CHEMICAL RECOVERY

ANNUAL PROGRAM REVIEW

MARCH 21, 1996

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Black Liquor Gasification:

KRAFT RECOVERY FURNACE MODELING CAPABILITY

ANNUAL PROGRAM REVIEW

February, 1995 - February 1996

PROJECT TITLE: KRAFT RECOVERY FURNACE MODELING CAPABILITY

PROJECT STAFF: T. Grace, S. Lien, W. Schmidl

BUDGET:		
	DOE	$302,000 (Oct. 31, 1995 through Jan. 31, 1997)
	Member Funded Research Program (MFRP)	$170,000 1995-96
	Other	$50,000

DIVISION: Chemical and Biological Sciences

PROJECT NUMBER: F016/3605-02 (DOE)

OBJECTIVE:

The overall objective of the work on recovery boiler modeling is to upgrade the capability of kraft recovery boilers through the application of computer-based models of fireside processes. The work is in conjunction with a large DOE supported project on validated recovery boiler models. The current objective of the DOE work is to bring closure to this recovery boiler modeling project in an effective manner that maximizes the usefulness of the total effort to the kraft pulp industry. All of the effort on recovery boiler modeling at IPST in 1996 will be directed toward bringing the DOE modeling program to a successful completion in January 1997.

GOALS:

The following are the goals for the DOE recovery boiler modeling project in 1996.

1. Complete the development of enhanced furnace models that have the capability to accurately predict carryover, emissions behaviour, dust concentrations, gas temperatures, and wall heat fluxes.

2. Establish the validity of these enhanced furnace models so that users will have confidence in the predicted results.

3. Obtain fundamental information on aerosol formation, deposition, and hardening so as to develop the knowledge base needed to relate furnace model outputs to plugging and fouling in the convective sections of the boiler.

4. Facilitate the transfer of codes, black liquor submodels, and fundamental knowledge to the US kraft pulp industry.

SUMMARY:

In January 1995, Tom Grace took over responsibility for the recovery boiler modeling program at IPST following the resignation of Dr. Robert Horton. At that time recovery boiler modeling involved three separate activities.

1. DOE Model Project
2. GA Consortium Project
3. MFRP Modeling Efforts

The original 4-year DOE model project had been extended in Fall 1994 for 3 more years. The objectives of this extended project were to complete the development of the furnace models, validate the models against experimental data, and develop the basis for addressing boiler fouling and plugging.

IPST was the lead institution on the extended project. There were four subcontractors;
University of British Columbia
Oregon State University
Babcock & Wilcox,
Tran Industrial Research.

IPST responsibilities on this extended project were:
1. Project Oversight
2. Implement Emissions and Fume Models
3. Improved Char Bed Model
4. Improved Treatment of Liquor on Wall
5. Improved Spray Model
6. Model Simplification Strategies
7. Sensitivity Studies
8. Validation Coordination
9. Convective Section Modeling and Validation

The Georgia Consortium modeling project involved the application of existing recovery boiler models to specific boilers within Georgia. At the beginning of 1995, two cases had been completed. These were a Tampella boiler at Georgia-Pacific, Brunswick, and the new Tampella boiler at Union Camp, Savannah. The third case, the B&W boiler at Stone Savannah River in Port Wentworth had been started.

During 1995, the third case was completed using simulations with the In-Flight model at IPST and hot flow simulations by UBC with their recovery boiler model. Assessment of these first three cases indicated that the existing models were adequate for dealing with boilers that had problems with carryover of burning black liquor drops, but not really applicable to boilers that had plugging problems associated with fume deposits as was the case for both the Brunswick and Stone Savannah River boilers. The fourth case was a relatively small boiler at the Inland-Rome, Rome mill. This boiler was not encountering any particular problems, but the mill offered to run it as an experimental boiler in order to help validate recovery boiler model simulation predictions. We are using this case for this purpose.

The objective of the IPST Funded Research Program effort in recovery boiler modeling was to upgrade the capability of kraft recovery boilers through the application of computer-based models of fireside processes.

The specific IPST program objectives were:
1. Support fireside model development
2. Cost-effective model utilization
3. Simulations to develop general knowledge about recovery boilers
4. Transfer model technology to users
5. Model validation

Several factors played a big role in what actually happened in the modeling program during 1995:
1. The inability to staff up effectively in this area,
2. The retirement of Stan Sobczynski from DOE,
3. Finding significient deficiencies in the existing FLUENT-based furnace model at IPST and the lack of internal resources to redo the codes in a timely manner,
4. Carrying out a critical review of recovery boiler computer models and their applicability to recovery boiler problem solving.

Internal changes in DOE led to the need to do a renewal proposal after the first year of the extended effort. This was, in effect, treated as if it were a new proposal and thus an opportunity to refocus the efforts and redefine tasks to maximize the utility of the effort. This redefinition of tasks drew heavily on the critical review of recovery boiler modeling that had been carried out.

The overall objective of the renewed project, which began on October 31, 1995, is to bring closure to this recovery boiler modeling project in an effective manner that maximizes the usefulness of the total effort to the kraft pulp industry. The specific objectives of the work are as follows.

1. Complete the development of enhanced furnace models that have the capability to accurately predict carryover, emissions behaviour, dust concentrations, gas temperatures, and wall heat fluxes.

2. Establish the validity of these enhanced furnace models so that users will have confidence in the predicted results.

3. Obtain fundamental information on aerosol formation, deposition, and hardening so as to develop the knowledge base needed to relate furnace model outputs to plugging and fouling in the convective sections of the boiler.

4. Facilitate the transfer of codes, black liquor submodels, and fundamental knowledge to the US kraft pulp industry.

Highlights of the Recovery Boiler Modeling Effort in 1995 Were:

1. Completion of a critical review of computer modeling of recovery boilers.

2. Restructuring of the DOE modeling project to address the critical areas needed to develop a model with the capability to address important operating concerns.

3. Identifying the Inland-Rome boiler as a suitable unit for model validation and as one where operating conditions may be changed substantially to determine the effects on furnace performance.

4. Reaching the decision to abandon the redevelopment of a FLUENT-based recovery furnace model and instead work with and use the UBC model where simulations are required.

5. Establishing effective working relationships with the research on boiler fouling and plugging ongoing at the University of Toronto and Oregon State University.

1996 Recovery Boiler Modeling Effort:

All of the effort in 1996 will be directed toward bringing the DOE modeling program to a successful completion in January 1997. The Georgia Consortium work at Inland-Rome and work on the Member Funded Research Program will be used to support the objectives of the DOE program.

The work is carried out by the five organizations listed below. Major responsibilities are also indicated.

Institute of Paper Science & Technology (IPST) - leadership, bed modeling, validation
University of British Columbia (UBC) - CFD code development, flow validation
Oregon State University (OSU) - fundamental black liquor data, rate equations
Babcock & Wilcox (B&W) - radiation heat transfer
Tran Industrial Research (TIR) - fouling and plugging

IPST Highlights so far in 1996:

1. Three boilers for validation tests have been identified and plans for testing are well underway.
   E.B.Eddy at Espanola, Ont. - take advantage of a U of Toronto project - the testing is scheduled to take place during March 11-15.
   Inland-Rome - tie in with Georgia Consortium work
   James River Naheola mill - tie in with B&W

2. A project team has been formed to deal with char bed modeling - the char bed reactor is being made operational to provide additional data on burning rates and on fume formation during bed burning

3. U of Toronto student is at IPST to do experimental work on fume formation during char bed burning

4. A UBC project team member will come to IPST for two months in April and May to bring the current UBC code to IPST and show us how to run it. This will be used for model validation simulations. In addition, he will work with us on code issues connected with char bed modeling

5. The capability for field testing of recovery boilers is being developed as part of the model validation effort.

STATUS

BLACK LIQUOR COMBUSTION - VALIDATED RECOVERY BOILER MODELING

INTRODUCTION

Monthly status reports are prepared for DOE covering the entire effort in recovery boiler modeling. Activity from all participants is included in these reports. Several of these monthly summaries have been combined for the following section. In addition to giving the current status, a sequential picture of key activity is provided by this method of presentation.

HISTORY:

The project began September 1990 as a cooperative effort between IPST, the University of British Columbia (UBC), Oregon State University, OSU, and T.M.Grace Company. IPST was the recipient of the grant and had the responsibility of overall project management, UBC had primary responsibility for development of the CFD code, and IPST, together with OSU and T.M.Grace Company, had the responsibility to develop the various black liquor submodels that would be incorporated in the CFD code.

UBC has developed CFD codes tailored to the special conditions that exist in recovery boilers. Isothermal flow predictions made with the UBC code have been validated against measurements made on two largescale physical models and one full-size recovery boiler. Work is continuing on developing the code coupling black liquor combustion and non-isothermal flow conditions. The current black liquor combustion models are oversimplified and focus primarily on particle mass changes and trajectories as the liquor burns. They do not yet incorporate all of the critical chemical reactions needed to describe furnace operation.

