

STATUS REPORTS
to the
W E T E N D C H E M I S T R Y
PROJECT ADVISORY COMMITTEE

March 6 - 7, 2000

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

ANNUAL PROGRAM REVIEW

WET END CHEMISTRY

March 6-7, 2000

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(For IPST Member Company's Internal Use Only)



February 4, 2000

TO: MEMBERS OF THE WET END CHEMISTRY PROJECT ADVISORY
COMMITTEE

Attached for your review are the Status Reports for the projects to be discussed at the Wet End Chemistry Project Advisory Committee meeting being held at the Institute of Paper Science and Technology. The Program Review is scheduled for Monday, March 6, 2000, from 1:00 p.m. - 3:30 p.m. and the PAC Committee Meeting will meet on Tuesday, March 7, from 1:00 p.m. to 4:15 p.m.

We look forward to seeing you at this time.

Sincerely,

Sujit Banerjee, Ph.D.
Professor & Senior Research Fellow

SB/map

Attachments

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**WET END CHEMISTRY
PROJECT ADVISORY COMMITTEE MEETING**

March 6, 2000

**Institute of Paper Science and Technology
Atlanta, Georgia**

PROGRAM REVIEW AGENDA

Seminar Room

12:00 p.m.	Lunch	
1:00 p.m. - 1:10 p.m.	Opening Remarks Review of Antitrust Statement and Confidentiality Statement	Charlie Neal
1:10 p.m. - 1:30 p.m.	Welcome from Vice President of Research	Gary Baum
1:30 p.m. - 1:40 p.m.	Overview of IPST Wet End Chemistry Research	Sujit Banerjee
1:40 p.m. - 2:30 p.m.	Project F043 Wet End Chemistry in Closed Water	Yulin Deng
2:30 p.m. - 2:40 p.m.	Break	
2:40 p.m. - 3:30 p.m.	Project F027 Wet End Chemistry Control Advisor	Yulin Deng and Bill Scott
3:30 p.m.	Adjourn	

Note: Dinner is provided at 5:30 p.m.

**WET END CHEMISTRY
PROJECT ADVISORY COMMITTEE MEETING**

March 7, 2000

**Institute of Paper Science and Technology
Atlanta, Georgia**

COMMITTEE DISCUSSIONS AGENDA

Room 173

12:00 p.m.	Lunch	
1:00 p.m. - 1:10 p.m.	Convene Antitrust Statement Confidentiality Statement New Members Acceptance of Fall, 1998 Minutes Review of Agenda	Nigel Sanders
1:10 a.m. - 2:10 p.m.	Subcommittee discussion of Yulin Deng's project	Committee
2:10 p.m. - 2:20 p.m.	Break	
2:20 p.m. - 3:30 p.m.	Subcommittee discussion of Bill Scott's project	Committee
3:30 p.m. - 4:00 p.m.	Portfolio Management/Research Lines	David Orloff
4:00 p.m. - 4:15 p.m.	Final Discussion/Adjourn	

TABLE OF CONTENTS

	Page
Project F043	Wet-End Chemistry in Closed Water 1
Project 27	Wet End Chemistry Control Advisor (WECCA) 33

WET-END CHEMISTRY IN CLOSED WATER

STATUS REPORT

FOR

PROJECT F043

Yulin Deng (PI)
Yufeng Xu

March 6 – 7, 2000

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, Georgia

DUES FUNDED PROJECT SUMMARY

Project Title: WET-END CHEMISTRY IN
CLOSED WATER
Project Number: F043
PAC: Wet End Chemistry

Project Staff:
Principal Investigator: Yulin Deng
Research Support Staff: Yufeng Xu

FY 99-00 Budget: \$88,000

Time Allocation:
Principal Investigator: 25%
Research Support Staff: 65%

RESEARCH LINE/ROADMAP: Line #12: Reduce pulp and paper product costs by 25% through increased productivity and improved pulp, paper, and product uniformity achieved with new developments in sensors and process controls. Increase paper-machine productivity by 30% over 97's levels via focusing on breakthrough forming, dewatering, and drying concepts.

PROJECT OBJECTIVE: Identify the metal ions, inorganic anionics, organics, fines, conductivity, cationic demand, surface tension, pH, and zeta potential of fine particles in the filtrate of thick stock of BLK and in the white water.

1. Study the interaction between cationic polymers and anionic organics. This includes studying:
 - (a) what the real anionic trash species are and which anionic substances do not contribute to charge neutralization
 - (b) the relationship among cationic demand, zeta potential, and total soluble organic content
 - (c) the reaction equilibrium and kinetics of charge neutralization reactions. The relationship among the structure, charge density of polymers, anionic substances, and molecular weights
2. Study the competition between the charge neutralization and polymer adsorption.

PROJECT BACKGROUND: This project was started in July 1999. The Project Advisory Committee (PAC) believed this project would significantly benefit the paper industry. Many useful suggestions were given during the PAC meeting in the fall of 1999 as PAC members expressed that the objectives of the research program should be well defined and that an extensive literature search was needed. Dr. Yulin Deng also had many discussions with the Chair and Vice-Chair about the objectives and focus of the program. Since this project was started, we have completed a literature search, review, and member-company survey. The contaminants in BLK furnish have been analyzed. The study of the interaction among cationic polymers and these contaminants is under way.

MILESTONES: *There are four milestones for FY99-00.*

1. *Project initiation: This includes the literature search and review, member company survey, experimental design, and equipment setup. This milestone was accomplished in the first quarter of the project (July-September, 1999).*
2. *The chemical analysis of contaminants in BLK: This was done in the second quarter of the project (October-December, 1999).*
3. *The interaction between cationic polymer and anionic trash: The experiments were started in the second quarter of FY99-00. The results are given in this report.*
4. *The competition between charge neutralization reaction and adsorption: the experiments have been designed.*

DELIVERABLES:

1. *A model for predicting the buildup of contaminants in closed white water will be delivered.*
2. *The information about the charge neutralization between cationic polymer and anionic trash will give a guideline for our member companies to control wet-end chemistry, particularly for white water closure systems.*
3. *By developing a fundamental understanding of the wet-end chemistry in closed white water, the member companies can significantly save chemicals and improve product quality. It will also improve the paper-machine runnability by reducing contaminant deposition.*

SCHEDULE:

Tasks	1999 Jul- Sept	1999 Oct - Dec	2000 Jan- Mar	2000 Apr- Jun
Literature review and member-company survey	---- X			
Contaminants analysis		----- X		
Study of the interaction between cationic polymer and anionic trash		----- X	----- X	---- X
Study of the competition between charge neutralization reaction and polymer adsorption				---- X

SUMMARY: *Much research has been focused on water closure and retention. Some paper mills claim that they have reached 100% water closure. But in America, this is only true for paperboard production. The buildup of inorganic and organic electrolytes in closed white water system has been reported, but the data are case specific. Although a mathematical model exists in the literature, this model needs to be modified.*

It is generally known that the buildup of electrolytes and anionic trash will affect retention when an ionic retention system is used. However, some questions remain unanswered. These questions include:

- 1) Can all anionically charged soluble organic substances in white water be categorized as "anionic trash"? Which substances, such as lignin, hemicellulose, fatty acid, etc., have the most detrimental effect on retention-aid performance?*
- 2) When a charge neutralizer such as polyDADMAC [poly(diallyldimethylammonium chloride)] is used, what is the ratio of neutralizer reacted with anionic trash? How much of the neutralizer will adsorb onto fibers, fines, and fillers? Will the adsorbed neutralizer positively or negatively affect the retention?*
- 3) Does the anionic trash effect solely depend on the charge characteristics or does it also depend on the chemistry of the organic substances?*
- 4) Which filler is the most effective for adsorbing and removing the anionic soluble substances?*
- 5) Are there significant differences between fresh fillers and organic contaminated fillers?*

To develop an effective retention program, it is important for papermakers to know which anionic organic substances are the most detrimental to retention and which mechanisms are involved. For example, if lignin strongly interacts with cationic retention aids but fatty acid does not, the cationic retention aids may still be used in fatty acid-rich white water. If this is true, the clarification of white water should focus on removing lignin rather than fatty acids.

It is also important to know what competition reactions exist among cationic processing polymers, fibers, fines, and fillers because this fundamental understanding will help papermakers to optimize the polymer systems and the addition point of the polymer additives.

The general conclusions from this study include:

- 1. Retention is very important for reducing the buildup of contaminants in white water. If 50% of the contaminants can be removed from the system by retention, adsorption or clarification, the buildup will not be significantly.*
- 2. Not all of the anionic materials will stoichiometrically react with cationic polymers. The lower the molecular weight of anionics, the less reactive they are with cationic polymers.*
- 3. Cationic demand can be used for controlling the electrostatic properties of pulp furnish. However, cationic demand usually is not equal to the total amount of anionics in pulp furnish.*

PROJECT PROGRESS, EXPERIMENTAL RESULTS AND DISCUSSION

PART I: MEMBER-COMPANY SURVEY: In order to focus on the needs of the member companies, a survey was sent to the PAC members in April 1999. Eight PAC members responded. The following is the summary from the survey.

1. Fine paper, tissue, paperboard, and coated paper are the major products. Most of the fine-paper and coated-paper mills add fillers. Most of them use dry-strength agents, and some of them use wet-strength agents.
2. Cationic retention aids are the most widely used retention aids. Only one fine-paper mill, one paperboard mill, and four coated-paper mills use microparticle retention aids. No one uses PEO as a retention aid.
3. Most mills use fresh water in the range of 1,000 to 10,000 gallons/ton. No mills are operating at a fresh water consumption of less than 1,000 gallons.
4. Most paper mills have significantly reduced their water consumption in the last two years, and many mills would like to further reduce water consumption in the next two years.
5. Most paper mills use white water for thick stock dilution; also, some mills use white water for wire cleaning. If there were extra water, 6 companies said they would send them to pulping plants, 2 companies said they would send the water to bleaching mills, and 4 said they would discharge it.
6. The problems they are considering are in the order of microbiology > deposits > reduced efficiency of wet-end chemicals > machine runnability > reduced paper strength > corrosion.

The suggested research areas are broad. The following issues were addressed in the member-company survey.

- a. Temperature in effluent
- b. Reduced efficiency of wet-end chemicals
- c. Importance of good first-pass retention
- d. Cleaning issues
- e. Bacteria buildup and biological deposition
- f. Chemical deposition
- g. Increased conductivity, anionic trash, dirt, salts
- h. Decreased performance of sizing chemicals
- i. Method for monitoring the buildup of dissolved colloids in streams
- j. Recommendations for alternatives to current chemicals as machines are closed
- k. The impact of white water closure on the use of wet-end cationic starch that is needed for strength
- l. Models predicting soluble chemicals, organics, and biological buildup
- m. Identification of major materials in white water
- n. Impact of major materials on retention and sizing
- o. Ways to convert troublesome organics to inert or beneficial species
- p. Wet-end polymers that are active at high salt concentration.

PART II: LITERATURE REVIEW

The Buildup of Contaminants in Closed White Water System

General review

To study the effects of white water closure on wet-end chemistry, it is essential to know how the detrimental substances build up in white water. The paper machine white water system contains a large variety of suspended, dissolved and colloiddally dispersed inorganic and organic substances. Some of these substances are introduced via the fresh water supply, for example, salts and humic acids, but the majority originates from raw materials. Suspended substances are mainly fines and fillers that are not fixed on the fiber as well as those coming with recycled fibers, such as large ink and stickies particles. Colloidal and dissolved substances consist of salts and various water-soluble organic constituents of wood, like hemicellulose and lignin derivatives and carryover chemicals from pulping and bleaching processes. In addition to these, white water contains process additives. These can be sizing agents, wet/dry-strength agents, surfactants, defoamers, dyes, and also retention and drainage aids that have not been completely fixed on the fibers and fillers.

In an "open" water system, where a relatively large percentage of water is discharged, there is a continuous and substantial purge of dissolved and suspended substances from the system. Another portion of the substances is removed via paper. As the mill closes up the water system by circulating a greater percentage of its water, the dissolved and suspended solids will increase according to the degree of retention of that material in the paper sheet itself. The concentration of these substances is largely dependent on the degree to which the wet-end system of the paper machine is closed. When present in sufficient concentrations, a large proportion of these substances will cause severe production difficulties such as increased deposits, foaming, biological activity, corrosion, poorer retention and web formation, and they will also impair paper strength properties.

Buildup level

Totally closed water systems are found in paperboard production. Linerboard mills typically don't have extensive treatment facilities already in place, and their product quality is less demanding than for many other paper products. Even in completely closed mills, slightly over 1 m³/ton of fresh water is required to make up the water loss in the drying section and evaporation process [1, 2]. Paper machines that use less than 750 gallons (~3 m³) of fresh water for a ton of paper are sometimes classified as "100% closed" [3].

With completely closed operation, the level of dissolved solids in white water typically rises to 10,000 mg/L or higher [4]. In a linerboard mill that uses 100% post-consumer fibers (OCC and mixed waste), the total dissolved solids in white water increased from less than 2000 ppm for a fairly open system to around 14,000 ppm after fresh water usage was reduced to a level of 1.5 m³/ton [5]. In recycled gypsum linerboard mill, the dissolved solids rose up to 15,000 ppm after closing the white water system [6]. Table 1 is a summary of the water analysis of nine fully closed paperboard mills. The final equilibrium concentrations of these substances depend on the degree of closure. The concentrations of these materials increase dramatically only after the fresh water use is

reduced to less than 20 m³/ton [8]. Little information was found on the buildup levels in newsprint and fine-paper mills.

Table 1. Reported contaminants in white water [7].

	Min.	Max.	Ave. (9 mills)
Cl (ppm)	204	708	326
Hardness (ppm)	170	1370	596
Na (ppm)	1580	6600	3643
Ca (ppm)	121	1190	587
Mg (ppm)	49	190	119
Mn (ppm)	1	5	2
Conductivity (umhos)	7990	18400	12790
PH	5.6	7.7	6.9
Lignin (ppm)	1012	11400	1019
TDS (ppm)	7160	12500	9620
TSS (ppm)	237	12840	4084
TOC (ppm)	7780	7860	9285

Laboratory work was also done to monitor the buildup. Heller and his coworkers [9] ran a pilot paper machine for 4 days under closed white water conditions. All the white water off the paper machine was reused, and the water in the paper web was the only water that left the system. The paper grade manufactured was an 89 g/m² high-opacity offset paper. No other experimental details, such as thick stock consistency, filler and wet-end chemicals were given. Ash, acidity, chloride, sulfate, calcium, magnesium, manganese, aluminum and iron concentrations in headbox, silo and machine chests were monitored. Many of these components did not reach equilibrium concentrations during the run and they were fitted to a first-order exponential function. The functions were extrapolated to very long times, and the associated concentrations were used as equilibrium concentrations. The obtained equilibrium concentration data in the headbox are given in Table 2. Although these are the only laboratory data reported in the literature, it was not clear how many cycles of the white water had been passed through the paper machine.

