fixed partial pressure becomes

$$\log K' = \log K - \log P_{CO_2} \quad (8)$$

To define a problem where an aqueous phase is in equilibrium with the atmosphere, the partial pressure of  $CO_2$  is set to  $10^{-3.5}$ .

The solution to the problem is found by making an initial guess for the  $X_i$  and iterating by a multidimensional Newton Raphson method to the roots of the equations.

The solution hinges on the computation of the Jacobean matrix consisting of the partial derivatives of  $Y$  with respect to  $X$ . Each element of the Jacobean matrix is given by  $Z_{jk}$

$$Z_{jk} = \sum_{i=1}^m a_{ij} a_{ik} \frac{C_i}{X_k} \quad (9)$$

The elements of  $Z$  are derived by expanding the partial derivatives for  $Y$  in terms of  $X$  using the above equations as follows:

$$\frac{\partial Y_j}{\partial X_k} = \sum_{i=1}^m \left( \frac{\partial Y_j}{\partial C_i} \right) \left( \frac{\partial C_i}{\partial X_k} \right) \quad (10)$$

Since

$$\frac{\partial Y_j}{\partial C_i} = a_{ij} \quad (11)$$

and

$$\frac{\partial C_i}{\partial X_k} = a_{ik} X_k^{a_{ik}-1} K_i \prod_{\substack{l=1 \\ l \neq k}}^n X_l^{a_{il}} \quad (12)$$

The final result is obtained by substitution and rearrangement of the two equations above.

For one or more solid (non-fibrous) phases the activity of activity of solid i,  $C_{ii}$  is constrained to 1. This allows the concentration  $X_{jj}$  to be determined from Eq. 1 as follows,

$$X_{jj} = \left[ K_{ii} \prod_{\substack{j=1 \\ j \neq jj}}^n X_j^{a_{ii,j}} \right]^{\frac{-1}{a_{ii,j}}} \quad (13)$$

$$Y_j = \sum_{\substack{i=1 \\ i \neq ii}}^m a_{i,j} C_i + a_{ii,j} S_{ii} - T_j \quad (14)$$

For the specific case of component jj, setting  $Y_{jj}$  to zero and solving for  $S_{ii}$  we obtain,

$$S_{ii} = \frac{-\left( \sum_{\substack{i=1 \\ i \neq ii}}^m a_{i,ii} C_i - T_{jj} \right)}{a_{ii,jj}} \quad (15)$$

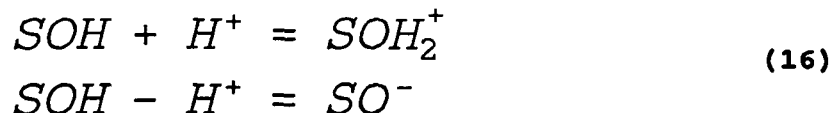
Here subscripts ii and jj are specific values of subscripts i and j respectively and not double subscripts.

Now substituting  $S_{ii}$  into the equations for  $Y_j$  the equations for the remaining Y's are independent of solid concentration  $S_{ii}$ . The problem is reduced by one dimension from  $n \times n$  to  $(n-1) \times (n-1)$ . After solving the reduced system of equations  $S_{ii}$  is solved from the above equation.

For multiple solid phases, the above procedure is extended in a sequential fashion. In each case the equations are transformed and the dimensionality of the system is reduced by 1 for each new phase.

### Equilibrium Between Trace Cations and Fiber Solids

Protonation/deprotonation reactions at amphoteric surfaces can be represented by the reactions



where SOH represents a surface hydroxyl group (e.g. FeOH, AlOH, TiOH). Since the surface may be at a potential  $\Psi$  with respect to the bulk of the solution, the coulombic energy of charged surface groups,  $zF \Psi$ , must be accounted for in the mass action laws for Reactions I and II in Eq. 16:

$$\begin{aligned} [SOH] [H^+] \left[ e^{\frac{-F\Psi}{RT}} \right] K_+ &= [SOH_2^+] \\ [SOH] [H^+]^{-1} \left[ e^{\frac{-F\Psi}{RT}} \right] K_- &= [SO^-] \end{aligned} \quad (17)$$

The positive charge on the surface can now be defined as the excess of positive groups over negative groups,

$$T_\sigma = [SOH_2^+] - [SO^-] \quad \left[ \frac{mol}{L} \right] \quad (18)$$

or in electrostatic units,

$$\sigma = T_\sigma \left( \frac{F}{Sa} \right) \quad (19)$$

In addition the charge may be defined from an electrostatic relationship (for instance a Helmholtz constant capacitance).