In September 1994, Babcock & Wilcox (B&W) and Tran Industrial Research (TIR) joined the team to provide additional expertise on radiation heat transfer and on boiler plugging. The current phase of the program started in October 1995. This final phase of the research will provide revised submodels that incorporate aerosol production and sulfur release and recapture as well as an expanded char bed model describing the chemical reactions and physical changes that occur on the char bed. These updated submodels need to be integrated into the CFD code. The other major issue being addressed is validation of the submodels and the global model. This work is expected to be completed by January 1997.

Status (November 30, 1995).

The contract for the project has been signed and subcontracts have been sent out to all subcontractors. A set of milestones has been put together and reviewed with the subcontractors.

The summary report on the first five years of the modeling project is progressing.

UBC has continued work on multigridding methods and convergence schemes. They are ready to incorporate a more advanced black liquor combustion into their code. This will be accomplished through meetings between workers at OSU and UBC. It will take place during December.

The black liquor model development work is continuing at OSU. First generation black liquor drop models incorporating sulfur and sodium release have been developed, but need further refining. There is also a need to test certain assumptions in the treatment of char burning reactions and in the handling of internal heat and mass transfer processes. Discussions have been held concerning the use of a more advanced single drop burning code at B&W to check and validate the more simplified drop model being developed by OSU for incorporation in global furnace models. The drop burning model will serve as the first case for the proposed looseleaf notebook burning model documentation. We are targeted to have the initial version of this complete by the end of February, 1996.

There are several steps underway to improve char bed models. A thesis student from the University of Toronto, Saied Kochesfahani, will come to IPST in early 1996 to carry out experiments on fume release during char burning using the char bed reactor on the DOE black liquor burning facility at IPST. In addition, the existing char bed model will be closely examined. B&W has indicated that they got unreasonably low burning rates when they incorporated it into their recovery boiler model. We plan to work directly with B&W to try to find out the reasons for the low burning rate predictions and modify the model accordingly. We are still awaiting the assembling of the complete model project team at IPST for assigning specific people to the char burning model effort.

Significant progress has been made on plans for validation of the complete models. We may have four different boilers involved. These are the one at the E.B.Eddy mill in Espanola, Ontario, a boiler at Inland-Rome, in Rome, GA, a wall-fired unit in the Southern U.S., and the Weyerhaeuser boiler at Kamloops, BC. A visit was made with people from Honghi Tran's group to the Eddy mill on November 8, to discuss data acquisition plans. This would piggyback model validation tests on an existing test program that Honghi Tran has as part of his program on boiler plugging. The validation tests would probably be carried out in early spring, 1996. The Inland-Rome boiler is one that IPST is working with as part of a Georgia Consortium project. This test will take place in late spring 1996, following the tests at E.B.Eddy. There is also a possibility of a cooperative validation test with B&W on a large boiler at a Southern US mill. Details of such a test are being discussed. Discussions have also been held with UBC about the inclusion of data being acquired by them and Paprican from the Weyerhaeuser boiler at Kamloops, BC and the initial response was positive.

B&W has completed and submitted their report on part one of their work on radiative heat transfer properties for black liquor combustion. This completes the measurement phase of the study. This report will be included as part of the summary report on the first five years of the study.

In general, work on deposition and plugging at OSU and at the University of Toronto is proceeding satisfactorily. OSU will concentrate on aerosol formation in black liquor combustion. Dr. Frederick reports that there is currently some delay with the work at Sandia, because Sandia has not yet received the DOE funds for this program. This is a frustration, but not a critical delay at this time. A full-day meeting of Tom Grace, Honghi Tran, Jim Frederick, and possibly Rick Wessel to review all available information of fume formation is planned for January 10 in Orlando, FL during the TAPPI Kraft Recovery Operations Short Course.

Discussions have been held with UBC about the possibility of transferring the existing, interim full furnace code to IPST for IPST to use for carrying out simulations when necessary. UBC has agreed to do this and a person from UBC will spend several months at IPST to assist with the transfer of the code and with teaching us how to run it. He will also be available to help with the incorporation of advanced char bed models into codes.

At present the project appears to be proceeding well with no major delays in meeting milestones anticipated.

Status (December 31, 1995)

The summary report on the first five years of the modeling project is progressing. The issuance of the report should occur this January.

UBC has worked on modeling turbulent flows across tube banks including the effects of pressure drop and heat transfer. A methodology adopted from Ganapathy and Welty was used for radiative heat transfer.

The black liquor model development work is continuing at OSU. No particular landmark events occurred in the past month.

Work has begun at IPST on modifying the char bed reactor which will be used by Saied Kochesfahani, a thesis student from the University of Toronto, to study fume release during char bed burning. A new staff member, Wolfgang Schmidl, has joined the project team at IPST to work on the char bed model development task. He will be full time on this effort starting in January.

Progress continues on planning for model validation. B&W has agreed to provide a special camera for the upcoming tests at the E.B.Eddy mill in Espanola, Ontario. B&W has agreed to make available data they are obtaining on a James River boiler at the Naheola mill, if James River agrees. Discussions on this matter will be held with James River on January 12. We continue planning for the measurements to be made on the boiler at the Inland-Rome mill in Rome, GA.

B&W has begun work on the second phase of their study of radiative heat transfer properties for black liquor combustion. This completes the measurement phase of the study.

A full-day meeting of Tom Grace, Honghi Tran, Jim Frederick, and Rick Wessel will be held on January 10 in Orlando, FL during the TAPPI Kraft Recovery Operations Short Course. This meeting will review all available information on black liquor burning and fume formation to clearly identify what is known and unknown and to facilitate planning for the remainder of the years work in this area. In addition, model validation planning will be covered.

Tom Grace will visit OSU on January 22 and 23 and will meet with Jim Frederick and Larry Baxter (from Sandia) to review the work that Scott Sinquefield is doing at Sandia. Discussions will also be held with Kaj Wag with regard to facilitating the transfer of the latest knowledge of black liquor burning to UBC for incorporation in their model. Discussions will also be held with Jim Frederick on how to document the current black liquor drop burning model in the proposed looseleaf notebook format. The initial version of this document is targeted to be completed by the end of February.

At present the project appears to be proceeding well with no major delays in meeting milestones anticipated.

Status (January 29, 1996)

The principle investigator spent several days at IPST in early January in order to get the char bed modeling work started, coordinate the validation planning, and deal with contract issues. Meetings were held with Rick Wessel of B&W and Honghi Tran of the University of Toronto in Orlando, FL and site visits were made to OSU and UBC. Larry Baxter of Sandia was present at the meetings at OSU. Thus, meetings were held with all participants in the project during the month.

The summary report on the first five years of the modeling project has been delayed because of time constraints of the principle investigator, T.M. Grace. It was felt more critical to devote the month of January to getting all of the different project activities coordinated. All of the remaining writing on this report needs to be done by T.M. Grace. This will require about six full time days to complete. Grace will be spending most of the month of February at IPST and will complete the report this coming month.

A full time staff member, Wolfgang Schmidl, has been assigned to the char bed modeling activity at IPST. He is spending the month of January reviewing all available information on char beds and will begin active model development work in February. We have set a target to have a first generation bed model available by the end of April.

The validation tests at the E.B.Eddy mill in Espanola, Ontario are scheduled to take place in the time period between February 26 and March 8, 1996. Steve Lien of IPST has been in contact with B&W about learning how to use the special camera and to arrange for its shipment to the mill site. The data acquisition plan is reasonably complete but is still being embellished. IPST will assume responsibility for getting the necessary liquor analyses done.

Preliminary discussions have been held with B&W and James River about using the B&W boiler at the Naheola mill as an additional boiler in the validation effort. Work is continuing with Inland-Rome on the tests planned on this unit.

Saied Kochesfahani, from the University of Toronto, will come to IPST in February to carry out experiments on fume formation during bed burning on the char bed reactor at IPST. He will not be able to get to IPST before February 19, because of paper work requirements to get his visa to enter the US.

Dan Tse will come to IPST for two months during the period from mid-March to mid-May. His primary responsibility will be to facilitate the transfer of the current UBC hot flow model with black liquor combustion to IPST. He will also work with IPST on code interface issues as the char bed model is being developed. He will take back with him the first generation char bed model developed by IPST for incorporation into the UBC code.

A number of issues dealing with the black liquor drop burning model and with predictions of fume formation and deposition were raised during meetings with various subcontractors this month. The principle investigator will be working closely with OSU in the next few months to resolve these issues.

The progress on documenting the existing black liquor drop burning model was reviewed. The first version of the looseleaf notebook documentation is due to be completed by the end of February. It appears that this schedule can be met. The main task now is to put the model in concrete form for use in CFD furnace models. There remains too much of an orientation toward the specific experimental setups from which the data were obtained.