Table 2. Inorganic substances in the white water obtained from a fully closed pilot machine operating 4 days [9].

Inorganic substance	Concentration, mg/L
Ash	2583
Chloride	48
Sulfate	2968
Calcium	126
Magnesium	41
Manganese	5
Aluminum	117
Iron	45
Hardness	1224

Buildup prediction

What is important to papermakers is how to predict the buildup level once a specific mill white water system is closed. Heller and his coworkers [9] also simulated a steady-state buildup level of the closed paper machine under different first-pass retentions, ranging from 0 to 100% at an interval of 10%, and three closure levels (0, 6,190 and 36,940 gal fresh water per ton of paper) using the data obtained from the pilot operation mentioned above. The simulation was made using a general purpose simulation program, GEMS (Edwards, L. L., Generalization Energy and Material Simulator, developed at the University of Idaho). The results from their study indicated that for large values of first-pass retention, there is little change in the ash concentrations when the closure degree is increased, while at the lower end of the retention scale a small change in the water closure degree produces a large change in concentration. Thus, it was concluded that for all degrees of closure, high equilibrium component levels were predicted only at the levels of first-pass retention less than 25%.

Alexander and Dobbins [10] defined a term called enrichment factor, which provides an understanding of nonsubstantive materials buildup in closed white water:

$$EFr = [1/(1 - r)]$$

Enrichment factor is defined as the ratio of the headbox concentration of a given species at r degree of recycling to that of zero recycling (completely open). As white water is circulated, some of the dissolved solids return to headbox. The greater the fraction of water recycled, the higher the equilibrium concentration will be. For example, the enrichment factor increases from 50% recycling ($EF_{0.5} = 2$) to 80% recycling ($EF_{0.8} = 5$) or to 90% ($EF_{0.9} = 10$). This allows the mills to predict the increase in dissolved solid content that accumulates in circulated white water system. However, the limitation of this enrichment factor theory is that it can only be used for substances that do not adsorb on the solids in pulp suspensions. For example, this model cannot be used to predict the buildup of anionic trash because there is strong adsorption of anionic trash on fillers, and the filler retention will be significantly different from mill to mill. Therefore, the Alexander's model needs modification to apply it to a more complicated system.

A major concern about white water closure is that the dissolved materials will reach their solubility and eventually precipitate out from the water [7, 10, 11]. The accumulation of the detrimental substances is limited by their solubility, meaning that they agglomerate and are seeded onto the active surfaces of the solid materials and are finally removed via paper. In the worst cases, they deposit together with other components of the paper stock and cause runnability problems [12].

Heller and his coworkers [9] noticed that the predicted headbox Fe^{3+} level is much greater than that allowed by the solubility of Fe at pH 4-5. They expected that most of the iron predicted by the model would be present in a colloidal manner and adsorbed onto filler and fibers. Although the above published works addressed the possibility that the concentration of dissolved substances can be higher than their solubility and eventually precipitated from white water as the closure degree increases, there is no direct proof from either an experimental study or a theoretical model found in the literature.

Effect of Anionic Trash on Retention

Interaction of anionic trash with cationic polymer retention aids

There is a large amount of negatively charged dissolved and colloidal substances present in pulp furnishes. Most of these substances are residual wood derivatives coming from pulping and refining processes, but anionic papermaking aids also contribute. In addition, a small amount of anionic substances comes from fresh water. These anionic colloids and wood polymer materials are often called "anionic trash", since these have a strong anionic charge. This term has been used for many years, and still no papermaker really knows what the "anionic trash" in his paper stock actually consists of. Just as paper stocks differ distinctly from one paper mill to another, or even from one paper machine to another, anionic trash is usually different from case to case. In general, a paper mill using wood pulp and waste paper has the highest anionic trash content. Chemically, these detrimental substances can be of a different organic and inorganic nature and of different origin. Materials commonly considered to be anionic trash are shown in Table 3. A similar table can also be found in a paper authored by Bley [13].

It has been generally known that the interactions between organic anionic trash and cationic polymers result in a decrease in the efficiency of processing polymers, such as sizing agents [1], wet strength agents [14] and polymeric retention aids [15-17]. In the worst cases, cationic retention agents cannot be used unless the anionic trash has first been inactivated [15-17]. Studies have also shown that the addition of model hemicelluloses [18, 19], lignin [12] and humic acid [12, 20, 21] increases the cationic demand of fine paper suspensions and decreases the effectiveness of cationic retention/drainage aids. Linhart et al. [12] judged the influence of detrimental substances onto cationic polymers by comparing the drainage effect of several retention aids. The retention aids they tested are listed in Table 4. They are all high-molecule-weight polymers. Commercial TMP pulp was used and the drainage time was determined by measuring the time a given amount of white water needed to pass the Schopper-Riegler freeness tester. The detrimental substances added to the stock were lignosulfonate, kraft lignin, water glass (sodium silicate), humic acid and a hot water extract of spruce with a COD of 2200 mg/L. Their results showed that all cationic polymers are impaired, but the highly cationic pure PEI and pure polyquaternary polymer were least influenced by the anionic materials. If a large amount of detrimental substances is present, all products are blocked.

Table 3: Common anionic substances in paper white water [12].

Chemical Nature	Origins
Sodium silicate	Peroxide bleaching, deinking, waste board
Polyphosphate	Filler dispersant
Polyacrylate	Filler dispersant
Organic acids	Pitch dispersant
Carboxymethylcellulose	Broke (coated)
Starch	Waste paper, broke, strength agents
Humic acids	Fresh water
Lignin derivatives	Kraft pulp, wood pulp
Lignosulfonates	Sulfite pulp
Hemicellulose	Wood pulp
Fatty acids	Wood pulp

Table 4. Polymer retention aids used in Linhart's study [12].

Retention aid	Amount applied, %
Pure polyethyleneimine	0.08
Modified polyethyleneimine	0.08
Polyamidoamine	0.08
Low cationic polyacrylamide	0.04
Medium cationic polyacrylamide	0.04
High cationic polyacrylamide	0.04
Polyquaternary polymer	0.08
Nonionic polyvinylamide	0.04

It is generally believed that the mechanism involved in the interaction between cationic polymers and anionic trash is charge neutralization. Many researchers have been focused on the relationship among the total cationic demand, anionic trash, zeta potential, and surface charge. It is expected that the inhibition of cationic retention aids by anionically dissolved materials is caused by the formation of inactive complexes [22]. Pelton et al.[22] studied the different behaviors of PEI in washed pulp, dialyzed pulp and untreated pulp. They suggested that most of the cationic retention aid would react with the dissolved anionics before having an opportunity to adsorb onto the surfaces of the dispersed solids. This view is confirmed by the observation that PEI influenced the electrophoretic mobility of the fines only when the pulp had been washed. The direct reaction between cationic retention polymer and anionic contaminants was also shown by Strom, Pilipp and Horn [23-26]. Strom and his coworkers [23,24] studied the complex formation between cationic polyethyleneimine, polyacrylamide and the anionic model compounds such as pine xylan and lignin sulphonate. The experiment was carried out by mixing anionic and cationic solutions, and the complex formation was determined by measuring the changes and turbidity of the system. The interactions were found to result in soluble complexes, colloids or macroscopic precipitates, depending on the molecular weight, polymer ratio and charge character of the complex formed. The complex formation between xylan and a cationic polymer was found to be non-stoichiometric and that between high-molecule-weight lignin sulphonate and a cationic polymer was stoichiometric. Similarly, the complex formation between cationic polymer and humic acid/fulvic acid was studied by Narkis and Rebhun [20, 21]. The reaction was found to be stoichiometric. They also found that the presence of organic matter in solution or as a complex on the mineral clay particle surface inhibits the process of flocculation by cationic polymer.

Ahrabi et al. [27] studied the complex formation kinetics using a stopped flow spectrophotometer. They found that the formation of a solid polyelectrolyte complex between cationic polyacrylamide (CPAM) and lignin sulphonate is faster than that between xylan and CPAM. The half-time of the reaction between CPAM and lignin sulphonate increased with the charge density of the CPAM. The authors proposed that the interaction involves a two-step formation process. The first step includes formation of small particles and is mainly diffusion controlled. In the second step, the primary particles agglomerate, and this is controlled by the colloidal stability of the system.

Linhart [12] indicated that the detrimental substances interact with wet-end chemicals not only through ionic mechanisms but also through nonionic mechanisms. They studied the effect of anionic lignosulfonate, kraft lignin and humic acid on the drainage

efficiency of a nonionic high-molecule-weight polyvinylamide, together with some other cationic polymers. Polyvinylamide has no motivation to form a complex with these anionic materials on an electrostatic basis. Nevertheless, its drainage effect is greatly inhibited by the lignosulfonate. The authors thought this was an indication that nonionic interactions are probably of about the same importance as electrostatic polymer complex formation. Experimental results support this conclusion by showing that the inhibition of cationic retention aids by detrimental substances is not proportional to charge density, even though the polymers have the same structure and the same molecular weight. Laleg and Pikulik [28] studied the effect of dissolved materials and fines in white water on the efficiency of cationic aldehyde starch, and they indicated that the principal deactivators of cationic polymers are fines rather than the soluble wood components. This conclusion was based on the large reduction of polymer efficiency (from 53% to 17% and 13%) when additional 10 and 20% fines were present in the white water. They suggested that the cationic polymer adsorbs first onto an anionic surface it encounters. If it is a fine particle, the reactive group on the aldehyde starch will be blocked by a chemical reaction. Clearly, there are conflicts in the literature about the roles of "anionic trash".

It can be seen from the above review that the mechanisms of the interaction between anionic organics and cationic polymers have been extensively studied. Both stoichiometric and non-stoichiometric reactions are found. The interactions are charge dominated but can also be affected by the chemistry of polymers and anionic trash. However, there are still some unanswered questions, e.g. in the area of interaction kinetics. This will be discussed below.

A general method reducing detrimental effects is to use high-charge-density, low-molecular-weight cationic materials to neutralize the anionic trash. Pre-addition of alum is thought to be an effective and economically feasible method to combat organics buildup as long as the alum amount is well controlled [29, 30]. Excessive addition of alum can negatively affect the synthetic organic retention aid and contribute to scale problems on the machine wire [31]. Because of the pH requirement of aluminum hydroxide polymer formation, it is only suitable for acidic papermaking conditions. In neutral papermaking environments, a highly charged synthetic coagulant, such as poly(ethylene imine) (12), polyDADMAC [13] can be used instead. Linhart [12] reported that an introduction of 0.05% modified polyethyleneimine increased the first-pass retention from 54 to 62% and the filler retention from 15 to 31%. The use of inorganic or organic coagulants can reduce the cationic demand, but the amount typically required increases the solids loading of the system.

Another approach is to simply increase the dosage of cationic polymer additives. Lagace et al. [32] studied the effect of polymer dosage change on retention under simulated zero-discharge conditions, and they indicated that the retention requirement could be met by using a higher dosage of polymer. However, they also indicated that the dosage change did not have a significant effect on the retention results from dual polymer systems and microparticle systems under zero-discharged conditions. Allen et al. [33] used dosages of cationic polymers 15-20 times those normally used in the mill to compensate for the cationic demand and believed that cationic polymers with higher charge density may provide a more optimistic picture.

In addition to charge neutralization, application of suitable polyelectrolytes that could precipitate detrimental substances onto fines or fiber in an early stage of the

papermaking process was also proposed [1]. However, the research in this area is rather limited.

Although many researchers have indicated that adding a coagulant could significantly improve the retention, many questions remain. The pulp furnishes are “dirty” systems that are significantly different from pure polymer solution. The interactions between cationic polymers and anionic trash are not only controlled by charge density and chemistry but also by reaction kinetics, shear forces, temperature, etc. The competition between the adsorption on solid substances and the reaction with oppositely charged substances will significantly affect the papermaking process and the efficiency of polymer additives. For example, if a neutralizer (such as polyDADMAC) is added to furnishes, will the neutralizer react with the soluble anionic trash first, or adsorb on fines, fillers, and wood fibers first? If they react with soluble anionic trash first, the efficiency of adding neutralizer can be maximized. However, if they react with filler, fines, and fibers first, the adsorbed cationic neutralizer will block the adsorption of cationic retention aids, which may result in a decrease in the adsorption amount and retention efficiency. Therefore, how effectively papermakers can use the neutralizer will strongly depend on the interaction and adsorption kinetics. By understanding the reaction kinetics, papermakers can optimize the neutralizer and retention-aid addition points. However, almost no such type of information is available in the literature.

Interaction of anionic trash with anionic and nonionic retention aids

Anionic and nonionic retention aids are also widely used in papermaking. The negative effect of white water closure on the performance of anionic and nonionic retention aids, which is much less significant compared to cationic polymers, has been reported [29, 30, 33]. Allen and his coworkers [33] determined the performances of five different retention-aid systems at closure levels of 55, 20 and 3 m³/ton in TMP newsprint. The retention-aid systems studied include bentonite/polyacrylamide, PEO/phenolic resin, PEI, polyDADMAC and chitosan. Different closure levels were achieved by using simulated white water that was obtained by diluting the thick pulp, pressing the diluted pulp and diluting the thick pulp again using the pressate. This process was repeated until the desired contaminant levels in the white water were achieved. Their results showed that at high degrees of closure, the PEO/phenolic resin system is the best choice, as it improved the first-pass retention of fines and drainage rate. Cationic demand due to white water closure tended to result in poor performance of cationic polymers. Springer et al. [29, 30] evaluated the effectiveness of three retention-aid polymers (a low-molecule-weight cationic polymer, high-molecule-weight cationic, and anionic polymer) under varying simulated closed system conditions by adding organic and inorganic contaminants. The organic contaminants were simulated by a blend of kraft lignin, xylan and D-glucuronic acid- α -lactone, while the inorganics were simulated by a blend of chlorine salts of Fe, Ca, Mg and Mn. They found that high-molecule-weight anionic polymer is the most effective when organic contamination is encountered. The results, however, show that organics did reduce anionic polymer effectiveness when it was used in conjunction with a cationic coagulant.

Several questions remain unanswered in Allen and his co-workers' study. For example, although the closure level was reduced to 3 m³/ton, the salt concentration in the water they used seems too low. The cationic and microparticle retention systems used in Allen's study are also questionable because no improvements in the retention efficiency

of fines was achieved by adding the cationic PEI and bentonite/polyacrylamide even at a zero closed water system. This suggests that the poor retention of fines observed in this study might not be caused by increased salt concentration and anionic trash but by poor choice of retention systems.