The problem of computing equilibrium including adsorption onto a charged surface becomes one of incorporating the above equations into the framework of equilibrium presented above.

The first step is to add the electrostatic potential to the set of chemical components. The "total concentration" of this new component is written as

$$T_{\sigma} = C \Psi \left( \frac{sa}{F} \right) \quad (20)$$

where this quantity is in molar units.  $\Psi$  is the electrostatic potential,  $F$  is the Faraday constant (96487 C/mol),  $s$  is the solids concentration (consistency) and  $a$  is the specific surface area of the solid (derived from CSF),  $C$  is the capacitance.

The surface hydroxyl concentration  $SOH$  must also be added to the component list. The concentration of this component for a pulp surface is proportional to the specific surface area, the pulp consistency and to the carboxylate concentration. The units of  $SOH$  are also in moles/l. For mass action equations for the basic system involving  $SOH$ ,  $H^+$ ,  $OH^-$ , and electrostatic potential are given by

$$\begin{aligned} [OH^-] & \quad [H^+]^{-1} \quad K_1 = [OH^-] \\ [SOH^{2+}] & \quad [SOH] \left( e^{\frac{-F\Psi}{RT}} \right) [H^+] \quad K_2 = [SOH_2^+] \quad (21) \\ & \quad [SOH] \\ [SO^-] & \quad [SOH] \left( e^{\frac{-F\Psi}{RT}} \right) [H^+]^{-1} \quad K_3 = [SO^-] \end{aligned}$$

The Jacobian elements of the system are the same as described previously except  $z_{\Psi\Psi}$ . Thus

$$\begin{aligned} Z_{j,k} &= \sum_{i=1}^n \left( \frac{a_{i,j} a_{i,k} C_i}{X_k} \right) \\ Z_{\Psi,\Psi} &= \sum_{i=1}^n \left( \frac{a_{i,\Psi} a_{i,\Psi} C_i}{X_{\Psi}} \right) + C \left( \frac{sa}{F} \right) \left( \frac{RT}{FX_{\Psi}} \right) \quad (22) \end{aligned}$$

which includes an extra term for the electrostatic potential.

## Redox Reactions

Oxidation-Reduction (Redox) reactions are also handled through the use of the electron as an additional component. Normally the  $p\epsilon$  defined as

$$p\epsilon = -\log_{10}\epsilon \quad E_H = 0.59 \log_{10}\epsilon \quad (23)$$

will be fixed at a given value for a computation. Thus the electron is included as a type 3 (fixed component) species. If the  $p\epsilon$  is to be calculated, the electron must be defined as a type 6 species (not included). Basic data for 17 redox reactions are provided. These include reactions involving iron, copper, mercury, sulfides, manganese, chromium, sulfates, cobalt and tin.

## Ionic Strength

Normally the equilibrium is assumed to be independent of ionic strength at high dilutions. However, an ionic strength correction can be determined based on the Davies approximation in the following way. The Davies approximation for the activity coefficient  $f$  of an ion in a medium of ionic strength is

$$\log f = -AZ^2 \left( \frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.2\mu \right) \quad (24)$$

where  $Z$  is the ionic charge and  $A$  is a function of temperature and dielectric constant (approximately 0.5 for water at 25 C).

The ionic strength is defined by

$$\mu = \frac{1}{2} \sum_i Z_i^2 C_i \quad (25)$$

where  $C_i$  is the concentration of species  $i$  and  $Z_i$  is the ionic charge of species  $i$ .

The equilibrium constant for a reaction

$$a_1 X_1 + \dots + a_n X_n = C \quad (26)$$

where a's are stoichiometric coefficients defined by

$$[X_1]^{a_1} \dots [X_n]^{a_n} K = [C] \quad (27)$$

where the a's represent activity. This can be written in terms of activity coefficients f. After rearrangement this becomes,

$$[X_1]^{a_1} \dots [X_n]^{a_n} \frac{f_1^{a_1} \dots f_n^{a_n}}{f_c} K = [C] \quad (28)$$

We can define a constant corrected for ionic strength as

$$(29) \quad K^* = \frac{f_1^{a_1} \dots f_n^{a_n}}{f_c} K$$

Using the above definitions for ionic strength and log f,  $K^*$  can be defined as

$$\log K^* = \left[ \sum_j a_j Z_j^2 - \left( \sum_j a_j Z_j \right)^2 \right] A \left( \frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.2 \mu \right) + \log K \quad (30)$$

#### Solution Technique

The Newton Raphson method for the determination of the roots of the equation

$$y(x) = 0 \quad (31)$$



yields the following iterative formula for the  $n+1$  st iteration for  $x$  given the value of  $x$  and  $dy/dx$  at the  $n$ th iteration,

$$X^{n+1} = X^n - \frac{y^n}{\left. \frac{dy}{dx} \right|_{x^n}} \quad (32)$$

The matrix equation

$$(33) \quad \bar{Y}^n = \bar{Z}^n (\bar{X}^n - \bar{X}^{n+1})$$

where  $Z$  is the Jacobean of  $Y$  with respect to  $X$  is solved for  $X^{n+1}$  by Gaussian elimination.