Status (February 23, 1996)

The summary report on the first five years of the modeling project is about 85% complete. Every attempt will be made to complete the report before March 1.

Reactivation of the char bed reactor system at IPST has begun. Saied Kochesfahani will come to IPST on February 26 to start work on measuring fume formation during char bed burning. We plan to carry out at least one char burning test on the reactor before mid-March.

The validation tests at the E.B.Eddy mill in Espanola, Ontario are firmly set for March 11 - 15. The test plan is complete and the necessary equipment for carrying out the test is being assembled. There are only two things that could cause a delay. An unscheduled outage at the mill or a failure of Diamanod Power to get their high resolution bed cameras to the site on tixne. Paprican is developing a dirty pitot tube velocity probe and if their initial test of this probe in a fumace next week are successful, they will try to take it to Espanola for the validation test at Eddy.

Work is continuing with Inland-Rome on the tests planned on this unit but this will be a low level effort until after the test at Eddy.

Dan Tse will come to IPST for two months during the period from the last week in March until the end of May. His primary responsibility will be to facilitate the transfer of the current UBC hot flow model with black liquor combustion to IPST. He will also work with IPST on code interface issues as the char bed model is being developed. He will take back with him the first generation char bed model developed by IPST for incorporation into the UBC code.

Oregon State has made considerable progress on documenting the existing black liquor drop burning model with a target to have the first version of the looseleaf notebook form completed by the end of February. There are some issues with details of the formulation of the drying and devolitilization model that need to be resolved.

Code development work at UBC is proceeding satisfactorily.

THE PYROLYSIS OF FUEL NITROGEN FROM BLACK LIQUOR

A Thesis Submitted by
Denise M. Martin

B.S. 1989, Viterbo College

M.S. 1991, Institute of Paper Science and Technology

in partial fulfillment of the requirements
of the Institute of Paper Science and Technology
for the degree of Doctor of Philosophy,
Atlanta, Georgia

September, 1995

SUMMARY

NO_x emissions resulting from the combustion of black liquor arise from the fuel NO_x mechanism, that is NO_x is formed by oxidation of the chemically bound nitrogen in the fuel. The mechanism is complex and involves numerous reactions. Identification and characterization of many of these reactions has been reported and largely involve HCN and NH_i intermediate species. However, little information exists on the details of the fuel nitrogen species decomposition to form the fuel NO_x intermediates. Thus, the present work focuses on understanding the formation of fuel NO_x intermediates during pyrolysis of black liquor.

A four-part experimental program was employed to 1) determine the chemical form of nitrogen in black liquor, 2) evaluate the analysis for nitrogen species in a total nitrogen measurement, 3) study pyrolysis with respect to the black liquor composition and operational parameters, and 4) provide an understanding of the formation processes through the formation pathway and depletion kinetics involved.

Black liquor nitrogen was found to be predominantly organic with the nitrogen bound in heterocyclic rings, both five- and six-member, and in straight-chain amines. Multiple species were present with individual compounds below the analytical detection limit for individual species making up 79% of the total organic nitrogen. The nitrogen was primarily associated with the acid-insoluble fraction of the liquor, which contains predominantly larger molecular weight organic compounds. Little nitrogen was associated with the acid-soluble liquor fraction. Thus, emphasis was placed on nitrogen bound in organic compounds. The types of nitrogen identified in the liquors varied between and within the tree species from which the liquor was generated. Multiple forms of nitrogen suggest various pathways for NO_x formation during black liquor combustion. Model compounds were selected based on the black liquor nitrogen

characterization and were used to evaluate the conversion for the total nitrogen measurement and to study nitrogen conversion to NO_x or NO_x precursors during pyrolysis.

The fuel nitrogen recovery for the analytical measurement varied from 35-91% (by weight) of the original fuel nitrogen content depending on the nitrogen species chemical structure. The nitrogen chemistry proved to be more important as compared with the kinetics and thermodynamics of the experimental system. The fractional recovery of the inorganic fuel nitrogen did not change for nitrate- and ammonium-type species regardless of the compound from which the nitrogen evolved. The organic forms of nitrogen, amines, and heterocyclic compounds, varied with respect to their individual bonds and structures. The variation observed indicates that intermediate reactions that lead to both N_2 and NO_x are important in understanding the overall formation of fuel NO_x.

The addition of alkali, as NA_2CO_3 and NaOH, to aqueous solutions of organic fuel nitrogen model compounds decreased the fuel nitrogen recovery by approximately 10%. Increased inorganic concentrations further decreased the recovery. No effect was observed for Na_2SO_4. It is theorized that sodium carbonate decomposed and sodium hydroxide vaporized at the reaction temperature of 1100°C such that sodium species entered the gas phase allowing reactions to occur which deplete NO_x and the NO_x precursors. Sodium sulfate does not enter the gas phase at these temperatures and had no effect. An opposite result was found for inorganic fuel nitrogen as NHCl. As the Na_2CO_3 concentration, i.e. the alkali concentration, in solution increased, more NH_3 was driven into the gas phase to be detected.

Pyrolysis was assumed to initially evolve a series of gas phase NO_x precursors termed GPNP. These are the sum of all gas phase nitrogen intermediates that eventually lead to NO_x or N_2. The oxygen concentration (0-22% 0_2) did not affect the total nitrogen released. The pyrolysis heating rate employed also had little effect on the total nitrogen released at 1-150°C/min or on the gas phase composition at rates from 10-1000°C/sec. Potential pathways have been provided for fuel nitrogen conversion for pyrolysis conditions which form the HCN and NH_i intermediate species. These pathways offer further insight into the otherwise limited information for this portion of the fuel NO_x formation mechanism.

The depletion of the GPNP species to form N_2 was investigated kinetically and found to follow a first-order homogeneous irreversible gas phase reaction,

$$\mathbf{N_{GPNP}} \dashrightarrow N_2$$

The activation energy for an assumed first-order reaction was found to be 850 cal/mol indicating a low temperature sensitivity. The low activation energy is suggestive of radical or catalytic reactions occurring in the depletion process.

The knowledge gained for the effects of fuel composition on the fuel nitrogen conversion provide a greater understanding to the overall fuel NO_x mechanism and is applicable to general stationary combustion processes and specifically to the combustion of black liquor during recovery boiler operations. Both individual nitrogen species and related inorganic matrix have an effect of NO_x generation. Conditions that provide time for the GPNP species to react prior to oxidation may lead to lower NO_x emissions.

A complete copy of this thesis is available from IPST's Information Services Division.

CLOSED MILL OPERATIONS

CLOSED MILL OPERATIONS

TECHNICAL PROGRAM REVIEW

February, 1995 - February, 1996

PROJECT TITLE: Closed Mill Operations

- Impact and Control of Nonprocess Elements (NPE's)
- Fundamentals of Dregs Removal
- Electro-membrane Purging of Chloride
- Analysis and Prediction of VOC

FYR 1996 BUDGET:

Total	$595,000
NPE's	300,000
Dregs Removal	110,000
Chloride Removal	130,000
VOC	30,000
Other	25,000

PROJECT STAFF: Bryant (NPE's), Empie (Dregs Removal), Pfromm (Chloride Removal), Malcolm (general), Rudie (NPE's), Zhu (VOC).

PROJECT CODE: CLDMIL
PROJECT NUMBER: F017
PAC(s): Chemical Recovery, Chemical Pulping and Bleaching
DIVISION: Chemical and Biological Sciences
LONG RANGE AREA: Minimization of Environmental Impact (RAC area 1).

PROGRAM OBJECTIVES:

Overall - Develop the technology required to move toward low effluent operation. This includes the pulping, bleaching, and chemical recovery technology needed to promote mill closure. Close coordination with Projects F013, F015, and F019 is required.

Impact and Control of Nonprocess Elements (NPE's) - Develop a scientific understanding of the material balance and partitioning of nonprocess elements in pulp and paper mill process streams. Provide member companies with mathematical models that predict the behavior of NPE's with different configurations and operating conditions. Determine the impact of NPE's on mill operations.

The Nature and Removal of Hard to Remove Iron - Evaluate novel metals removal strategies, with an emphasis on improving the removal efficiency of iron. Determine the nature of "hard to remove" iron in pulp.

Fundamentals of Dregs Removal - Determine the effect of elevated levels of NPE's on the composition, settling, and filtration rates of green liquor dregs with the goal of improving dregs separation from green liquor in support of reduced effluent operations.

Electro-membrane Purging of Chloride - Evaluate the selective removal of chloride and potassium by electrodialysis of dissolved electrostatic precipitator catch (ESP catch). Show technical feasibility with simulated and actual mill materials. Estimate economic feasibility. Pursue external funding.