The effect of filler and fines retention in closed white water using anionic and nonionic retention systems is considered to be due to the presence of high salt concentration (salting-out effect); however, less attention has been paid to the effect of organic trash on these two types of polymers. It is generally believed that there is no chemical reaction between anionic trash and anionic or nonionic polymer retention aids. However, the phrase "no chemical reaction" should be carefully used because many researches have found that surfactants can form micelle-like aggregates with water-soluble polymers [34-38], such as polyethylene oxide and polyacrylamide. Because anionic trash in white water, such as sulfonated lignin and fatty acids, can be surface active, they may also form aggregates with polymeric retention aids. However, how these aggregates can form and how they will affect the performance of the anionic and nonionic polymer retention aids have not been studied. Even by assuming there is no strong chemical reaction between anionic trash and anionic and nonionic polymers, it does not mean that the buildup of organic substances will not affect the anionic and nonionic retention-aid performance. For example, the adsorption of anionic and nonionic polymers on filler and fiber surfaces can be significantly affected by the presence of anionic trash. Clearly, the papermakers need to understand the effect of anionic trash on the performance of anionic and nonionic retention aids.

The literature indicates that nonionic or slightly ionic additives are effective retention aids [39]. Their niche appears to be high-conductivity systems, particularly systems that contain high levels of small fiber fines and colloidal anionic materials, such as wood extractives [40]. One of the most promising nonionic retention systems is polyethylene oxide (PEO) plus a cofactor. A great deal of research conducted on the PEO systems has been concentrated on newsprint furnishes [41-43], probably owing to the high wood extractive content in the furnish. Because of the high anionic trash level in a closed white water system, it is expected that this retention system will behave well combating the problems due to anionic trash. There is no information regarding the effects of water closure on the filler retention in fine and coated papermaking using nonionic PEO systems.

Adsorption of anionic trash on the surfaces of fillers, fines and fibers

The interaction between polymer retention aids and organic substances is not the only reason for poor retention performance. It is believed that anionic trash will strongly affect the adsorption of polymers on the filler, fines and fiber surfaces because anionic trash will also adsorb onto the substrates [12], particularly if they are neutralized by cationic polymers [27]. When the filler, fiber and fines absorb anionic trash, the surface properties, including charge characteristics and hydrophobicity of substrates, are changed. For cationic polymers, the higher the negative charge of the substrate surface, the larger the adsorption amount will be. However, the increase in the charge density of anionic trash will also affect the configuration of the cationic polymers on the surface.

Much research has been done on the adsorption of cationic polyacrylamide on wood fiber surfaces [44, 45]. Hendrickson and Neuman [44] looked at the effect of salt concentration on the polyacrylamide adsorption onto bleached oak kraft pulps. A variety

of salt types, including the chloride salts of sodium, calcium and aluminum and sulfate salts of sodium and aluminum, were studied. They reported a significant drop in cationic polyacrylamide adsorption with increasing salt concentration. However, they did not study the effect of anionic trash on the adsorption. Das and Lomas [46] found that unbleached kraft fines pretreated with dilute NaOH at room temperature showed an appreciable drop in adsorption of polyethyleneimine. The alkaline extract, when analyzed for dissolved organics, was found to contain substantial quantities of soluble lignin. Therefore, reduction of ligneous materials from fines surfaces will reduce the adsorption of cationic polymers.

In contrast to the cationic retention aids, the adsorption of anionic and nonionic polymeric retention aids on negatively charged fillers, fibers and fines strongly depends on the hydrophobicity of the substrate because Wan der Waals force should be the dominating attraction force for the adsorption. However, there have been very few studies in this area. Ishimaru and Lindstrom [47] studied the adsorption of eleven different nonionic polymers on different cellulosic fibers. They found that the polymers could be divided into three different classes with respect to their interaction with three different pulps, unbleached kraft, bleached kraft and mechanical pulp. Some polymers adsorb on one kind of pulp but not others, and some, including nonionic polyacrylamide, do not adsorb on any of the three kinds of pulp. In another study by Lindstrom and Glad-Nordmark [48], it was found that polyethylene oxide adsorbed onto unbleached fibers but adsorbed onto mechanical pulp or bleached fibers. The interaction with phenolic and catecholic groups was suggested as the main driving force for adsorption. Because the lignin content in white water systems will increase when mill streams are closed, the adsorption of PEO on solid substance surfaces must be significantly affected.

Anionic trash and other organic extractives in pulp furnish will affect the hydrophobicity of fillers, fines and fibers if they adsorb onto the surface. Unfortunately, no report has been found in the literature regarding the effect of anionic trash on the hydrophobicity of fillers, fibers and fines.

The adsorption of anionic trash on the solid surfaces will help clean up the anionic trash. Little is known about the relationship between the properties of anionic trash and filler and fiber surface chemistry. Miyanishi et al. [49] studied the adsorption of oleic acid and abietic acid on the surface of PCC. They found that PCC adsorbed both oleic and abietic acids. Oleic acid was adsorbed on PCC 10 times more than abietic acid was. Therefore, an increase of PCC retention can reduce dissolved colloidal substances in the papermaking system. They also concluded that the adsorption is chemical in nature. The difference in adsorption behavior between oleic acid and abietic acid was attributed to the different equilibrium constants of calcium fatty salts. An improvement in the effectiveness of retention aids can also be achieved by adding certain "active fillers" alone or in combination with polyelectrolytes. Positive results have been obtained with bentonite [50]. A unique property of bentonite, when used in a wet-end, is its ability to adsorb and absorb dissolved and colloidal material from the white water stream. By acting as a microscopic "sponge", and by being highly retained in the paper sheet, a significant proportion of the water-soluble trash is innocuously removed. Bentonite contains micropores and an amphoteric charge structure, giving it particular properties for the retention of colloids and complex dissolved solids, as well as fiber fines and mineral fillers. Other microparticles such as silica and organic microparticles do not contain an amphoteric surface, or a porous structure capable of a absorption/adsorption

[5]. Other minerals that could have similar effect include aluminum silicate hydrates, althonites, montmorillonites and the like [1]. Such minerals can adsorb dissolved or suspended substances, inactivate them and take them out of the system through retention on the fiber furnish.

Although the adsorption of processing polymers (cationic, anionic, and nonionic) on wood fibers, fines and mineral fillers has been studied, the adsorption of anionic trash, such as lignin, hemicellulose, etc., has not been systematically studied. More importantly, how adsorbed anionic trash affects the adsorption of processing additives in a closed environment has not been fully understood.

Difference between fresh and circulated fillers and fines in white water

Filler and fines retention strongly depends on the filler and fines surface charge, surface hydrophobicity, particle size, particle shape, etc. As a result, the fines and fillers that circulate in white water may be different from fresh fines and fillers. It has been indicated [51] that if fines are not retained in a sheet, they pass into the white water system and form colloidal linkages with polymer additives and other fines. These unbound fines are saturated by contaminants in white water and may be more difficult to retain on the paper sheet. However, little is known as to how the surface properties of fibers and fillers will be affected by organic anionic trash adsorption.

Effects of Inorganic Salts

General review

The effects of inorganic salt concentration on water-soluble polymer properties have been well known for more than a hundred years. The effect of inorganic ions on polyelectrolyte is much more significant than nonionic polymers. Much research, including experimental studies, mathematical approaches and computer simulations, has been done in this area. A full review of this area is beyond the scope of this report. Therefore, this report focuses only on the effects of salt buildup in white water on the performance of polymeric retention aids and the surface chemistry of solid suspensions.

There is a definite order of affinity between fibers and various positively charged ions in a solution. Small, highly charged ions such as sodium, magnesium, calcium, lithium and potassium are non-substantive and have relatively little adsorption onto cellulose, whereas larger ions with lower charge densities are more readily adsorbed and will be removed with the sheet in large percentages. Aluminum, barium silica, titanium and iron are included in this category. A dissolved salt, such as sodium, which has virtually no retention in the paper, will cycle-up based solely on the degree of closure. A fully closed mill can expect sodium to cycle-up to very high levels. Calcium, chloride and sulfate concentrations will also increase within the white water closure.

The overall level of these materials, as measured by conductivity, influences wet-end chemistry. Ionic salts influence the interactions between wet-end materials through their ability to shield the charged groups on particle surfaces and on polymer chains. A positive effect of the increased ionic concentration is that the cations, mainly divalent and trivalent, reduce the electrostatic double layer thickness, a beneficial effect in

terms of retention [52-55]. As a result, this enables two fine particles to approach more closely, which, in turn, promotes coagulation and decreases the bridging distance. In high ionic concentration, the diffuse layer may not exist at all [17]. The chlorides of sodium, calcium and lanthanum raised the fines retention of a bleached hardwood pulp from around zero in deionized water to about 20% maximum [56]. The optimum concentrations were about 100 mg Na/L, 13 mg Ca/L and 2 mg La/L, in approximate agreement with the well-known Schulze-Hardy rule for ion effectiveness against hydrophobic colloids. Similar work [55] on TiO_2 retention showed a wider range in the active concentration range of these ions with maximum retention (about 40%) occurring at higher ion concentrations.

The high salt concentration shields the charge of the polymers, which affects the conformation of polymers. Increased salt levels allow the polymer chains to become less extended, and more coiled, thus resulting in a collapse of the effective volume [7], available polymer surface area and bridging capability. Aloï and Trsksak [57] reported that a conductivity above 5000 μS will almost certainly impact the performance of the modern retention systems, while 10,000 μS may have a destructive impact. However, it is interesting to see if these effects are also chemically dependent, i.e., it is not clear if the salt effect for cationic polyacrylamide is the same as cationic polyethyleneimine and starch. It is also not clear how these effects will depend on the polymer charge density and molecular weight.

The effects of salt on different polymer retention aids

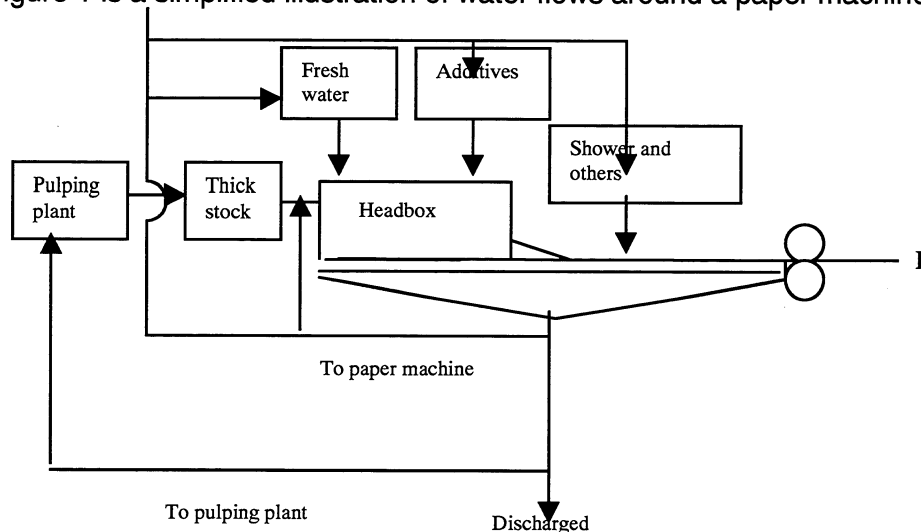
Allan et al. [58] studied the effects of sodium chloride, sodium sulfate and aluminum sulfate on the performance of a cationic polyacrylamide using bleached kraft pulp and titanium dioxide. They found that at 10^{-5} to 10^{-2} M, sodium chloride and sodium sulfate caused negligible changes in the first-pass retention of titanium dioxide. Aluminum at 10^{-5} to 10^{-4} M at pH 4.0-4.5 increased retention, but higher concentrations gave lower retention. Buontempo et al. [59] studied the performance of four cationic flocculants (not specified) with charge densities of 0.14, 0.65, 1.19 and 2.78 meq/g with and without starch addition. Their results indicated that with no starch in the furnish, the 0.65 and 1.19 meq/g cationic flocculants maintained a high level of retention. With starch added to the furnish, each flocculant showed a marked decrease in performance when salt levels are increased.

Other researchers examined the effect of inorganic materials on retention together with other interfering materials [29, 30, 33], as it is difficult to isolate the organic materials.

PART III: EXPERIMENTAL, RESULTS AND DISCUSSIONS

Mathematical Model

Figure 1 is a simplified illustration of water flows around a paper machine.



To simplify the situation, the contaminants coming into the headbox are divided into two parts: those are from outside a paper machine (thick stock, fresh water, and additives) and these recycled inside a paper machine. In this study, we also assume that the contaminants in thick stock are constant. This assumption is practically reasonable because, even though the water closure degree is increased, the pulps are washed before they are sent to a paper machine. After washing, a constant level of contaminants in the thick stock can be achieved. In other words, we assume that the contaminants brought into a paper machine from thick stock, fresh water, and additives are a constant if the paper machine runs under an equilibrium condition.

For a given interested species in a paper machine, we defined

$$K = (\text{total amount retained by a paper web}) / (\text{total amount in the headbox})$$

It is further assumed that K is a constant during the water closure process. In other words, if the total amount of interested species in the headbox increases, the total amount of the same species on the paper web increases proportionally.

Based on these assumptions and the mass balance, the following equation will be true for the first cycle of papermaking:

$$(FC_{f,1} + TC_{t,1} + AC_{a,1} + RC_c) * (1-K) = SC_{s,1} + GC_{g,1} + RC_{r,1} \quad (1)$$

Where the concentration at the n th cycle is defined as

F = Fresh water added directly to the manufacturing process

A = Water with additives

T = Water coming with thick stock

R = Total white water re-entering the paper machine, including the waters being reused for thick stock dilution, additive dilution, shower and others.

G = White water being sent to pulping plant

S = White water being released as sewage

$C_{f,1}$, $C_{t,1}$, $C_{a,1}$, $C_{s,1}$, $C_{g,1}$, and $C_{r,1}$ are the concentrations of any interested species (can be dissolved or dispersed) in fresh water (f), thick stock (t), additives (a), sewage water (s), water sent to the pulping plant(g), and water recycled in the paper machine (r), respectively, where the second subscript "1" in the concentration term denotes the recycle number of white water in a paper machine.

Because $C_{s,1} = C_{g,1} = C_{r,1}$ and the total white water $W_t = S + G + R$

$$\begin{aligned} C_{r,1} &= (FC_f + TC_t + AC_a + RC_c)(1-K)/W_t \\ &= (Y + RC_c)(1-K)/W_t \end{aligned} \quad (2)$$

where Y is the total mass of interested species coming into the system from fresh water F, thick stock T, and additive water A. The cycle numbers for $C_{f,n}$, $C_{t,n}$, and $C_{a,n}$ are omitted in the equation (2) because they are constant for different cycles. $C_{r,1}$ is the concentration of interested ion species in the white water of the first recycling system, which means a complete open system.