Convergence on the solution must include checks on physically meaningless negative solutions and other anomalies.

When the test for  $Y_j$  sufficiently close to zero is satisfied, the system is solved. Since each  $Y_j$  is the sum of terms which vary widely in order of magnitude, the convergence criterion is chosen to reflect the magnitude of  $Y_j$  relative to the maximum of the terms of which  $Y_j$  is the sum. Thus the criteria for convergence is

$$\frac{|Y_j|}{\max(Y_j)} \leq \epsilon \quad (34)$$

where  $\max(Y_j)$  is the maximum of the absolute values of the set of terms

$$(a_{i,j}C_i) \quad i=1, m ; \quad T_j \quad (35)$$

### Stand-alone Equilibrium Programs

Three stand-alone public domain programs were obtained for this project. All programs included source code and sample data files and extensive documentation and theory. MINEQL, developed by John Westall, is a fortran program which computes multi-phase equilibrium but does not include solid adsorption. This program also includes an extensive data base. MICROQL is a program in BASIC which performs only solid phase adsorption using one of four adsorption isotherm models. A third more comprehensive equilibrium code, MINTEQA2/PRODEFA2 developed by Jerry Allison, David Brown

and Kevin Novo-Gradac of the Environmental Research Laboratory, EPA, Athens, GA. was also obtained. This program is a comprehensive geochemical equilibrium speciation model capable of computing equilibria among dissolved, adsorbed, solid and gas phases. All three stand-alone programs are being run separately for standard problems to validate the MAPPS calculations.

### **MAPPS Equilibrium Calculations**

The MAPPS equilibrium model is based primarily on the MINEQL source code and databases with supplemental models for adsorption taken from MIQROQL. The large number of MINEQL components was reduced to a feasible set of 46 components. In order to make the equilibrium calculations feasible in MAPPS, all of these components were added to the default stream definition of the PULPING stream. This redefinition of the PULPING stream was done as part of a general restructuring of the MAPPS stream structures described in a second report.

The components selected for the MAPPS equilibrium, shown in Table I, can be changed or expanded in the future.

Table I. MAPPS Equilibrium Components

Symbol	Symbol	Symbol
Ca(2+)	Zn(2+)	TiO(2+)
Mg(2+)	Al(3+)	NH3
K+	Cs(+)	S(2-)
Na+	Cu(+)	SiO2(OH)2 (2-)
Fe(3+)	H+	S2O3(2-)
Fe(2+)	e-	CN-
Mn(2+)	CO3(2-)	AC-
Cu(2+)	SO4(2-)	ACAC-
Ba(2+)	Cl-	CIT(4-)
OX-	ENO	GLU(2-)
SAL(2-)	DIP0	NTA(3-)
DCTA(-4)	SUSAL(3-)	EDTA(4-)
PHTH(2-)	PHE(-)	SCN-
NH2OH	NO3-	TRIS
surface charge	SOH	

Some of the more unusual components are defined in Table II.

Symbol	Name
AC-	acetate
ACAC-	acetylacetone
CIT(4-)	citrate
OX-	oxylate
SAL(2-)	salicylate
EN0	ethylenediamine
DIP0	dipyridyl
GLU(2-)	glutamate
NTA(3-)	nitrilotriacetate
EDTA(4-)	ethylenediamine-tetraacetate
DCTA(4-)	1,2 diaminocyclohexane tetraacetate
PHTH(2-)	phthalate
PHE-	phenylalanine
SCN-	thiocyanate
TRIS	tris(hydroxymethyl)-aminomethane
SUSAL(3-)	sulfosalicylate

Based on the smaller set of component, the several thousand equilibrium reactions in the MINEQL data base defining the MINEQL species was reduced to 470 potential reactions involving MAPPS components. Of the 470 species defined by these reactions, only a small portion are included in the MAPPS stream definition. Those species which are not in the MAPPS stream definition must be handled in a special way which is described below. For MINEQL species which are MAPPS components, the calculated species from the equilibrium are passed to the outlet stream directly.