VOC Analysis and Prediction - The goal of this research program is to develop a VOC computer model which will enable users to simulate the partitioning of hazardous air pollkutants (HAP's) in the liquid streams of pulping and paper making unit operations. The subtask has four objectives: (1) Experimental study of vapor-liquid phase equilibrium of model and actual mill streams to obtain liquid activity coefficients which will be used for model prediction; (2) Computer model development for the prediction of VOC generation and release; (3) Model validation; and (4) Development of control strategies to reduce VOC's in Kraft mills.

CLOSED MILL OPERATIONS

Task: Impact and Control of Nonprocess Elements (NPE's)

Patrick Bryant

Summary

Work began in August 1994 to develop a scientific understanding of the material balance and partitioning of non-process elements (NPE) in pulp and paper mill process streams and to provide member companies with mathematical models that predict the behavior of NPE's in pulp and paper mills with different process configurations and operating conditions. The research plan includes mill sampling, laboratory experiments, full-mill simulation, predictive model development, and model verification.

Mill Base-Line Studies

We are working with three member companies to develop three bleached kraft mill NPE material balances. This work involves sampling and analyzing process streams at each mill for NPE's and developing a full-mill process simulation for each mill.

The purpose of conducting mill base-line studies is to develop a better understanding of the partitioning of NPE's in bleached kraft mills, to develop NPE material balances for mills from different geographical areas that have different process configurations, and to develop full-mill simulations that can be used to validate NPE predictive models.

Three member company mills are participating in the NPE material balance base-line studies. The first mill (A) is a Southern single line market kraft pulp mill with conventional continuous kraft cooking and ECF bleaching. The mill campaigns runs of hardwood and softwood for periods of 1-2 weeks. The mill has white liquor pressure filters in place of conventional white liquor clarifiers. The mill has a single low odor recovery boiler.

The second mill (B) is a Southern dual line (SW and HW) integrated kraft pulp mill with conventional continuous kraft cooking, medium consistency O_2 delignification, and conventional C/D bleaching. The mill has white liquor and lime mud pressure filters in place of conventional clarifiers. The mill has two liquor recovery operations with low odor recovery boilers, but processes the liquor as mixed liquor from both pulping lines.

The third mill (C) is a Northern dual line (SW and HW) integrated kraft pulp mill with conventional continuous kraft cooking of HW and MCC continuous cooking of SW, medium consistency O_2 delignification, and conventional C/D bleaching of HW and ECF bleaching of SW. The mill has combined liquor recovery operations with three recovery boilers all using direct contact evaporators. The mill uses conventional clarifiers in liquor recovery.

Mill A was sampled in December 1994, Mill B in May 1995, and Mill C in June 1995. Chemical analysis of the samples has been delayed due to organizational problems, personnel turnover, and equipment failure within our Chemical Analysis Group. These problems have been addressed by hiring three new staff members and by purchasing a new inductively coupled plasma (ICP) atomic emission spectrometer for metal analysis. Chemical analysis of Mill A is scheduled to be complete in March 1996, Mill B in May 1996, and Mill C in June 1996.

A full-mill simulation for Mill A was completed in February 1995. Construction of full-mill simulations for Mills B and C are in progress and scheduled for completion by May 1996. Completion of NPE material balances for each mill is scheduled for September 1996.

Laboratory Experiments

The Beneficial Effects of Dissolved Organic Carry-over When Closing the Bleach Plant

Mill and laboratory studies indicate that carry-over or carry-back of dissolved solids into the acid wash (A) or acid chelation (Q) stage improves manganese removal from pulp and results in lower hydrogen peroxide consumption and higher pulp brightness. This improvement in manganese removal is a result of ion exchange with sodium and a poorly understood reaction between dissolved organics and cations that occurs under acidic conditions. It appears that under acidic conditions, dissolved organics irreversibly bind to metal cations forming a colloidal suspension. This irreversible reaction reduces the amount of freely dissolved cations that can participate in ion exchange with the pulp fibers. Detailed experimental procedures and results are presented in the task status section.

Sorption of Cations onto Unbleached Kraft Pulp

Laboratory experiments have been completed to characterize the sorption of cations onto pulp fiber using three different commercial unbleached kraft pulps using two different chelants at different pH's. Data from these experiments will be used to determine sorption constants for cations onto pulp in multicomponent systems. Experimental procedures and results are given in the following status section.

Binding Capacities and Equilibrium Constants

Two M.S. students (Ryan Mills and Eddie Gravely) are developing experimental procedures to measure the binding site concentrations and equilibrium formation constants for the binding of cations with pulp and with dissolved organics using single or binary cation systems. Preliminary experiments using ion-selective probes to measure the binding capacity and formation constants of calcium and sodium to weak black liquor are yielding positive results.

Impact of Fines on Cation Sorption

Initial experiments investigating the impact of primary and secondary fines on NPE behavior yielded indeterminate results. Recently published work by Heijnesson et al. from Chalmers University of Technology lead to the following conclusions:

1. Primary fines have a significantly higher lignin content and acid group content relative to average fibers.
2. Lignin-rich surface material (secondary fines) can be removed by mild mechanical treatment. Secondary fines generated in this way have a higher acid group content relative to average fibers.
3. The metal content of primary and secondary fines correlates with their lignin and acid group content.

Heijnesson's work clearly shows that the ion-exchange capacity of pulp increases as the fines content increases. No further PAC research is planned for this topic.

Literature Cited:

Heijnesson, B., Simonson, R., and Westermark, U., Metal Ion Content of Material Removed from the Surface of Unbleached Kraft Fibres, *Holzforschung* 49(1):75-80 (1995).

Heijnesson, B., Simonson, R., and Westermark, U., Removal of Lignin-rich Surface Material from Unbleached Kraft Fibres, *Holzforschung* 49(4):313-318 (1995).

Aqueous Phase Chemical Equilibrium Model

The beta release of a general aqueous phase chemical equilibrium model is in testing. The purpose of the equilibrium model is to determine which of three phases NPEs will partition into: 1) dissolved solid, 2) suspended solid, 3) pulp-bound solid. Integrating the equilibrium model within a process simulation system (WinGEMS) enables one to evaluate different closure and purge scenarios and to predict NPE concentrations under those scenarios. Final release of version 1.0 is scheduled for September 1996.

Status Section

STATUS

As noted in the summary, further details on "The Beneficial Effects of Dissolved Organic Carry-over When Closing the Bleach Plant" and the "Sorption of Cations onto Unbleached Kraft Pulp" are given in the status section.

INTRODUCTION

The Beneficial Effects of Dissolved Organic Carry-over When Closing the Bleach Plant

Abstract

Mill and laboratory studies indicate that carry-over or carry-back of dissolved solids into the acid wash (A) or acid chelation (Q) stage improves manganese removal from pulp and results in lower hydrogen peroxide consumption and higher pulp brightness. This improvement in manganese removal is a result of ion exchange with sodium and a poorly understood reaction between dissolved organics and cations that occurs under acidic conditions. It appears that under acidic conditions, dissolved organics irreversibly bind to metal cations forming a colloidal suspension. This irreversible reaction reduces the amount of freely dissolved cations that can participate in ion exchange with the pulp fibers.

Introduction

The quantity of each cation that binds to pulp fibers in the fiberline is determined by the following:

1. The total number of carboxylic acid binding sites on the pulp, typically 0.1 mole/kg o.d. fiber for unbleached kraft pulp and half that for fully bleached pulp.
2. The concentration of each ***freely*** dissolved cation.
3. The concentration of competing ligands. Competing ligands include chelants such as EDTA and DTPA and dissolved organics generated in pulp and bleaching reactions.
4. The relative affinity of each cation for each competing ligand, i.e., its formation constants.

Recycling acidic bleach plant filtrates to the alkaline brownstock washers can create a "metal trap." The metal trap occurs because under acidic conditions most cations are desorbed from the pulp by ion exchange with hydrogen ions, and under alkaline conditions most of the cations are sorbed by the pulp by ion exchange with hydrogen ions. This sorption/desorption phenomenon between acid and alkaline wash stages results in a buildup of cations within the loop.

The concentration of cations in the filtrate must increase to the level where the amount being carried over with the pulp mat liquor in the bleach washer and the amount being carried back to recovery in the weak black liquor is equal to the amount entering the fiberline from the digester.

Mills running closed and partially closed bleach plants have seen increased calcium concentrations because of the metal trap phenomenon.[1-3] In contrast, several mills report reductions in manganese when running the Q stage countercurrent.[2-4]

Linden[3] postulates that the presence of HS^- in the washer filtrates keeps manganese in the +2 oxidation state, making it easier to chelate compared to the higher oxidation sates of manganese. In its Mn(II) state, manganese forms a very stable complex with the chelants EDTA or DTPA and should remain soluble.