If we further assume that $RC_c \ll Y$ (i.e., the amount of interested species in the dilution water of the first cycle of papermaking is much smaller than the sum of the same species from thick stock, fresh water, and additives), equation (2) can be simplified as

$$\begin{aligned} C_{r,1} &= (FC_f + TC_t + AC_a + RC_c)(1-K)/W_t \\ &= Y(1-K)/W_t \end{aligned} \quad (3)$$

For the second cycle, the concentration of interested species in the white water is

$$C_{r,2} = (Y + RC_{r,1})(1-K)/W_t \quad (4)$$

Substituting $C_{r,1}$ by Equation (3), it gives

$$\begin{aligned} C_{r,2} &= Y(1-K)/W_t + RY(1-K)^2/W_t^2 \\ &= C_{r,1}[1 + (1-K)R/W_t] \end{aligned} \quad (5)$$

If this process continues to n cycle, we have

$$C_{r,n} = C_{r,1}[1 + R(1-K)/W_t + R^2(1-K)^2/W_t^2 + \dots + R^{(n-1)}(1-K)^{(n-1)}/W_t^{(n-1)}] \quad (6)$$

If we define the recycle degree r as the ratio of white water recycled in a paper machine (R) to the total white water generated in the machine (W_t), i.e., $r = R/W_t$, equation (6) can be rewritten as

$$C_{r,n} = C_{r,1}[1+r(1-K) + r^2(1-K)^2 + \dots + r^{(n-1)}(1-K)^{(n-1)}] \quad (7)$$

Because r (recycle ratio of white water in a paper machine) is <1 , and $(1-K)$ (the fraction of un-retained substance) is <1 , equation (6) can be further simplified as

$$C_{r,n} = C_{r,1}[1 - r^n(1-K)^{(n-1)}]/[1-r(1-K)] \quad (8)$$

or

$$EF = C_{r,n}/C_{r,1} = [1 - r^n(1-K)^{(n-1)}]/[1-r(1-K)] \quad (9)$$

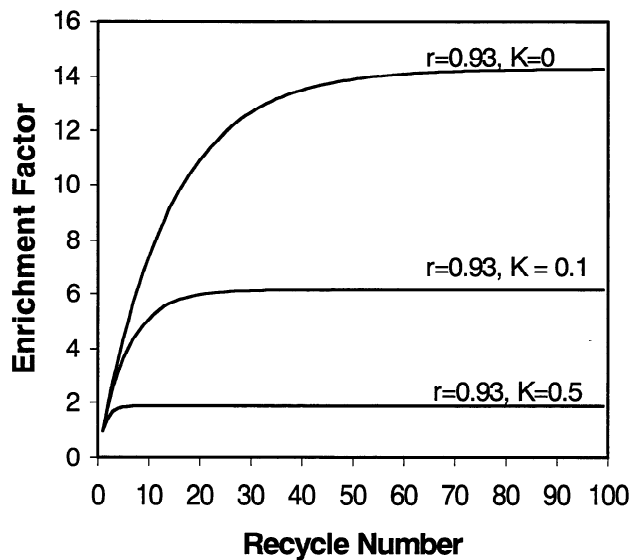


Figure 2. The effect of recycle number of white water on the buildup of contaminants at 93% of water closure and different retention levels (K).

Figure 2 shows the effect of recycle number of white water on the buildup of contaminants at different retention levels. It should be noted that the "retention level" is a general term that indicates how many substances are retained by the paper sheet, which includes all materials of interest on the paper sheet (physically entrapped and adsorbed, chemically bonded and retention aid enhanced). This term can be used for all substances in white water, including water-soluble and suspended solids.

Two conclusions can be drawn from Figure 2:

- 1) The retention level of the substances on the paper sheet (indicated by K) is very important for controlling the buildup. For $K=0$ (no substance is retained by the paper sheet), the enrichment factor can be as high as 14 at 93% of white water closure when it reaches equilibrium. The enrichment factor can be further increased (see below) if the closure degree is increased. However, for $K=0.5$ (50% of substance is retained by sheet), the enrichment factor is less than 2. This suggests that if the paper mills can control their retention level above 50% of the total input substances, the buildup of these substances should not be significant. This conclusion can be applied to any substances. However, it should be noted that the results are based

on the assumption that the substances in thick stock are constant during the water closure. If the input level changes, e.g., if the contaminant levels in thick stock are not constant, the conclusion will be varied.

- 2) The cycle numbers needed for buildup equilibrium strongly depend on the retention level K . For the instance showed in Figure 2 ($r=0.93$), it needs only about 5 cycles are needed for white water to reach the equilibrium if the retention level K is 0.5, but about 60 cycles are needed to reach the equilibrium if the retention level K is zero.

Figure 3 further indicates the relationship among the retention level K , closure degree r and the enrichment factor. No significant buildup is evident if the closure degree r is less than 0.75. However, if the closure degree is further increased, the substance concentration in white water sharply increases. In a case of $K=0$, the buildup level is an infinite number for 100% water closure. However, it should be noted that based on the water flow balance, a paper machine (does not include pulping plant) can never reach a 100% water closure because the amount of water coming off the machine during web formation always be less than the water coming in with the thick stock.

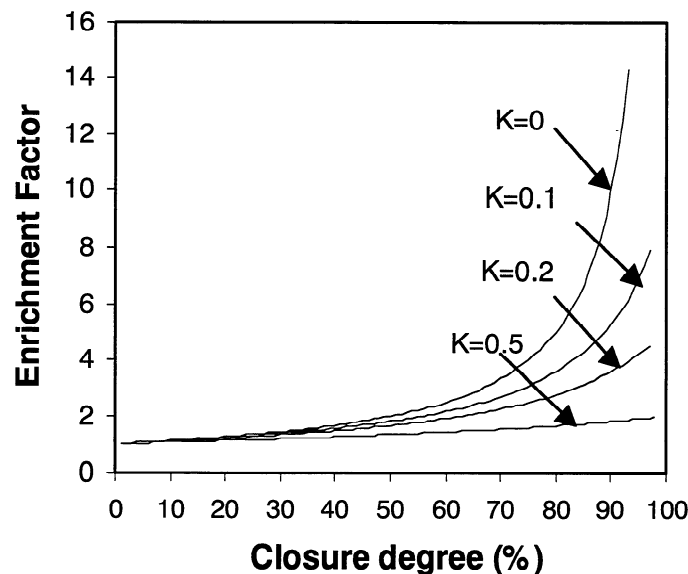


Figure 3. The relationship among white water closure degree, the retention level and the enrichment factor.

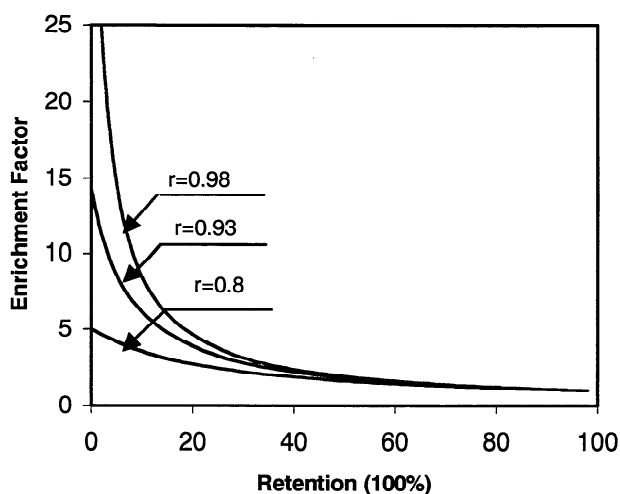


Figure 4. The effect of retention on the buildup of substances in white water at different closure degrees.

Figure 4 indicates the effect of retention constant K on the buildup at different closure degrees. It can be seen that even for the system with 93% white water reuse ($r=0.93$), there is no significant buildup if 50% of the substance can be removed from the system. The general conclusions from the above discussions are:

- 1) Retention of contaminants on the paper sheet (or removed from the system by other methods, such as clarification) can effectively avoid the buildup.
- 2) The buildup rate increases sharply at high closure degrees. However, the actually increased rate depends on the retention ratio.
- 3) If the retention ratio is higher than 50%, the buildup reaches its equilibrium quickly if the retention is high, but it takes ~65 cycles to reach the equilibrium if no contaminants are removed from the system.

Anionic Trash in Bleached Kraft (BLK) Pulp

Materials and Experimental Methods

Several bleached northern soft wood kraft samples, including thick stock, headbox sample, dry pulp, and white water sample were provided by one of our member companies.

The filtrates of the thick stock and white water were chemically analyzed. The filtrates were obtained using VWR 413 filter paper (pore size 5 μ m). White water filtrate was concentrated 5 times by boiling the sample before analysis. The organics in 500 ml samples were extracted with methylene chloride three times, with 30 ml methylene chloride for each time. The organic phase was concentrated to 1 ml and was used for GC/MS analysis.

The total organics in the filtrates were analyzed using a Shimadzu TOC-5050 analyzer, and the lignin contents were analyzed by a UV/VIS spectrum at 280 nm. The surface tension was measured by a dynamic contact angle analyzer (Cahn DCA 312) using a glass plate. The samples for surface tension measurements were diluted by adding different amounts of deionized water to the thick stock filtrate.

The interactions between anionic materials and cationic polymers were studied by colloidal titration, and the end-points were determined using a Rank Brothers Charge Analyzer II, with a streaming current detector cell. Both forward and backward titration methods were employed. A dynamic contact angle analyzer (Cahn DCA 312) was used to measure the surface tension of liquid against a glass plate.

Results and Discussions

The contaminants in the samples are given in Table 5:

Table 5. Properties of the samples

	Thick Stock	Thick stock filtrate (••m filter paper)	5 times diluted thick stock passing DDJ	White water	White water filtrate (••m filter paper)
Solid consistency, %	4.715				
Fines content, %	11.31				
Dissolved solid content, ppm		444		668	250
TOC, ppm		85.44			48.65
pH	6.98	7.05		7.36	7.48
Conductivity, mS/cm	0.587	0.576	0.203	0.399	0.406
Z-potential, mV		-24.6	-18.3	-15.0	-1.5
Surface tension, dyne/cm		55.95			59.58

Table 6. Chemical analysis results of the BLK pulp and white water

	Concentration of total extractives	Concentration of extractives	Lignin	Specific Organic Detected
Thick stock filtrate	4.0 ± 0.3 (mg/L)		48 mg/L	Dehydroabietic acid > Palmitic acid > Stearic acid, Other fatty acids were present at lower conc.
Thick stock filtrate	160 (mg/L)			
Dry thick stock pulp		780 (mg/kg O.D. basis)		Hydrocarbon and/or silicone oil: >700 mg/kg C12: Laric acid: 7mg/kg C18: Stearic acid: 3 mg/kg C22: Arachidic acid: 1mg/kg Dehydroabietic acid: 1 mg/kg C20: Arachidic acid: 1 mg/kg C24: Lignoceric acid: 1 mg/kg Other fatty acids were present at lower conc.

Table 5 indicates that the BLK fibers are slightly negatively charged with a low conductivity and total organic contents. Table 6 shows more details about the contaminants in the samples.

Table 6 indicates that the pulp furnish and mill white water are relatively “clean” compared to other furnishes (see Tables 1 and 2), such as CTMP and TMP.

Surface tension has been suggested by some member companies as a method for monitoring the level of water contaminants. In this study, the thick stock filtrate was diluted by deionized water and the surface tension was measured. Figure 5 shows that the surface tension of the filtrate increases as the dilution degree increases, and this decrease has a linear relationship with contaminate level in the white water in the range from original filtrate to that diluted 5 times. However, the relationship between surface tension and contaminate level may be more complicated than is shown in Figure 5, particularly if the contaminants level is very high, in which the anionic fatty acids are expected to form micelles. It is well known that the surface tension will be a constant if the concentration of surface agent is higher than its critical micellization concentration. This suggests that if the concentration of contaminants in white water is too high, the sensitivity of surface tension measurement may remarkably decrease when it is used as a monitor for anionic trash. The salt and pH effects may also need to be considered.

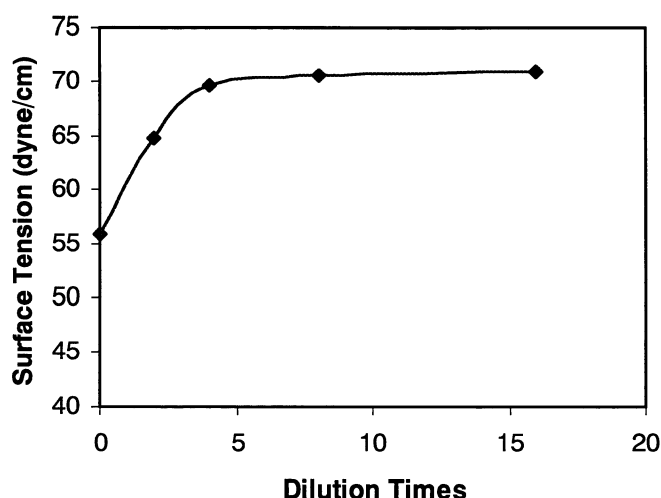


Figure 5. The surface tension of white water as a function of dilution degree.

Anionic trash and cationic demand are two terms that are often used by paper makers. However, as discussed in the introduction section, the relationship between these two has not been well understood. For example, what materials can be defined as anionic trash? Will anionic trash react with cationic polymers stoichiometrically or non-stoichiometrically? Will cationic demand depend on the chemical structure of anionics and cationic polymers? In this study, the colloidal titration was first used as a tool to study the interaction between anionics and cationic polymers. Although only the results from colloidal titration were reported in this progress report, and more work on the characterization of anionic organics are ongoing in our lab, any conclusions given in this report are only under our experimental conditions. More general conclusions may be reported when the whole project is completed.

For studying the charge neutralization reactions, the reliability of our streaming current titrator was first examined using standard solutions of 0.0001 N potassium polyvinyl sulfate (PVSK, Nalco Chemicals) and 0.0001 N polyDADMAC (Nalco Chemicals). The results are shown in Table 7.

Table 7. Dependability of charge analyzer

(5 ml 0.0001N titrate, 10 ml 0.0001N titrant, diluted to 140 ml for titration)

	Titrate	Excess	Titrant	PolyDADMAC/ PVSK ratio
Forward Titration	PolyDADMAC	-	PVSK	1
	PVSK*	-	polyDADMAC	1.007
Backward Titration	PVSK	polyDADMAC	PVSK	1.017
	PolyDADMAC	PVSK	polyDADMAC	1.051

* The pH of 5 ml PVSK in 140 ml DI water is 5.31.