A total of 104 new MAPPS components were created for the equilibrium calculations. Of these 24 are equilibrium components and 80 are equilibrium species. In order to properly handle precipitates, all species created by precipitation are passed as MAPPS components. Otherwise, separation of precipitates from solution could not be accomplished.

Those species which are not in the stream definition are "decomposed" into MAPPS-MINEQL components and added to the equilibrium mixture. Thus, the calculated stream from the equilibrium may not be the same as the actual equilibrium calculation. However, the calculated values are sent to a report each time the equilibrium is successfully completed.

Because of the complex nature of the chemical equilibrium and the potential for slowing down the simulation, it was decided to isolate the calculations into a single MAPPS block called EQUIL01. When an equilibrium composition is needed in a flowsheet, the EQUIL01 block is inserted into the flowsheet at that point.

The module computes the equilibrium and determines the pH of the entering stream. Titrations are handled by mixing acid or base with the stream entering the EQUIL01 block. To titrate to a desired pH, a flow control block, PCONT2, should be placed after EQUIL01 to adjust the acid or base flow until the pH from EQUIL01 reaches the desired value.

### New Data Structures

The stand alone MINEQL program reads in a data file describing the MINEQL components and the various species reactions to consider. In the MAPPS implementation, the input functions are performed automatically by EQUIL01. Thus, the entering stream may contain a wide variety of MAPPS components such as equilibrium components, species and components which do not participate in the equilibrium such as fibers, fines, dissolved lignin,  $\text{Cl}_2$  etc. Species which are adsorbed onto pulp fibers are treated as separate components. These will be discussed later.

Each MAPPS component which is to participate in the equilibrium must be identified as either a MINEQL component or a MINEQL species. This is accomplished by a new phase code in the MAPPS stream/component data base. Once the MAPPS component is identified as a species, a second data file is entered to determine the reaction which defines that species. This data file (MINEQL.DAT) defines a mapping between MAPPS component ID's and MINEQL ID's and stoichiometry. The stoichiometry of that reaction then defines the breakdown of that species into the basic components. Thus, the concentration of the components is incremented by "breaking down" each of the species in the entering stream. Hydronium ion is handled as a special component. If it is not present in the inlet stream, its concentration is computed from the  $\text{OH}^-$  concentration by assuming equilibrium. In other words,  $\text{H}^+$  must be a component of the equilibrium in all aqueous systems.

If pulp fibers are present, the surface charge and carboxylate concentration ( $\text{SOH}$ ), are also entered as components. The carboxylate concentration is entered through the new PAT variable CRBOX which will be defined initialized in other modules. The surface charge is based on the entering consistency and specific surface area of the fiber.

Once the component ID's and total analytical concentrations are obtained, the species are determined from a third data base, THRM2.DAT, which contains the 480 reactions with equilibrium constants for each. Depending on the components present the program selects the species and equilibrium constants for each from the data base. The ionic strength is then computed and the program then write a report summarizing the input conditions. The charges of each MINEQL component are read from a fourth new data base called IONIC.DAT.

The internal calculations are performed in a new utility module called EQUIL which is called through the MAPPS physical property interface. This method separates frequently used calculations from module input. In this way it will be possible to have other modules call the utility to compute local equilibrium as part of their internal calculations.

After the solution to the equations is obtained, the species determined by the equilibrium are compared to the list of MAPPS components to determine whether they are passed to the outlet stream or decomposed into MINEQL components. Once this procedure is accomplished, the final concentrations of MAPPS components are provided by EQUIL. The concentrations determined by EQUIL are then converted into mass flows in EQUIL01 and passed to the outlet (calculated stream). Module output includes the calculated pH which is put into position 6 of the outlet stream. The equilibrium carboxylate concentration is passed to the outlet performance attribute CRBOX.

The results of the equilibrium are added to the output in the special report file.

### Module Testing

The equilibrium module is currently undergoing testing in a papermachine flowsheet model and the results compared with output from MINEQL using standard cases. For the base case of  $\text{Ca}^+$ ,  $\text{CaCO}_3$ ,  $\text{CO}_3^{-2}$  and  $\text{H}^+$  and adsorption into fibers the results agree.

### CONCLUSIONS/RECOMMENDATIONS

When fully tested the new equilibrium feature of MAPPS will provide a sound basis for significant new studies in areas of corrosion, wet end chemistry effects and paper property effects previously beyond the reach of MAPPS or any other pulp and paper simulation program.

### FUTURE ACTIVITY

Additional cases will include the presence of a carbon dioxide atmosphere, multiple metal cations, variable pH and redox reactions.

This module will soon be "entered into service" to simulate the effects of closing up a papermachine white water system as part of a proprietary project. After testing the module and property system will be available in future versions of MAPPS

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