However, in a TCF fully countercurrent bleaching trial, Bryant and Edwards[4] found a reduction in manganese to the Q stage when the filtrates were run countercurrently back to the brownstock fiberline which included medium consistency O_2 delignification. The oxygen stage and postoxygen stage washer filtrates have oxidative potentials. Mn(II) is not thermodynamically favored in alkaline systems. Based on thermodynamics, Bryant and Edwards[5] have speculated that $MnOH^+$ should be the dominate species of manganese in alkaline filtrates. As a univalent ion, $MnOH^+$ would have a relatively low affinity for EDTA and DTPA and a moderate affinity for the acid sites on pulp. Formation of $MnOH^+$ would make manganese difficult to chelate in alkaline stages.

Lindeberg[6] has calculated that sodium concentrations in the A or Q stage can increase from 0.2 to 6 g/liter when closing up an alkaline hydrogen peroxide bleach plant. The increased sodium concentration in filtrates results in lower bound concentrations of other competing ions due to ion exchange. Further displacement of manganese can be accomplished by adding magnesium to the A or Q stage.

Laboratory studies were conducted to determine the impact of dissolved organic carry-over into a metals removal stage. This work follows up previous laboratory and mill studies by Bryant et al.,[7-9] which showed reduced binding of cations onto pulp when the dissolved organic concentration in the acid wash or Q stage increased. The studies also showed that if the WBL was acidified separately from the pulp and metal cations, it did not behave as a chelant when added to alkaline pulp slurries. The current hypothesis to explain this behavior is that under acidic conditions dissolved organics irreversibly bind to cations in a colloidal suspension. The metals bound to the colloidal suspension are not free to resorb to the pulp under alkaline conditions and because of their small size follow the filtrate split in washing operations.

Further studies are needed to determine if the underlying fundamentals of these observations can be used to manage the fiberline metal profiles with dissolved organics acting as natural chelants and sodium taking the place of hydrogen as a competitive ion under alkaline conditions.

Experimental

Laboratory experiments to determine the impact of dissolved organics on the sorption of cations onto pulp fiber were conducted using a commercial unbleached kraft pulp. The pulp was stored at 4°C as received. The characteristics of the pulp used in these experiments are given in Table A.1 and are referenced as *Pulp A*. The initial metal content of the pulp was measured by inductively coupled plasma (ICP) atomic emission spectrometry and is given in Table A.2. Pulp samples were prepared for metal analysis by drying, grinding, and digesting in hydrochloric and nitric acid following EPA method 3050.

The weak black liquor used in the experiments came from a single line Southern market bleached kraft pulp mill that runs campaigns of softwood and hardwood. ICP chemical analysis of the WBL is given in Table A.3.

Table A.1 Initial pulp characteristics.

	Pulp A
Wood Species	Southern Pine
Digester	Kamyr Vapor
O_2 Delignification	Sunds MC
Sample Location	2nd O_2 Wash Press
Initial Consistency, %	41.0
Kappa	18.0
% ISO Brightness	27.9
CSF, ml	745
Fiber Length, mm*	2.62
% Fines**	1.03
Carboxylic Acid Content (moles/kg o.d. fiber)	0.087

*Kajaani length weighted mean, **Kajaani < 0.100 mm

The starting pulp consistency for all experiments was approximately 40%. Pulp was diluted to 1% consistency with nano-pure water having 18 MΩ·cm resistivity at 25°C. Pulp slurry pH's were adjusted with either H_2SO_4 (EM Science TracePur Plus) or NaOH (EM Science ACS reagent grade). The pulp slurry pH was adjusted to either 2.0, 3.0, 4.0, or 5.0 and mixed for 30 minutes with a 2.5-inch diameter polypropylene U-shaped paddle at 200-300 rpm in a 2-liter glass-tempering beaker with circulating water in the shell to maintain a temperature of 75±0.5°C. After 30 minutes, the slurry was adjusted to a pH of 10.5 by addition of concentrated NaOH and mixed at the same temperature for 15 minutes.

WBL was added in the amount of 0.0, 0.1, 0.5, 1.0, or 2.5% of total liquid volume in the slurry either immediately after the slurry was acidified or immediately after it was taken alkaline. The 0.0% addition of WBL served as a control experiment. The pulp slurry was then vacuum dewatered across a Buchner funnel to approximately 25% consistency. The pulp was further dewatered by pressing to approximately 50% consistency. The pulp was then analyzed by ICP.

Table A.2. Initial metal content (mg/kg o.d. fiber) measured in four replicate unwashed Pulp A samples, 18 Kappa oxygen-delignified kraft from Southern Pine softwood.

	Sample Replicate				Statistics		
Element	1	2	3	4	Mean	Median	CV %
Na	2354.0	2124.0	2160.0	2103.0	2185.3	2142.0	5.3
Mg	436.0	430.0	409.0	390.9	416.5	419.5	4.9
Al	12.1	10.0	9.3	8.9	10.1	9.7	14.1
P	33.1	38.7	31.7	34.2	34.4	33.7	8.8
K	241.5	219.1	235.3	233.6	232.4	234.5	4.1
Ca	1104.0	1169.0	1026.0	1108.0	1101.8	1106.0	5.3
Mn	54.6	54.7	48.6	51.9	52.4	53.2	5.5
Fe	6.0	6.6	4.4	5.0	5.5	5.5	17.6
Zn	3.8	8.8	BQL	4.2	5.6	4.2	49.5
Cu	BQL	BQL	BQL	BQL	-	-	-
Co	BQL	BQL	BQL	BQL	-	-	-
Ba	6.4	6.3	5.8	5.8	6.1	6.1	5.4

Table A.3. Initial metal content (mg/liter of liquor) measured in three replicate WBL samples.

	Sample Replicate			Statistics		
Analyte	1	2	3	Mean	Median	%CV
TS (%)	15.8	15.5	15.8	15.7	15.8	1.0
Na	128200	128500	165900	140867	128500	15.4
Mg	72.0	74.0	74.8	73.6	74.0	1.9
Al	68.9	BQL	84.4	76.6	76.6	14.3
K	11710.0	1169.0	12703.0	8527.3	11710.0	75.0
Ca	202.0	176.9	210.1	196.3	202.0	8.8
Mn	54.8	56.3	54.1	55.1	54.8	2.0
Fe	37.6	BQL	23.9	30.7	30.7	31.5
Co	BQL	BQL	BQL	-	-	-
Cu	1.6	BQL	BQL	1.6	1.6	-
Zn	BQL	BQL	36.6	36.6	36.6	-
Ba	BQL	1.6	4.8	3.2	3.2	70.1

Results and Discussion

The effects of both sodium competition and acidified weak black liquor are shown in Figures A.1-A.3. The concentrations of bound manganese, magnesium, and calcium dropped substantially from their initial values due to sodium competition. The lower pH slurries required a greater amount of NaOH for neutralization. The higher sodium concentrations in the initially lower pH slurries resulted in the greatest reduction of bound cations due to sodium competition.

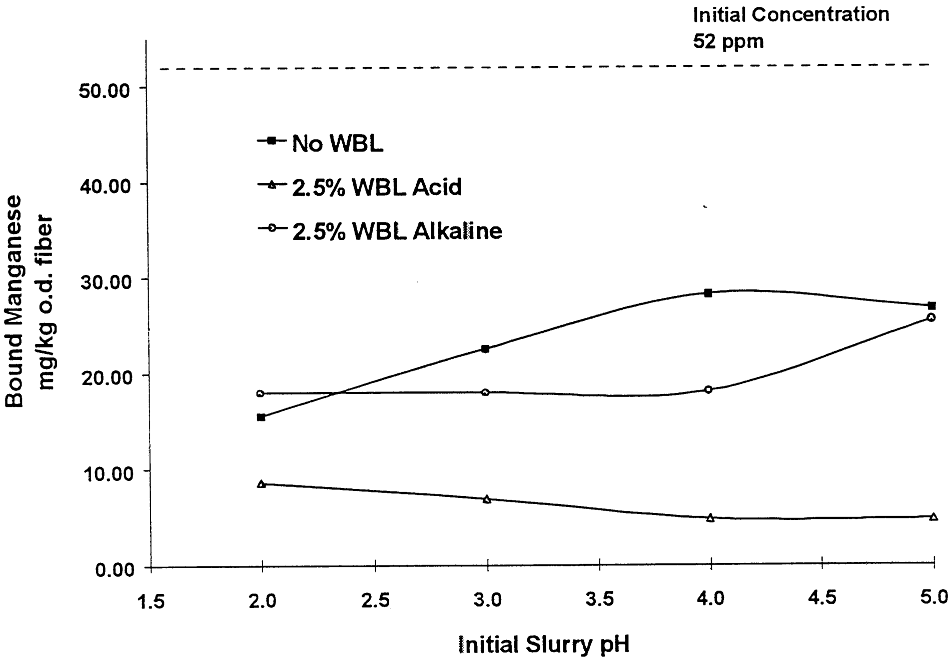

Figure A.1. Manganese bound to pulp fiber as a function of initial pulp slurry pH and pH when WBL is added. Slurry mixed in acid conditions for 30 minutes then at 10.5 pH for 15 minutes. Temperature 75°C.