Table 7 shows that the results from both forward and backward titration agreed very well (uncertainty is less than 1.7% for first three experiments and is 5.1% for the last one) when standard polyDADMAC and PVSK were used. This suggested that our titrator is reliable. It has been noted that backward titration in the order of polyDADMAC-PVSK-polyDADMAC (the last experiment in Table 7) gave a little higher cationic demand. This may result from the formation of particle precipitation when the first part of the polyDADMAC was mixed with PVSK.

In the papermaking wet-end, there are many different organic and inorganic contaminants. One of the contaminants is anionic trash. However, it is not known if all of the anionic organics can be classified as "anionic trash". In this study, the organics that were found in BLK fibers were first studied using a titration method. Although only the results from polyDADMAC as a titrate are reported here, more studies using various cationic polymers will be given in the next report.

Table 8. Calculated and experimentally determined charge density of different anionic substances at pH 6, 8 and 10 (5 ml 0.0001N titrate, 0.0001N polyDADMAC as titrant for all experiments)

Titrate	Calculated, •eq/L	pH=6, •eq/L	pH=8, •eq/L	pH=10, •eq/L
Sodium oleate	100	35.6	57.9	78.0
Lauric acid, sodium salt	100	14.3	18.5	31.7
Caprylic acid, sodium salt	100	5.9	18.1	21.1
Galacturonic acid, sodium salt	100	9.6	13.0	25.6
Polyacrylic acid, sodium salt (MW=1000)	100	109.2	126.5	150.2
Polyacrylic acid, sodium salt (MW=225,000)	100	101.7	134.2	150.6

Table 8 shows the titration results for different organic acid salts. All acids used in this study are analysis grade. Several conclusions can be drawn from Table 8:

1. The reaction between polyDADMAC and the acids examined here does not follow a stoichiometric rule. The results indicate that there is a remarkable amount of free acids in water at the end point of colloidal titration if a streaming potential detector is used. The reasons for non-stoichiometric reactions between fatty acids and polyDADMAC are complicated. First, it should be noted that, unlike an anionic polymer such as PVSK, the fatty acids examined here are low-weight compounds that contain only one charge group (carboxyl group) in their molecules. When these small acid salts react with a cationic polymer, only one ionic bond can form between these acids and polyDADMAC. Because one charge group may not perform a complete reaction with the cationic polymer, there must be many free anionic acids in the water at the end point of titration. Second, some acids can form micelles in water. The competition between

micelle formation and charge neutralization reactions may also reduce the opportunity for anionics to react with cationic polymers.

2. The lower the molecular weight of fatty acids, the lower the cationic demand. This may be because the complexes formed by very low-molecular-weight fatty acids and polyDADMAC have a higher dissociation constant than a complex formed between two oppositely charged high-molecular-weight polymers. The difference in the charge neutralization reactions between low-molecular-weight and high-molecule-weight anionics is shown in Figure 6.

It has been well known that some small anionic ions, such as Cl and SO_4^{2-} , do not form complexes with cationic polymer but polymeric anionics can strongly and completely react with cationic polymers. The anionic trash studied here (low-molecular-weight organic acids) lay between small anionic ions and high-molecular-weight polymers so it is reasonable to believe that the complex formation is not complete. Therefore, when these substances mix with a cationic polymer, there are remarkable free anionics that do not form a complex with cationic polymers. This suggests that if colloidal titration were used to study the reaction between low-molecular-weight and highly soluble small anionic and cationic polymers, the end point should not correspond to the stoichiometric reaction point. This also suggests that cationic demand obtained by colloidal titration only reflected the "demand" of cationic polymer to reach a "neutral" streaming point, but does not equal to the point at which all the anionics are neutralized by cationic polymers.

3. The cationic demand strongly depends on the pH when organic acids are used. This is not suppressed because anionic acid will be more negative and cationic polymer will be less positive when pH is increased.
4. It has been noted during experiments, but did show in Table 8, that all the anionic acids can form precipitates with polyDADMAC at high concentration of two oppositely charged polymers. The precipitation is more significant if the solubility of anionic acid is low. For the fatty acids that are not water soluble at experimental pH, the uncertainty of the colloidal titration increases. For some fatty acids, such as stearic acid, the results are not reproducible. This suggests that even for the furnishes that have the same amount of anionic acids, the colloidal titration may give a different number of cationic demand when pH is varied. This also suggest that colloidal titration cannot be used to predict the amount of anionic substances in water, particularly if the anionic substances have very low solubility in water.
5. Cationic demand for polyacrylic acid is higher than the calculated numbers at alkaline conditions. This may suggest that the reaction between polyacrylic acid and polyDADMAC is not stoichiometric.

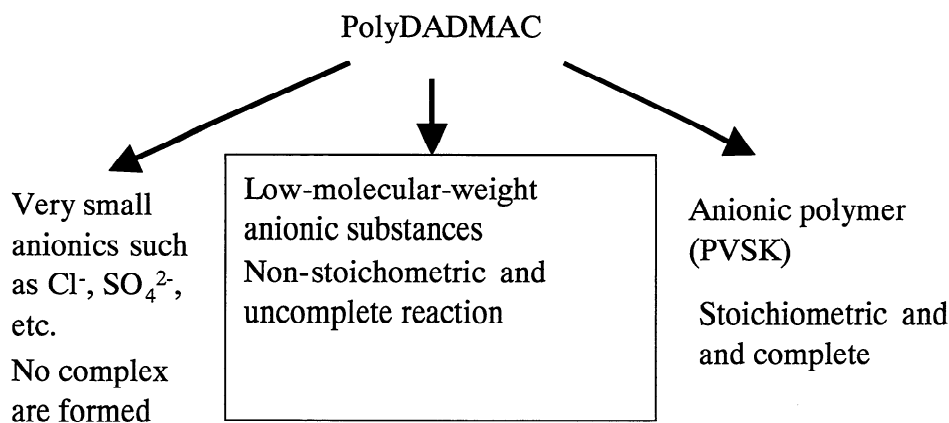


Figure 6. The dependence of charge neutralization reaction on the properties of molecules.

Table 9 shows the dependence of cationic demand on the anionic concentration. The general trend is that the cationic demand slightly decreases as the anionic concentration increases for all three chemicals tested in this study. Although the reason for this is not very clear, it may relate to the formation of precipitation of the complexes. It has been noted before that the interaction between cationic and anionic substances at high concentration resulted in precipitation. It is believed that some unreacted charges may be entrapped in precipitates. Therefore, the charge neutralization is difficult to follow a stoichiometric rule.

Table 9. Consumption of polyDADMAC for different titrates at different titration concentrations at pH 8 (0.0001 N polyDADMAC was used for all titrations)

Sodium oleate	Concentration	2 ppm	20 ppm	200 ppm	1000 ppm
	Consumption of polyDADMAC	1.90 meq/g	1.81 meq/g	1.53 meq/g	1.66 meq/g
Polyacrylic acid, sodium salt	Concentration	1 mg/L	10 mg/L	70 mg/L	350 mg/L
	Consumption of polyDADMAC	13.1 meq/g	12.1 meq/g	10.13 meq/g	10.52 meq/g
Lignosulphonic acid, sodium salt	Concentration	1 ppm	10 ppm	70 ppm	350 ppm
	Consumption of polyDADMAC	2.43 meq/g	2.06 meq/g	1.93 meq/g	1.97 meq/g

FUTURE WORKS

The future works in the next year include:

1. Continue the work of characterization of anionic trash. This work will focus on identifying the differences between "anionic trash" and cationic demand, which includes (a) what are the real anionic trash specie, and which anionic substances do and do not contribute to charge neutralization; (b) the relationship among cationic demand, zeta potential and total soluble organic content (i.e., if the total cationic demand corresponds to zero potential point, if the total cationic demand equals to the total anionic organic contents, etc.) (c) charge neutralization reaction equilibrium and kinetics; (d) studying the differences between the charge neutralization reactions of anionic substance with cationic fixation agents and retention agents.
2. Studying the charge neutralization and adsorption kinetics. Will cationic polymers react first with anionic trash or wood fibers? If they are simultaneous, how can we control the reaction?
3. Which anionic trash species are the most harmful for retention-aid performance (different retention systems will be involved) when BLK fibers and PCC filers are used?

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WET END CHEMISTRY CONTROL ADVISOR

STATUS REPORT

FOR

PROJECT WECCA
F027

Bill Scott (PI)

Collaboration Established Between
the
Institute of Paper Science and Technology
and the
Miami University Paper Science and Engineering Department

March 6 - 7, 2000

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, Georgia

DUES-FUNDED PROJECT SUMMARY

Project Title:	Wet End Chemistry Control Advisor (WECCA)
Project Code:	WECCA
Project Number:	F027
PAC:	Wet End Chemistry
Project Staff	
Principal Investigator:	Bill Scott (20%) (Miami U. and Adjunct IPST)
Research Support Staff:	None
FY 99-00 Budget:	\$50,000
Time Allocation:	
Principal Investigator:	20%

RESEARCH LINE/ROADMAP: No. 12: Reduce pulp and paper costs by 25% through increased productivity and improved pulp, paper, and product uniformity achieved with new developments in sensors and process controls.

PROJECT OBJECTIVE:General Objectives

- To develop and implement a first-pass retention control model that predicts retention upsets and guides the operator to the appropriate, preemptive response.
- Develop general guidelines and procedures for setting up and implementing predictive wet end chemistry control models in paper mills.

PROJECT BACKGROUND: The Wet End Chemistry Control Advisor (WECCA) project is the first endeavor in a wet end chemistry research collaboration established between IPST and Miami University Paper Science and Engineering Department. The overall goal of the collaboration is to promote improved paper quality and paper machine productivity through the development of new wet end chemistry process control strategies and tools. A broad preliminary proposal aimed at developing new wet end chemistry control tools was presented to the Recycled, Surface and Colloid Chemistry PAC in March 1998. It was decided that we should focus the initial project on the development of a predictive model that could be applied in retention control or, more specifically, tray consistency control. First-year funding was approved in July 1998, and a full-blown project proposal was accepted by the newly formed Surface and Colloid Science PAC at their fall meeting, 1998.

The first step in the project was to develop a predictive model for tray consistency. It was decided that the model should be based on mill data, rather than laboratory data, so that it could be more rapidly implemented in a production situation. The following nine-phase experimental program was proposed (Table I).

Table I

Nine phases in the WECCA experimental program	
1.	Test mill site selection
2.	Data set definition
3.	Time lag determination
4.	Data collection
5.	Data reduction
6.	Modeling strategy determination
7.	Model creation and refinement
8.	Implementation of the model in a supervisory mode
9.	Evaluation of the model as a tray consistency control tool

Phases 1 and 2 were completed during September 1998–February 1999. Process data collection and reduction (Phases 4 and 5) began in February 1999 and continue to the present time. Results from Phases 1, 2, 4, and 5 were reported at the March 1999 PAC meeting.

MILESTONES:

1. Phase 1: Selection of a mill that met the criteria defined for the project by October 1, 1998. Completed on time.
2. Phase 2: Definition of the set of process variables to be used in data collection by December 1, 1998. Completed on time.
3. Phase 3: Determination of time lag values for each variable in the process data set by March 1, 1999. This phase was deleted due to the modeling strategy adopted.
4. Phases 4 and 5: Data collection and reduction by June 1, 1999. Daily data sets were transmitted by the mill to Miami beginning in February 1999, approximately two-and-one-half months later than originally scheduled. Data collection continues and the most recent values will be used for model validation.
5. Phase 6: Modeling strategy determination by April 1, 1999. This phase refers to the selection of a modeling program and approach (i.e., first principles, empirical or semi-empirical). This phase was completed in October 1999, when the PAC confirmed that Simons Technologies' IDEAS simulation program would be appropriate for the project.
6. Phase 7: Model creation and refinement by September 1, 1999. This milestone has not yet been completed. It is expected that the model will be completed by the March 2000, PAC meeting.
7. Phases 8 and 9: Implementation of the model in a supervisory mode and evaluation of the model as a tray consistency control tool by April 1, 2000. This milestone will not be completed by the projected date. It is expected that model implementation and testing will occur during June-September 2000.

DELIVERABLES:

1. *Deliverable 1: A paper machine computer simulation, based on the Simons Technologies IDEAS program, that will enable an operator to predict the tray consistency on a paper machine as a function of current conditions throughout the stock preparation and paper machine system by September 1, 2000. Potential applications and benefits of this deliverable are described later in the report. Potential paybacks will be paper-machine-specific, but could be significant due to the relatively low implementation costs involved.*
2. *Deliverable 2: A set of guidelines for the procedures to follow when implementing Deliverable 1 in a given mill and for a given machine.*

STATUS OF GOALS FOR FY 99-00:

Goal: Install tray consistency prediction model on no. 93 paper machine in the Appleton Papers, West Carrollton, OH, mill, in a supervisory mode. Evaluate its effectiveness in reducing retention variability and improving operator control of the paper machine. As described above, this goal will not be met by the March PAC meeting but should be achieved by September 1, 2000.

SCHEDULE:

Phase	1999 Apr - Jun	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr - Jun
4. Data Collection	-----	-----	-----	-----	-----
5. Data Reduction	-----	-----	-----	-----	-----
6. Modeling Strategy	-----X				
7. Model Creation		-----	----X		
8. Model Implement.		-----	-----	-----X	
9. Model Evaluation		-----	-----	-----X	
10. Report and final recommendations					-----X

SUMMARY OF RESULTS: *A comprehensive set of process data has been collected from the No. 93 paper machine at the Appleton Papers, West Carrollton, OH, mill. The data set was found to be unsuitable for the development of an empirical retention control model. Instead, it was used in the development of a mass balance-based simulation of the paper machine. In addition, fines and cationic demand surveys were carried out around the thick and thin stock areas of the machine. The bookstock input stream was found to be the most significant source of cationic demand and fines.*

A dynamic mass balance simulation of No. 93 paper machine was developed using the IDEAS software package provided by Simons Technologies. The modeling process was found to be only moderately difficult and could be done by any experienced process engineer having up-to-date P&ID diagrams. The simulation will serve as the foundation for wet end chemistry modeling, which is the next stage in the project. As it currently exists, the simulation could be used to investigate white water closure strategies and contaminant buildup in the paper machine system.

SUMMARY OF KEY CONCLUSIONS:

- *The Internet provides a convenient way to acquire mill process data for use in off-site projects.*
- *No. 93 paper machine exhibits relatively stable, steady-state operation over very long time periods.*
- *The process data collected from No. 93 paper machine are unsuitable for the development of an empirical model.*
- *The bookstock stream provides most of the cationic demand introduced into the paper machine system. It also introduces the majority of the fines.*
- *On-line charge measurement is needed on at least the bookstock stream.*
- *A dynamic mass balance model could be developed from mill P&ID diagrams and the process data described above. The model will serve as the foundation for a wet end chemistry control model.*

DISCUSSION:**1. Phases 4 and 5: Collection of process data for model development**

- A. Significance: It was decided early on that the WECCA project would be mill-based, and that the characteristics of the collected data would determine the modeling approach to be taken. Thus, Phases 4 and 5 were highly significant to the project.
- B. Approach: A large number of process variables believed to have potential impacts on retention were selected for daily downloads from the mill PI data archiving system. The PI compression algorithm was turned off for this project and the data points were sampled every three minutes.

The logged variables covered significant fiber and chemical additive streams, headbox and tray solids and ash levels, the paper output stream, and the characteristics of many internal process streams. The data were transferred to an Excel spreadsheet and sent to Miami University via the Internet on a daily basis. This process began in February 1999, and continues today. Cumulative model validation data sets will be developed from the entire dataset. This process is currently underway.

In addition to the daily data sets, separate machine surveys were carried out pertaining to cationic demand and fines level, and an on-line cationic demand sensor was borrowed from Chemtronics to learn about the variability of the attribute in the bookstock stream.

C. Results:

Most of the logged variables were found to be essentially constant from day to day. This fact played a major role in the decision against an empirical modeling approach. Figures 1 - 4 illustrate the general nature of several representative variables. Additional information pertaining to many of the process streams is presented in Table V.

Cationic demand and fines surveys on No. 93 – Since it is known that cationic demand and fines levels play important roles in first pass retention chemistry, surveys were carried out around the No. 93 paper machine system. The results

are presented in Table II. The data in the table represent average values calculated from hourly measurements taken over a four-hour period. The sample points for the measurements are indicated on the process flow diagrams in Figures 5 and 9. Conductivity was also measured in order to determine whether cationic demand and conductivity were correlated. No such correlation was found, as is shown in Figure 6.

Figure 7 illustrates that the bookstock stream introduces most of the cationic demand found in the system. A similar balance done around the thin stock system (not shown) indicated that the stuff box stock stream was the only significant source of cationic demand for the thin stock system. Similarly, Figure 8 reveals that the bookstock is also the most significant source of fines in the thick stock system. The thin stock fines level is dependent upon the PCC addition rate and the first pass fines retention.

On-line measurement of cationic demand – Because cationic demand plays a key role in retention chemistry, and the cationic demand levels found in the bookstock stream were high, it was decided to determine its variability in the bookstock stream with the assistance of an on-line sensor. Chemtronics, Inc. agreed to provide an instrument for us to use in the project. The instrument was installed on the machine early in December. Figure 10 contains 100 hours worth of data collected with this instrument.

It is clear from Figure 10 that the bookstock cationic demand varies significantly over a 75 $\mu\text{eq./L}$ range. Peak-to-trough cycle times in the figure range from 1 hour to 15 hours, with 6-8 hours being the most common. These values are the same order of magnitude as the observed duration of retention swings.

D. Conclusions

1. Scientific Conclusions
 - a. The Internet provides a convenient way to acquire mill process data for use in off-site projects.
 - b. No. 93 paper machine exhibits relatively stable, steady state operation over very long time periods.
 - c. The process data collected from No. 93 paper machine are unsuitable for the development of an empirical model.
 - d. The bookstock stream provides most of the cationic demand introduced into the paper machine system. It also introduces the majority of the fines.
 - e. On-line charge measurement is needed on at least the bookstock stream.
2. Economics: None
3. Deliverables: None

F. Tables

Table II

Average cationic demand, conductivity, and fines levels measured at various locations in the No. 93 system

Stock	Cationic Demand	Conductivity	Fines
Softwood	45	1324	16
Broke	42	1338	23
Bookstock	128	1563	18
Machine Chest	80	1503	16
Stuffbox	80	1503	n.a.
Saveall	45		26
Primary Fan Pump	53	1430	35
Sec. Fan Pump	53	1472	37
Headbox	51	1414	35
Clarified WW	51	1508	n.a.
Machine WW	54	1511	n.a.
Knock-Down Shower	31	1300	n.a.

G. Figures

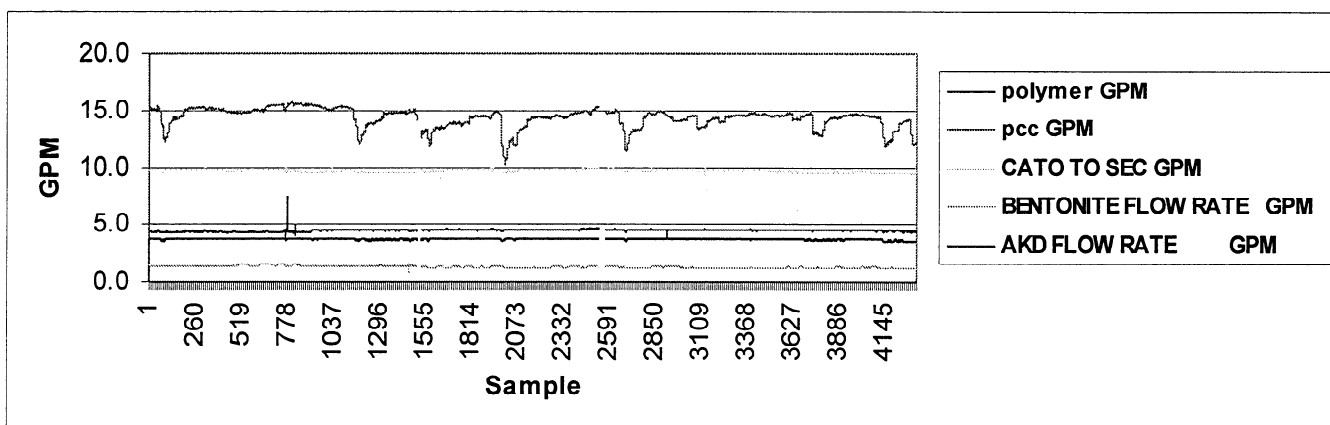


Figure 1. Volume addition rates of most important chemical additives. Data taken from the first two weeks in January 2000.

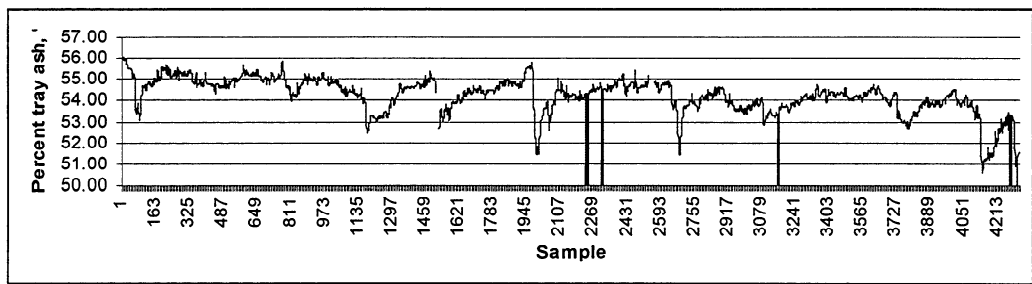


Figure 2. January tray ash data.

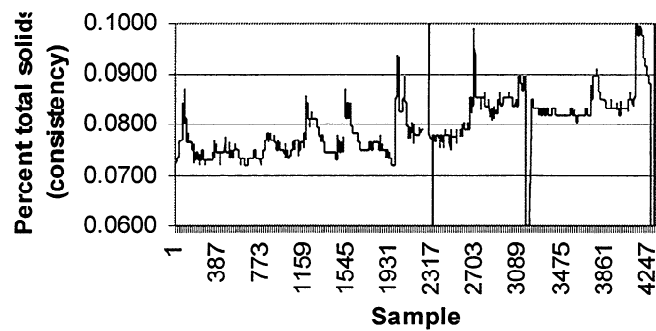


Figure 3. January headbox consistency data.

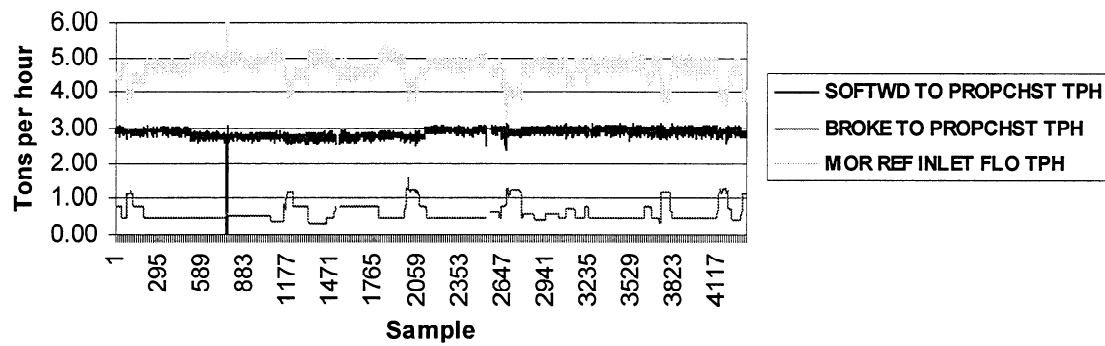


Figure 4. January fiber flows to proportioner chest.

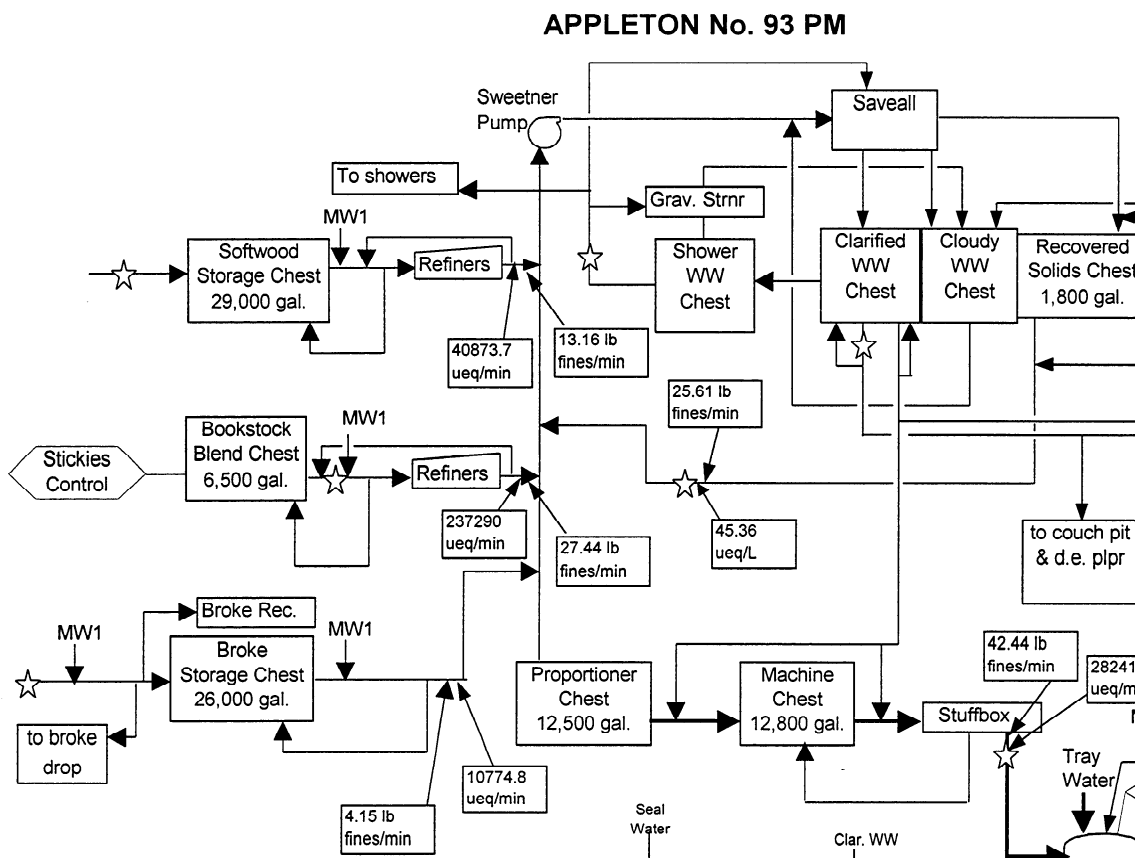


Figure 5. Thick stock area indicating sample points for fines and cationic demand determination.

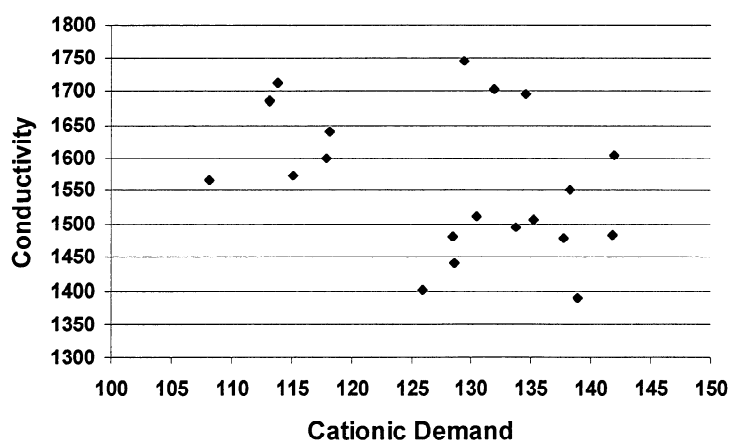


Figure 6. Conductivity vs. Cationic demand scatter plot. It is clear from the random distribution of points on the graph that no discernible correlation exists between these two parameters. Thus, conductivity is not a good indicator of cationic demand.

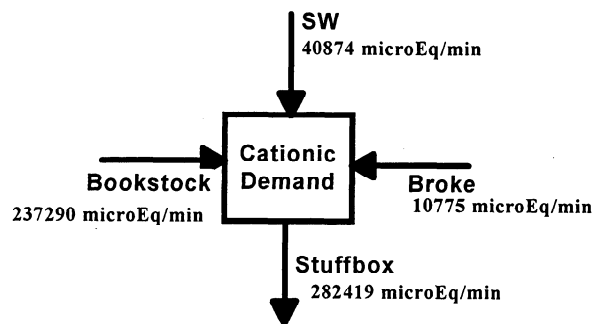


Figure 7. Cationic demand balance around the thick stock system.