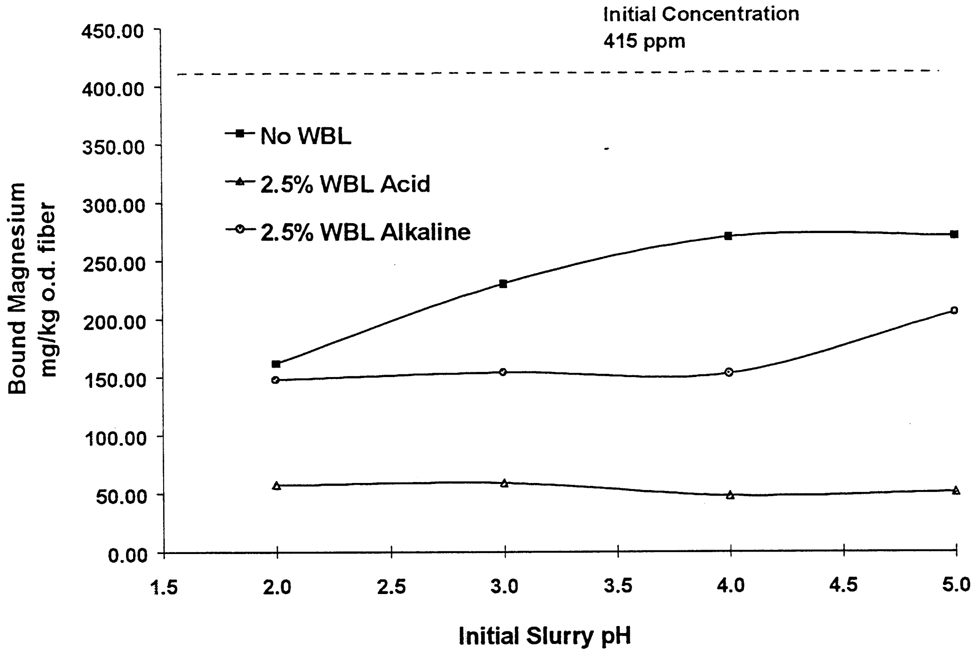

Figure A.2. Magnesium bound to pulp fiber as a function of initial pulp slurry pH and pH when WBL is added. Slurry mixed in acid conditions for 30 minutes then at 10.5 pH for 15 minutes. Temperature 75°C.

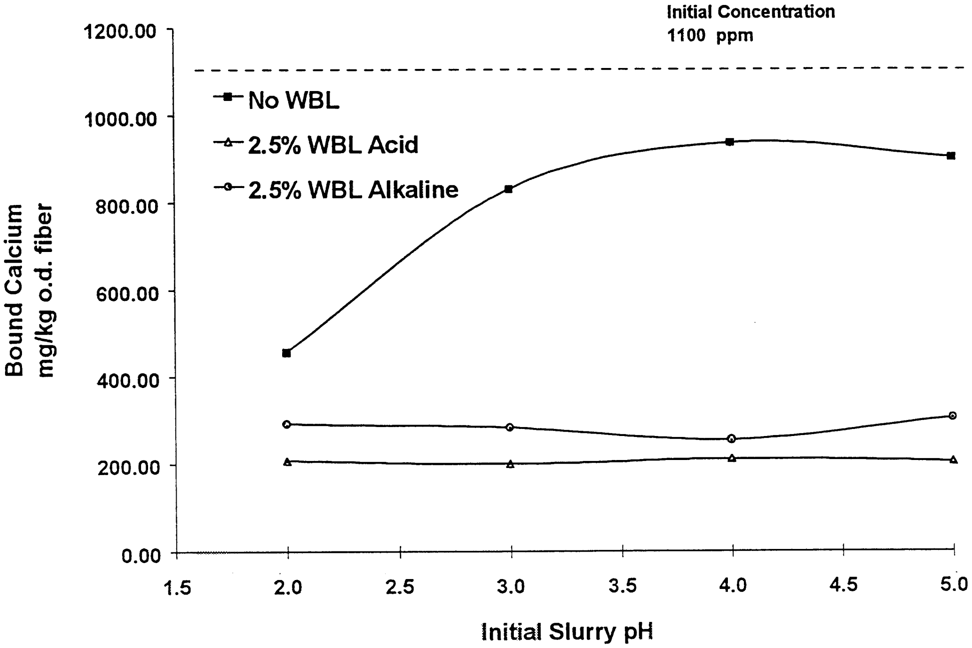

Figure A.3. Calcium bound to pulp fiber as a function of initial pulp slurry pH and pH when WBL is added. Slurry mixed in acid conditions for 30 minutes then at 10.5 pH for 15 minutes. Temperature 75°C.

Adding WBL in either alkaline or acid conditions lowered the bound concentration of all three cations. The reduction of bound Mn and Mg was slightly higher when WBL was added under alkaline conditions compared to the control case without WBL. The reduction of bound Mn and Mg was significantly higher when WBL was added under acid conditions. Bound Mn was reduced by 80% when WBL was added at a pH of 5.0 compared to either the control or compared to the case when WBL was added under alkaline conditions.

The reduction of bound Ca was significantly higher compared to the control when WBL was added in either acid or alkaline conditions. Calcium's unique behavior may indicate that it has a greater binding affinity for dissolved organics regardless of pH history.

Conclusions

Closing up the bleach plant often results in a decrease in pulp-bound manganese prior to a metals removal stage. This reduction results from increased ion exchange competition from sodium and an apparently irreversible reaction between dissolved organics and cations under acidic conditions. Further studies are needed to characterize these acid-promoted reactions.

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STATUS

INTRODUCTION

Sorption of Cations onto Unbleached Kraft Pulp

Experimental

Three commercial unbleached kraft pulps were used in the laboratory cation sorption experiments. Pulps A and B were stored at 4°C as received. Pulp C was centrifuged to approximately 35% consistency and then stored at 4°C. Table B.1 lists the characteristics of each pulp. The initial metal content of each pulp was measured by inductively coupled plasma (ICP) atomic emission spectrometry and is given in Tables B.2-B.4. Pulp samples were prepared for metal analysis by drying, grinding, and digesting in hydrochloric and nitric acid following EPA method 3050.

The starting pulp consistency for all experiments was approximately 35-40%. Pulp was diluted to 1% consistency with nano-pure water having 18 MΩ·cm resistivity at 25°C. Pulp slurry pH's were adjusted with either H_2SO_4 (EM Science TracePur Plus) or NaOH (EM Science ACS reagent grade). Pulp slurries were mixed for 30 minutes with a 2.5-inch diameter polypropylene U-shaped paddle at 200-300 rpm in a 2-liter glass tempering beaker with circulating water in the shell to maintain a temperature of 75±0.5°C. The pulp slurry was then vacuum dewatered across a Buchner funnel to approximately 25% consistency. The pulp was further dewatered by pressing to approximately 50% consistency. The pulp was then analyzed by ICP.

Experiments conducted with chelants used either 0.3% on a dry fiber basis Baker Chemicals ethylenediaminetetraacetic acid (EDTA) or 0.4% on a dry fiber basis Aldrich Chemicals diethylenetriaminepentaacetic acid (DTPA).

Results

Table B.1 Initial pulp characteristics

	Pulp A	*Pulp B*	*Pulp C*
Wood Species	Southern Pine	Mixed South. HW	Southern Pine
Digester	Kamyr Vapor	Batch	Kamyr Hydraulic
O_2 Delignification	Sunds MC	Sunds MC	none
Sample Location	2nd O_2 Wash Press	2nd O_2 Wash Press	Decker (pre-bleach)
Initial Consistency, %	41.0	29.1	17.1
Kappa	18.0	12.7	28.6
% ISO Brightness	27.9	42.2	23.5
CSF, ml	745	615	735
Fiber Length, mm*	2.62	0.98	2.52
% Fines**	1.03	3.16	0.92
Carboxylic Acid Content (moles/kg o.d. fiber)	0.087	0.090	0.088

*Kajaani length weighted mean, **Kajaani < 0.100 mm

Table B.2. Initial metal content (mg/kg o.d. fiber) measured in four replicate unwashed Pulp A samples, 18 Kappa oxygen delignified kraft from Southern Pine softwood.