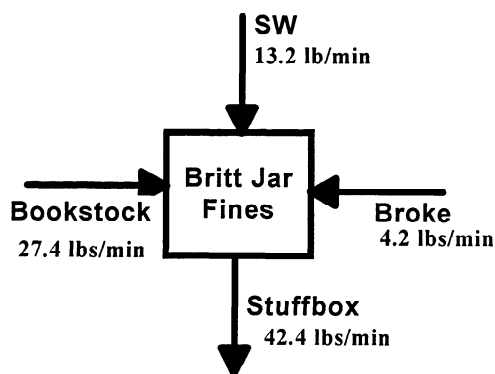


Figure 8. Fines level balance around the thick stock system.

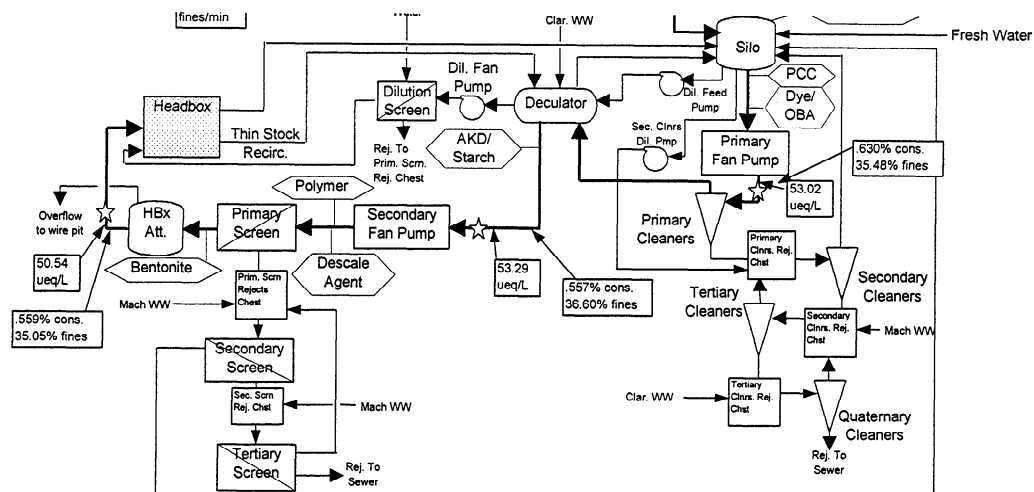


Figure 9. Thin stock area indicating sample points for fines and cationic demand determination.

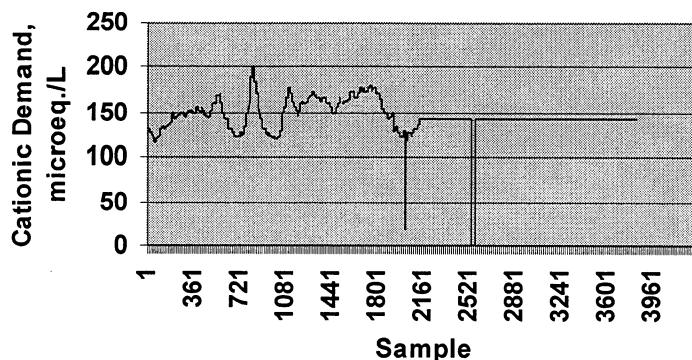


Figure 10. Cationic demand of bookstock stream going to the proportioner chest, as measured with a Chemtronics on-line charge analyzer.

2. Phase 6: Modeling strategy determination

- A. *Significance:* The control strategy underpinning the WECCA relies upon the existence of a process model that faithfully predicts wet end chemistry performance as a function of process conditions. The decisions made in Phase 6 determined the general modeling approach to be adopted (i.e., whether empirical or first-principles; steady-state or dynamic), and dictated the path followed in all future project phases. This was clearly a very significant milestone.
- B. *Approach:* PAC members indicated a preference for a modeling approach that would meet the criteria presented in Table III. Criteria 1-3 in the table indicate that an empirical model would not be desirable because they are often case-specific, are not modular, and exhibit little relationship to fundamental process characteristics. Also, the development of an empirical model relies upon widely distributed data points, which is not a characteristic of the process data collected from No. 93 paper machine.
- C. *Results:* The criteria listed in Table III clearly point toward the adoption of a “first-principles” approach to modeling. In addition, the process data points collected from No. 93 paper machine were not widely distributed throughout the experimental space. Consequently, the data set was very inappropriate for empirical modeling.

The modeling program selection process was influenced by several considerations. First, a dynamic simulation was needed because wet end chemistry phenomena occur over finite time periods in a paper machine system. Second, the simulation must be capable of modeling the physical processes in papermaking, as well as track material transport through the system and in recycle loops. Finally, the simulation program must be capable of calculating wet end chemistry phenomena at appropriate points in the system and take into account situations where a

calculation at one point in the process depends upon a prior event. For example, polymer added at a point in the process affects the flocculation of particles downstream, and information about polymer adsorption must be passed downstream to the flocculation calculation. Taking these considerations into account, the *IDEAS* (Integrated Design Engineering with Advanced Simulation) dynamic simulator (Simons Technologies) was selected for WECCA modeling. The program is capable of doing dynamic mass and energy balances and also has been previously applied to wet end chemistry situations (1,2).

IDEAS simulates the material and energy flows in industrial processes in a dynamic fashion (3). The program represents industrial processes accurately because they are described by the first principles of physics involved. The program is relatively easy to use. It allows the user to construct a process model by retrieving icon-based objects (pumps, pipes, tanks, transmitters, controllers, etc.) from various libraries and assemble them on a drawing worksheet. Individual equipment characteristics can be specified by entering information for each object.

The program runs on the types of small computers commonly found in paper mill control rooms and does not require any special hardware or software. Communication with common DCS systems and data archiving programs, such as *PI*, can be done readily through *Excel* with a dynamic data exchange function.

Simons Technologies' approach to wet end chemistry is to construct a parallel system of scalar calculations that pass material attributes related to wet end chemistry (polymer adsorption, flocculation, charge decay) from one unit operation in the process to another (1). The material-attribute data supplements the traditional description of fluid slurries by enabling the simulator to track parameters such as pulp freeness, fiber specific surface area, and fiber water retention value. Material attributes provide a measure of the amount of processing that fibers have received. The simulator uses specific mixing rules that ensure the correct combination of attributes when different slurries are mixed. A more complete description of this subject is presented in reference (1).

A second generation program based on *IDEAS*, called *Kodiak*, that takes a very user-friendly approach to the handling of stream attributes is under development, and it has been suggested by Simons Technologies personnel that it would be a better program than *IDEAS* for the WECCA project. Conversations are currently being held between IPST and Simons Technologies regarding this issue.

- D. *Scientific Conclusions*: Either Simons Technologies' *IDEAS* dynamic simulator program or *Kodiak* simulator program meet the criteria specified for the WECCA modeling approach, and also are appropriate for the collected process data.
- E. *Economics*: The cost to IPST member companies of purchasing the *IDEAS* program will be the subject of conversations between IPST and Simons Technologies. The cost of installing the program and interfacing with a mill's data archiving system will be very low because no special hardware is needed and commonly available software (*Excel*) is employed.
- F. *Deliverables*: None.

G. References

- (1) Shirt, R. and Manness, M. *Dynamic simulation of retention chemistry effects using a material attribute array structure*. A paper presented at the 1999 TAPPI Engineering Conference. (Attached.)
- (2) Shirt, R. W. *Modeling and Identification of Paper Machine Wet End Chemistry*, Ph.D. Thesis, University of British Columbia, Vancouver, BC, Canada, 1997.
- (3) *IDEAS User Manual*, Simons Technologies, Inc., Version 2.0, Rev. 0.0. 10/30/98.

F. Tables

Table III

Model criteria

1. Unit operations – process based (not “black box” model)
2. Modular – add additional features individually
3. Transportable from machine to machine and mill to mill
4. Low development and implementation costs

3. Creation of a dynamic mass balance simulation for No. 93 paper machine

- A. *Approach*: The model creation approach employed was first to create a dynamic mass balance model for No. 93 paper machine based on information contained in recent P&ID drawings. Next, the model stream flows and compositions were reconciled with actual process data. Separation efficiencies for the saveall, cleaners, and screens were also derived from process data.
- B. *Results*: Figure 11 contains a process flow diagram constructed by tracing pipes on No. 93 paper machine. This diagram was found to agree closely with the P&ID diagram used in model construction. The machine system has a total of 15 chests and associated streams. Table IV indicates the mean residence times associated with the chests. Input streams included the softwood, broke, and bookstock supply streams, the principal chemical additive addition streams, and a fresh water supply stream. Output streams included the paper to the presses and excess clarified white water sent to the mill white water chest from the saveall system.

Figure 12 depicts the complete *IDEAS* mass balance model of No. 93 paper machine. The thick stock system is found in the upper left hand corner of the figure. The thin stock system is found in the right middle section of the figure. The saveall system is in the lower left corner. The large rectangular icons in the figure are the chests, while the smaller icons represent mixers, controllers, pumps, and valves. The arrows represent flow streams. Individual views of the thick stock and thin stock systems are presented in Figures 13 and 14. Figure 15 presents a typical start-up curve for tray consistency. Note that nearly 3000 seconds elapse before the system comes to approximate equilibrium. This is mainly a function of the starting conditions defined for each chest.

Chest level control in the model is usually done by manipulating the flow rate of an incoming stock stream. Proportioner chest level is controlled by varying the flows of the softwood, broke, and bookstock streams, while maintaining their respective ratios. All controllers were set to a PI control configuration. Chemical additive

addition rates are controlled based on the consistency and flow rates of the stock stream to which the additive is introduced. Table V lists their respective addition rates; along with the fiber furnish composition.

C. *Conclusions:*

- a. *Scientific Conclusions:* A dynamic mass balance model of No. 93 paper machine could be constructed with process information gleaned from P&ID diagram of the machine system and daily process data collected from the machine PI data archiving system.
- b. *Economics:* None

D. *Deliverables:* There were no formal deliverables associated with this portion of the work. However, the mass balance model will be a key part of the final wet end chemistry model.

E. *References*

None

F. *Tables*

Table IV

Mean residence times associated with each chest, minutes

Softwood storage chest	165
Bookstock blend chest	23
Broke storage chest	1131
Proportioner chest	16
Machine chest	9
Cleaner chests	1-3 each
Screen chests	4 and 6
Machine silo	45 sec.
Machine white water chest	3
Shower white water chest	5
Recovered solids chest	16

Table V

Addition levels, concentration, and flow rates of principal chemical additives; and fiber furnish composition

PCC	215 lbs/ton	20%	15.5 gpm
Bentonite	5 lbs/ton	5%	1.69 gpm
Cationic Starch	12 lbs/ton	2%	9.8 gpm
AKD	3.5 lbs/ton	1.25%	4.0 gpm
Polymer	1.7 lbs/ton	0.7%	3.71 gpm
Softwood	35% of total fiber furnish		280 gpm
Bookstock	55% of total fiber furnish		450 gpm
Broke	10% of total fiber furnish		170 gpm

G. Figures

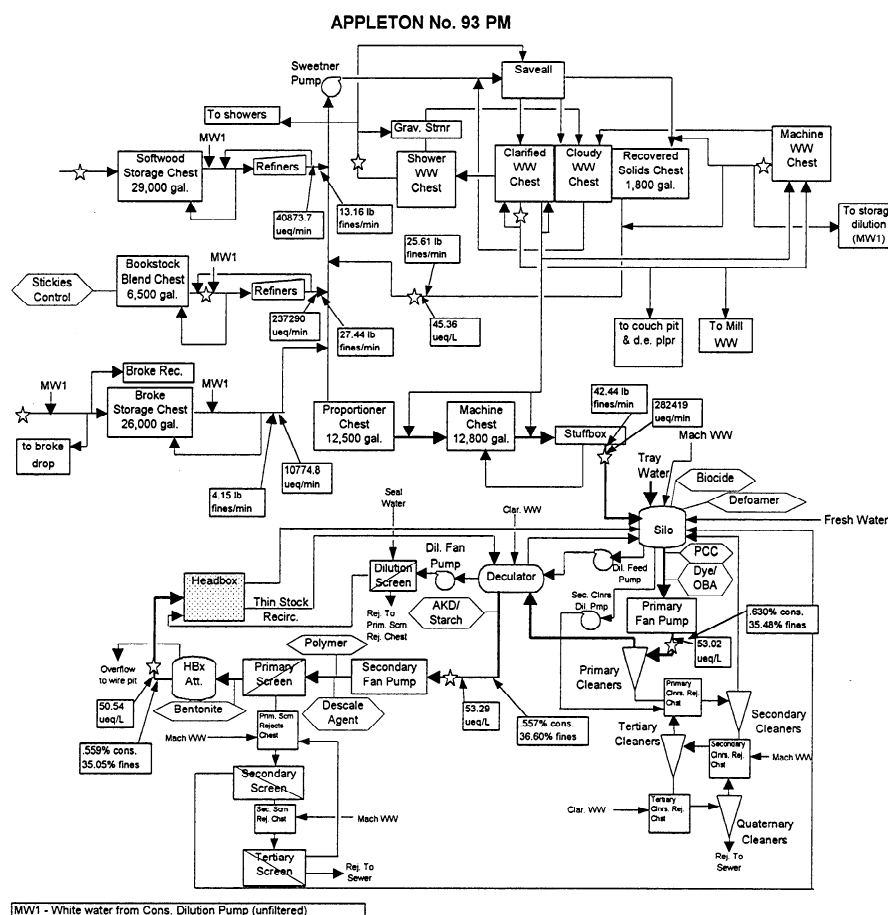


Figure 11. Process flow diagram of No. 93 paper machine.

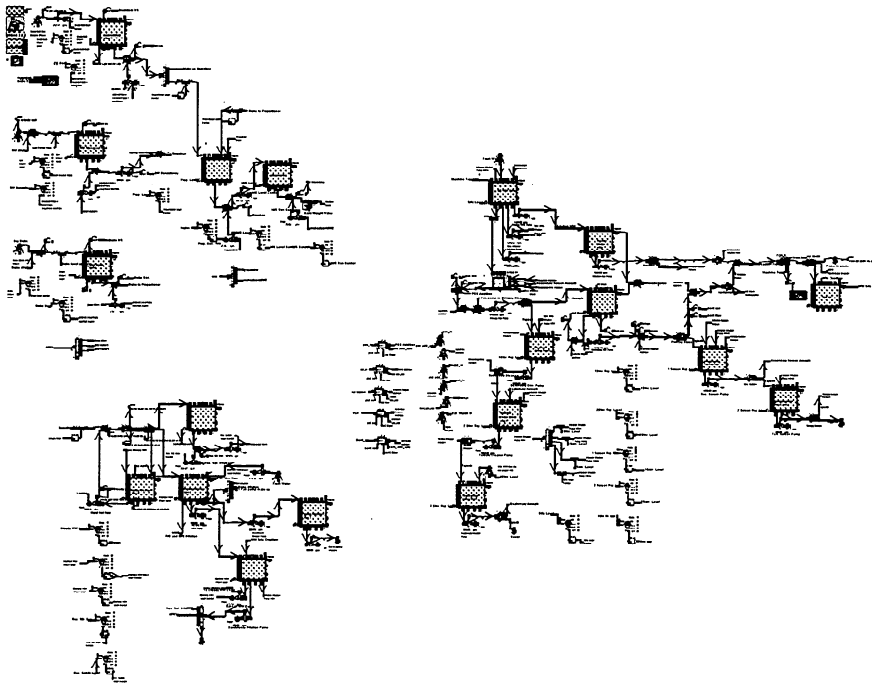


Figure 12. Overview of *IDEAS* mass balance model of No. 93 paper machine. The thick stock area is located in the upper left corner of the figure. The thin stock area is in the right middle portion. And, the saveall system is in the lower left portion of the figure.

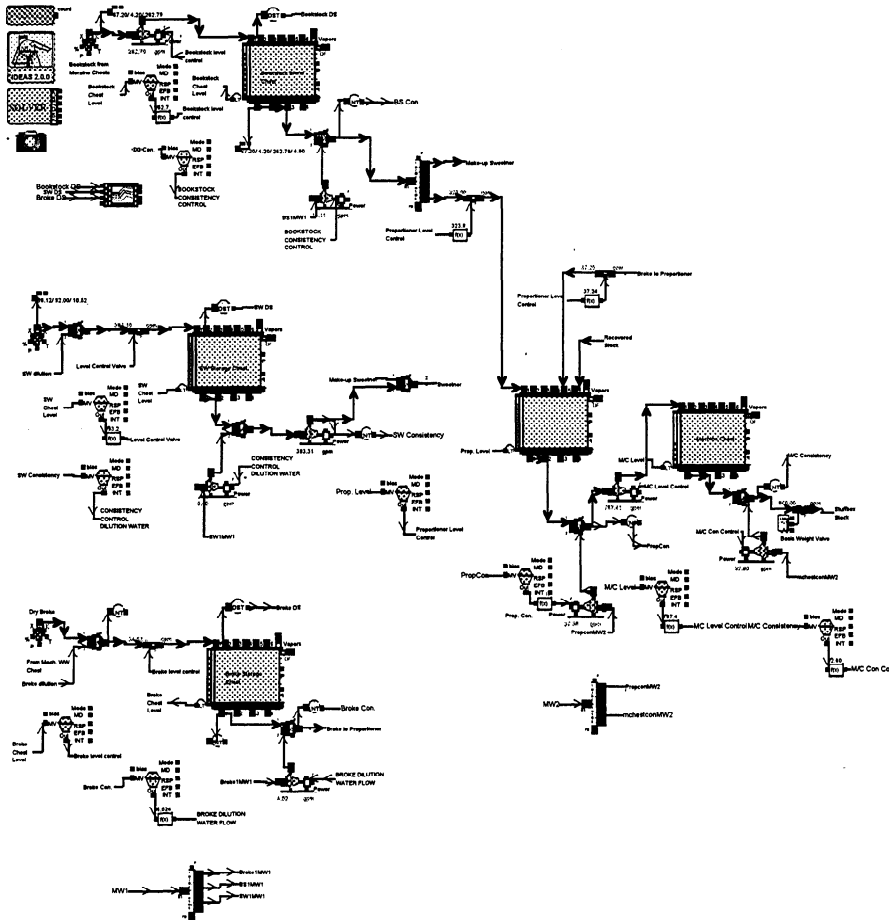


Figure 13.0 *IDEAS* mass balance model of the thick stock area.

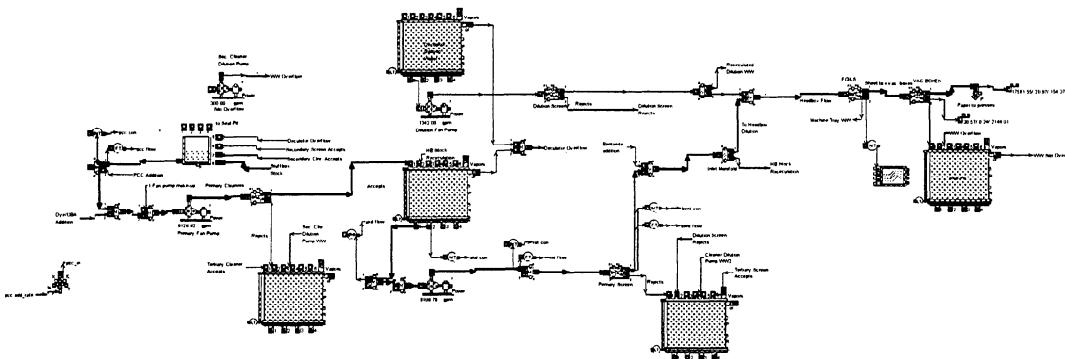


Figure 14. *IDEAS* mass balance model of the thin stock area.

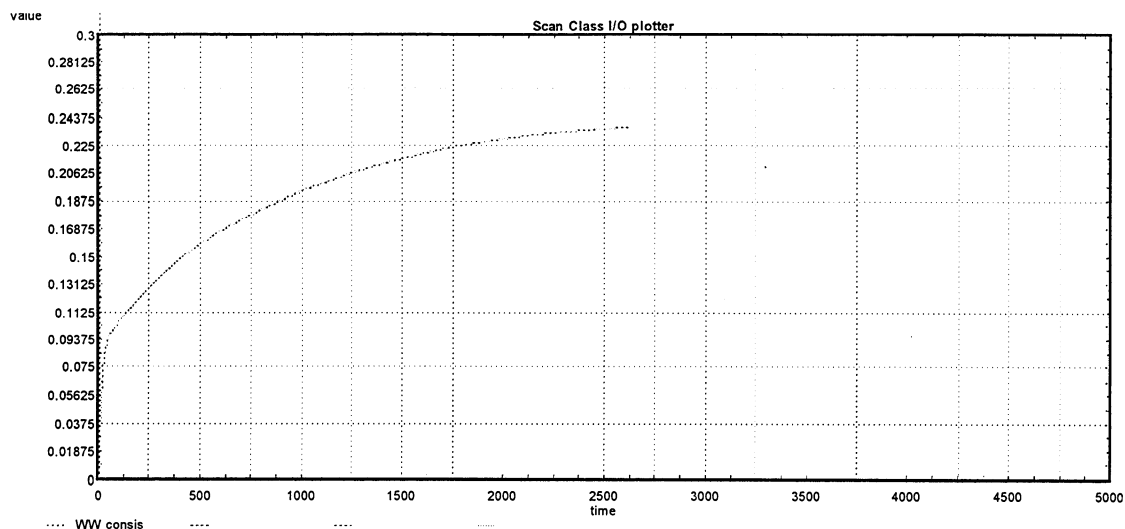


Figure 15. Plot of tray consistency from start-up of the mass balance model to approximately 40 minutes later. No chemistry has been included in the program, so the consistency is approaching 0.25%, which is much greater than the ca. 0.1% found in practice.

4. Developing a more focused view of how WECCA will assist a paper machine operator.

In order to understand how the WECCA predictive control strategy will enable an operator to improve productivity, we can consider the following scenario. Referring to Figure 16 below, suppose that a process upset occurs somewhere in the stock preparation area that leads to an out-of-control situation with tray consistency. Further suppose that there is a 20 minute transport lag between the process upset point and the tray consistency sensor. Thus, 20-minutes elapse before the operator becomes aware of the problem. If we assume that the operator does not recognize that a problem exists for 5 minutes, and that it takes 10 additional minutes to identify the source of the problem and make a correction, then the total time required to return the tray consistency to 0.1% is 55 minutes. This is summarized in Figure 17.

Effective application of a predictive model control strategy would eliminate the problem recognition time and the transport lag component of the problem by presenting the operator with a "picture" of future process performance. This would shave 25 minutes off the process upset duration and facilitate more rapid problem correction. This is illustrated schematically in Figure 18.

In summary, one clear benefit of employing a predictive strategy is that problems involving long transport times can be identified more quickly, thereby reducing process upset time. Thus, in the case of tray consistency control, the WECCA approach will be most effective when process upsets occur in the stock preparation area. The predictive approach has no advantage over traditional feedback control in the thin stock loop where transport lags are insignificant.

Two additional examples where the WECCA process model can be useful include:

- (1) wet end chemistry problem solving where the transport lag information on a WECCA plot can guide an investigation to particular process area; and
- (2) developing “what if?” scenarios for problem solving (e.g., testing effects of alternative furnish changes on predicted tray consistency)

Figures

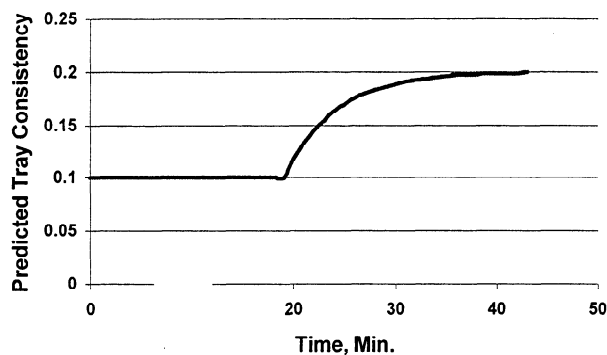


Figure 16. Time series plot of tray consistency when a process upset occurs somewhere in the stock preparation system at time '0'. The upset produces an increase in tray consistency. There is a 20-minute transport lag from the process-upset point to the tray consistency sensor.

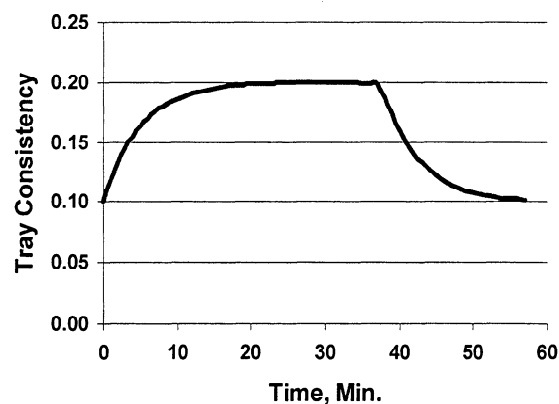


Figure 17. Process response without WECCA assistance. Total upset time = 55 minutes (5 min problem recognition time + 10 min prob. solution time + 20 min of in-process upset stock + 20 min. process response to return to 0.1%).

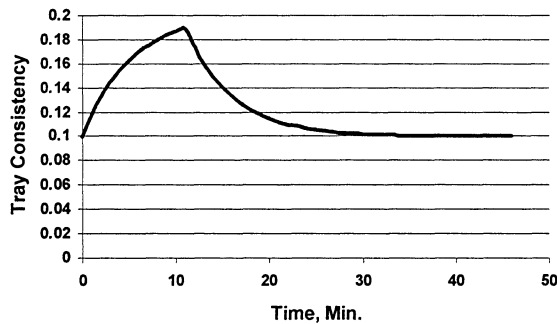


Figure 18. Process response with WECCA assistance. Total upset time = 30 minutes (10 minutes prob. solution time + 20 minutes process response time to return to 0.1%)

5. Incorporating wet end chemistry models in an IDEAS simulation

A. Approach

The *IDEAS* simulation of No. 93 paper machine described above tracks the flows of various furnish components throughout the system and does mass balance calculations around the various processing units. It also accounts for process dynamics in chests and tanks. In order to incorporate wet end chemistry into the simulation, it will be necessary to carry out parallel sets of calculations that relate to the basic phenomena involved, such as polymer adsorption, flocculation, and charge decay. These calculations will be associated with specific processing units (e.g., chests, mixing points) and will be introduced in the appropriate sequence. For example, flocculation occurs after polymer addition, so the calculations pertaining to polymer adsorption must be done before those related to flocculation. Also, mixing rules must be established that will define the correct material attribute values for the mixture when streams having different properties are mixed.

The retention system employed on No. 93 paper machine involves a cationic polyacrylamide and bentonite clay. Thus, one of the basic phenomena that must be taken into account in the wet end chemistry calculations is polymer adsorption. It is often assumed that the adsorption of polymers onto furnish particles can be described by Langmuir kinetics (4). In this case, the fractional coverage, θ , of a particle j 's surface by a polymer is given by the following equation:

$$d\theta_j/dt = k(n_0^j - \theta_j)(1 - \theta_j)$$

where n_0^j is the initial dosage of polymer relative to the amount required to completely cover the particle. This initial relative polymer dosage is calculated from the polymer concentration, c_0 (kg/m³), particle surface area, σ_j (m²/particle), particle number concentration, N_j (particles/m³), and maximal adsorption of the polymer onto the particle surface, Γ_j^{Max} (kg/m²) as

$$n_0^j = c_0 / (\sigma_j N_j \Gamma_j^{\text{Max}})$$

These parameters can be estimated for common papermaking furnish particles and extent of polymer coverage on each type of furnish particle calculated. This computation is inserted in the simulation at the point of polymer addition and surface coverages calculated for each component.

Immediately after the polymer is added, flocculation begins. Gregory (5) developed mathematical models that describe flocculation as follows. For two particles to form a floc the area covered by polymer on the first particle must come into contact with an uncovered area on a second particle. Assuming equal particle densities, the following equation can be written for the rate of flocculation between particles i and j

$$dC_{ij}/dt = k_{ij}C_iC_j \theta (1 - \theta) \{V_iV_j/(V_i+V_j)\}$$

where C_{ij} is the consistency of the flocs composed of particles i and j , C_i and C_j are the consistencies of unflocculated particles, V_i and V_j are the individual particle volumes and K_{ij} is rate constant. Particle volumes can be globally defined and the rate constant adjusted so that measured machine retentions match the calculated values. Integrating the equation over the time lag between the polymer addition time and sheet formation to give the final values of the floc consistencies.

Other assumptions must be made. For example, fixed retention values will be assumed for each of the different types of component particles in the furnish (long fiber, fiber fines, filler, flocs).

The above calculations refer to a single polymer system, plus fibers, fines, and fillers. The No. 93 paper machine system also employs bentonite for retention, which is added late in the system. A literature search will be undertaken to determine what theoretical models have been developed and to determine how they can be adapted for use in the IDEAS simulation.

B. References

- (4) van de Ven, T. G. M. *Particle deposition on pulp fibers*, Nordic Pulp and Paper Res. J., 1(8), 130-147(1993).
- (5) Gregory, J. *Polymer adsorption and flocculation in sheared suspensions*, Colloids and Surfaces, 31, 231-253(1988).