	Sample Replicate				**Statistics**		
Element	**1**	**2**	**3**	**4**	**Mean**	**Median**	**CV %**
Na	2354.0	2124.0	2160.0	2103.0	2185.3	2142.0	5.3
Mg	436.0	430.0	409.0	390.9	416.5	419.5	4.9
Al	12.1	10.0	9.3	8.9	10.1	9.7	14.1
P	33.1	38.7	31.7	34.2	34.4	33.7	8.8
K	241.5	219.1	235.3	233.6	232.4	234.5	4.1
Ca	1104.0	1169.0	1026.0	1108.0	1101.8	1106.0	5.3
Mn	54.6	54.7	48.6	51.9	52.4	53.2	5.5
Fe	6.0	6.6	4.4	5.0	5.5	5.5	17.6
Zn	3.8	8.8	BQL	4.2	5.6	4.2	49.5
Cu	BQL	BQL	BQL	BQL	-	-	-
Co	BQL	BQL	BQL	BQL	-	-	-
Ba	6.4	6.3	5.8	5.8	6.1	6.1	5.4

Table B.3. Initial metal content (mg/kg o.d. fiber) measured in four replicate unwashed Pulp B samples, 13 Kappa oxygen delignified kraft from mixed Southern hardwoods.

	Sample Replicate				Statistics		
Element	**1**	**2**	**3**	**4**	**Mean**	**Median**	**CV %**
Na	6042.0	6026.0	5998.0	5874.0	5985.0	6012.0	1.3
Mg	319.5	315.1	310.9	312.3	314.5	313.7	1.2
Al	9.4	5.6	0.9	9.8	6.4	7.5	64.4
P	69.7	70.8	69.6	70.8	70.2	70.2	0.9
K	775.8	774.2	758.7	718.0	756.7	766.5	3.6
Ca	2320.0	2312.0	2287.0	2394.0	2328.3	2316.0	2.0
Mn	88.2	89.9	88.8	93.1	90.0	89.3	2.4
Fe	14.7	14.4	10.3	9.9	12.3	12.3	20.8
Co	BQL	BQL	BQL	BQL	-	-	-
Cu	2.2	0.4	0.4	0.3	0.8	0.4	114.7
Zn	14.2	9.3	6.1	8.2	9.4	8.8	36.4
Ba	25.5	25.4	25.7	26.0	25.7	25.6	1.1

Table B.4. Initial metal content (mg/kg o.d. fiber) measured in four replicate unwashed Pulp C samples, 29 Kappa conventional kraft from Southern Pine softwood.

	Sample Replicate				Statistics		
Element	**1**	**2**	**3**	**4**	**Mean**	**Median**	**CV %**
Na	1127.0	1027.0	1276.0	1187.0	1154.3	1157.0	9.1
Mg	246.5	216.6	255.4	257.0	243.9	251.0	7.7
Al	11.8	10.7	12.6	11.1	11.6	11.4	7.2
P	22.1	22.7	23.0	23.7	22.9	22.8	2.8
K	156.8	165.1	183.0	169.8	168.7	167.5	6.5
Ca	1081.0	1037.0	1100.0	1104.0	1080.5	1090.5	2.8
Mn	80.0	77.1	82.7	82.0	80.4	81.0	3.1
Fe	7.9	5.8	10.5	8.1	8.1	8.0	23.5
Co	BQL	BQL	BQL	BQL	-	-	-
Cu	BQL	0.1	0.5	BQL	0.3	0.3	85.1
Zn	8.0	5.5	17.2	12.3	10.8	10.1	47.6
Ba	10.0	9.7	10.3	10.0	10.0	10.0	2.2

Table B.5. Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C without chelant. Pulp A, 18 Kappa oxygen delignified kraft from Southern Pine softwood.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	BQL	7.2	12.5	3.5	23.4	0.8	BQL	3.2	0.2
2.0	4.4	27.0	BQL	6.4	46.0	1.3	0.9	0.3	0.2
2.5	72.1	20.4	1.8	5.4	73.0	2.0	0.5	BQL	0.3
3.0	65.4	38.3	7.6	6.1	136.5	5.1	1.8	0.6	0.7
3.5	64.6	65.3	3.8	10.2	197.2	8.6	1.8	BQL	1.0
4.5	103.8	149.1	6.3	7.2	477.0	25.3	3.1	1.3	2.7
5.5	142.9	226.2	3.1	12.6	696.9	38.6	2.9	2.9	3.8
6.5	143.6	255.3	3.5	22.4	798.4	42.6	3.1	1.8	4.1
7.5	244.1	379.6	1.9	33.0	989.0	53.7	3.1	5.3	5.4
8.5	337.1	380.0	2.2	36.1	948.4	51.1	3.1	2.0	5.3
9.5	649.9	400.0	4.5	44.3	977.4	54.1	3.1	5.6	5.8
10.0	871.0	396.3	6.1	32.8	948.9	54.1	4.1	6.4	5.7
10.5	1288.0	415.9	12.5	13.9	908.5	54.9	9.1	9.1	5.5
11.0	2535.0	373.8	16.5	13.8	808.7	48.6	10.7	23.2	4.6
11.5	5926.0	270.3	21.4	19.7	715.6	49.8	11.8	2.8	3.4

Table B.6. Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C with 0.3% EDTA. Pulp A, 18 Kappa oxygen delignified kraft from Southern Pine softwood.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	18.7	10.5	3.6	12.2	24.1	3.1	4.7	6.5	0.1
2.0	18.8	12.0	5.6	20.4	45.0	0.9	9.3	18.1	0.2
2.5	35.2	23.6	4.1	25.7	86.3	1.9	3.1	21.4	0.3
3.0	40.5	40.8	4.5	16.3	129.7	2.1	4.2	14.8	0.7
3.5	61.0	85.8	7.4	11.2	241.5	1.1	5.6	24.6	1.2
4.5	95.5	169.8	10.5	10.1	448.2	0.3	5.6	33.6	2.5
5.5	164.1	360.4	9.1	21.8	739.6	1.9	5.6	21.9	4.4
6.5	210.0	467.6	10.6	29.1	847.5	5.6	8.8	16.9	5.3
7.5	284.1	495.7	10.6	40.4	840.1	17.5	7.9	20.6	5.3
8.5	397.6	513.7	15.6	49.8	871.1	29.8	8.9	25.6	5.8
9.5	619.5	564.6	13.3	53.8	814.0	40.3	13.1	10.6	5.3
10.0	868.4	499.2	16.8	34.4	789.9	43.0	9.0	45.4	5.7
10.5	1430.0	523.8	16.7	23.0	753.0	53.9	9.7	19.4	5.4
11.0	2400.0	535.6	20.2	16.2	732.8	54.2	8.2	35.8	4.7
11.5	4080.0	527.3	17.7	16.2	677.4	56.7	11.8	20.6	3.7

Table B.7. Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C with 0.4% DTPA. Pulp A, 18 Kappa oxygen delignified kraft from Southern Pine softwood.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	22.7	8.8	4.8	BQL	25.8	0.7	1.3	11.1	0.2
2.0	36.5	19.5	BQL	BQL	48.6	1.0	BQL	4.0	0.2
2.5	52.1	24.4	11.5	7.3	88.0	2.5	8.9	5.6	0.5
3.0	65.4	46.8	5.8	7.7	149.2	3.8	5.2	6.3	0.8
3.5	38.4	109.0	37.9	9.6	278.4	3.8	20.3	92.7	1.7
4.5	133.6	221.6	33.6	17.7	542.6	0.9	16.7	44.1	3.7
5.5	166.0	272.4	43.2	114.9	692.2	1.2	17.6	87.9	4.7
6.5	227.1	459.6	40.2	239.0	748.4	6.2	26.7	89.8	5.8
7.5	229.9	506.6	11.3	162.3	725.9	15.9	11.8	9.4	5.1
8.5	388.9	424.5	45.6	272.9	827.2	23.9	15.3	84.4	6.0
9.5	521.9	506.1	19.6	243.0	766.3	26.7	9.0	14.9	7.0
10.0	799.4	247.9	38.8	144.5	747.0	30.2	12.2	78.5	6.0
10.5	1100.0	773.3	30.2	95.3	695.9	37.3	14.7	54.9	7.4
11.0	1420.0	642.0	19.7	89.1	579.3	43.0	7.5	BQL	4.4
11.5	2980.0	490.6	14.0	49.4	602.2	48.3	4.0	11.7	3.9

Table B.8. Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C without chelant. Pulp A, 13 Kappa oxygen delignified kraft from Southern mixed hardwoods.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	69.2	5.6	5.3	5.8	70.7	1.0	2.6	BQL	1.1
2.0	97.8	12.1	3.8	10.3	119.9	1.9	6.2	0.2	1.2
2.5	133.5	21.0	10.7	10.4	200.1	5.0	5.3	26.8	1.9
3.0	191.8	33.4	5.1	20.5	283.9	8.6	5.3	14.0	2.7
3.5	295.3	55.3	3.1	BQL	528.1	17.9	9.2	4.1	4.6
4.5	413.8	135.4	4.1	56.9	1229.7	45.7	6.9	4.7	3.9
5.5	539.9	200.5	9.2	64.1	1560.2	66.6	9.8	5.3	3.5
6.5	784.9	224.8	7.4	103.6	1718.0	70.9	10.2	BQL	4.2
7.5	1037.0	245.2	12.6	130.9	1695.0	71.0	8.7	6.9	14.6
8.5	865.7	257.8	16.5	133.8	1109.0	77.0	10.5	8.8	3.5
9.5	1265.0	252.8	16.7	163.0	1297.0	73.7	12.4	8.6	4.7
10.0	1290.0	264.5	18.0	138.8	1299.0	76.0	7.7	5.6	3.1
10.5	1441.0	267.1	17.2	117.8	1251.0	78.9	9.4	8.6	3.5
11.0	1962.0	254.7	20.3	BQL	1181.0	75.8	12.0	16.5	12.7
11.5	4854.0	173.2	10.2	BQL	735.5	47.9	4.6	2.3	8.9

Table B.9. Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C with 0.3% EDTA. Pulp A, 13 Kappa oxygen delignified kraft from Southern mixed hardwoods.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	81.7	BQL	4.7	BQL	51.4	0.6	21.7	5.5	1.2
2.0	113.7	BQL	9.8	BQL	65.2	0.7	2.3	30.9	1.1
2.5	157.1	18.3	2.3	BQL	138.2	2.6	1.7	1.1	1.2
3.0	190.9	22.8	1.0	BQL	205.3	2.8	1.6	BQL	1.5
3.5	340.6	51.1	11.8	BQL	387.5	3.4	3.4	3.1	BQL
4.5	544.2	149.1	BQL	BQL	1268.5	5.7	7.3	10.0	0.8
5.5	794.7	205.6	28.5	BQL	1801.0	8.7	4.8	0.3	0.3
6.5	1108.9	235.2	BQL	106.9	1683.5	11.5	5.3	3.1	0.8
7.5	1456.1	231.7	BQL	152.7	1569.6	18.8	7.8	10.2	0.8
8.5	1885.9	264.7	24.5	156.5	1380.9	27.9	9.2	3.8	0.4
9.5	2070.1	243.0	18.0	143.0	1433.7	37.2	8.8	11.5	BQL
10.0	2687.5	275.3	31.2	142.8	1559.4	44.3	13.9	10.0	0.4
10.5	2719.0	272.3	21.1	BQL	1572.3	52.5	11.1	6.5	0.4
11.0	3356.3	269.5	BQL	BQL	1456.4	60.8	8.4	4.2	BQL
11.5	5960.7	247.0	24.4	BQL	1412.1	60.9	9.5	11.4	0.4

Table B.10. Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C with 0.4% DTPA. Pulp A, 13 Kappa oxygen delignified kraft from Southern mixed hardwoods.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	26.5	BQL	3.1	BQL	27.9	1.1	1.9	1.6	0.8
2.0	41.4	6.3	BQL	BQL	47.1	1.5	2.2	0.7	0.8
2.5	101.6	19.1	0.2	BQL	118.1	3.6	0.4	1.8	1.5
3.0	65.8	20.1	BQL	BQL	141.2	3.6	0.8	BQL	1.1
3.5	251.2	71.7	1.6	BQL	516.7	6.3	1.8	0.4	5.0
4.5	507.6	119.2	3.0	BQL	1447.0	3.9	0.3	1.8	9.5
5.5	541.2	186.7	13.4	66.2	1354.0	6.3	2.2	1.1	13.9
6.5	31.5	21.3	BQL	BQL	138.3	1.6	BQL	BQL	1.9
7.5	900.0	265.1	9.9	161.1	1000.0	21.7	9.0	14.2	18.0
8.5	850.6	166.5	14.1	136.2	816.6	16.7	5.0	4.8	2.7
9.5	1580.0	187.5	19.5	138.0	1263.0	28.5	8.4	8.9	4.7
10.0	1175.0	197.9	18.7	122.4	915.5	34.6	10.6	6.3	4.6
10.5	1460.0	185.1	20.5	85.7	976.6	35.0	11.2	1.7	5.8
11.0	1342.0	169.0	18.0	BQL	793.0	38.6	7.4	4.9	6.2
11.5	4378.0	205.7	15.9	BQL	1412.0	64.1	10.1	3.4	5.4

Table B.11. Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C without chelant. Pulp A, 29 Kappa conventional kraft from Southern Pine softwood.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	12.2	230.8	8.6	14.1	31.1	1.1	16.0	19.4	0.2
2.0	17.9	219.1	6.1	10.3	75.0	1.9	14.8	13.5	1.9
2.5	33.0	224.3	12.3	31.5	76.8	3.2	17.0	16.6	0.4
3.0	35.7	215.8	12.7	12.8	96.2	4.8	14.4	25.7	0.6
3.5	36.5	213.8	13.7	BQL	181.7	11.9	13.8	6.7	1.6
4.5	72.4	184.2	17.2	15.2	463.7	34.9	16.1	12.6	4.7
5.5	107.8	237.7	6.5	3.1	781.4	65.4	9.7	13.4	7.6
6.5	204.5	236.6	13.2	27.2	941.3	78.3	11.2	23.1	8.6
7.5	247.7	299.8	12.1	48.9	1016.0	85.1	13.3	12.8	9.9
8.5	317.1	281.4	13.7	47.8	1055.0	85.3	11.1	13.5	10.2
9.5	538.4	294.7	16.0	53.5	1044.0	85.4	9.7	12.9	10.1
10.0	763.6	288.5	8.5	42.4	993.8	84.7	11.2	11.0	10.0
10.5	1241.0	256.6	5.0	23.5	912.6	78.2	14.2	11.2	8.7
11.0	1965.0	321.1	16.3	12.9	993.3	83.0	11.6	12.9	9.5
11.5	3899.0	322.9	8.5	BQL	884.4	77.3	9.4	25.0	7.7

Table B.12. Concentration of metal bound to pulp (mg/kg o.d..fiber) as a function of pH after 30 minutes mixing at 75°C with 0.3% EDTA. Pulp A, 29 Kappa conventional kraft from Southern Pine softwood.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	18.4	199.9	8.2	BQL	33.7	1.1	18.9	13.7	0.2
2.0	19.9	199.6	3.7	BQL	41.3	1.3	17.0	6.9	0.2
2.5	30.0	184.7	9.7	7.1	68.0	1.9	25.9	9.3	0.4
3.0	42.5	194.7	8.0	BQL	101.1	2.9	21.6	7.1	0.7
3.5	40.1	158.8	3.1	11.5	176.9	2.1	15.9	3.1	1.5
4.5	71.5	201.7	13.3	13.8	466.0	0.9	19.7	6.8	4.5
5.5	138.7	256.3	19.2	24.6	831.6	1.5	17.5	8.2	8.4
6.5	193.5	273.2	16.8	39.3	850.9	2.3	16.1	BQL	9.2
7.5	333.4	300.1	19.0	55.2	919.6	8.2	18.3	BQL	10.1
8.5	429.2	295.6	17.5	62.9	884.0	16.4	13.5	BQL	9.9
9.5	649.3	291.9	23.6	53.0	849.8	26.7	12.1	2.0	9.7
10.0	882.6	299.0	16.7	34.4	852.8	40.7	10.7	BQL	9.8
10.5	1192.0	302.7	16.0	27.6	784.4	50.4	12.5	10.0	8.4
11.0	2128.0	315.9	15.1	16.3	731.5	70.9	13.2	4.6	8.5
11.5	3992.0	313.6	18.9	15.3	610.1	69.1	15.4	13.2	5.2

Table B.13. Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C with 0.4% DTPA. Pulp A, 29 Kappa conventional kraft from Southern Pine softwood.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	13.4	214.1	BQL	BQL	23.4	1.0	13.8	8.9	0.2
2.0	17.3	230.7	3.9	BQL	48.6	1.2	12.9	17.3	0.4
2.5	21.1	227.1	4.4	BQL	85.8	3.6	15.2	13.9	0.6
3.0	38.0	217.0	BQL	BQL	116.6	5.0	11.5	13.5	1.0
3.5	56.0	176.5	BQL	BQL	202.4	4.9	10.0	20.4	1.7
4.5	85.2	250.9	7.3	BQL	564.4	1.7	10.4	23.6	5.0
5.5	125.7	227.8	15.6	BQL	787.0	0.7	11.3	BQL	8.3
6.5	201.3	202.9	2.6	33.1	748.1	1.1	5.7	7.4	9.6
7.5	300.2	266.5	10.8	15.8	768.2	3.4	15.8	36.7	9.9
8.5	308.7	241.6	11.0	50.3	721.2	5.5	13.7	6.3	9.1
9.5	581.4	239.6	13.9	45.0	654.8	9.8	11.7	8.2	8.9
10.0	748.4	273.4	8.2	42.0	691.6	10.2	12.9	11.1	8.7
10.5	1127.0	291.7	17.4	24.8	682.6	18.0	16.6	5.1	9.0
11.0	2015.0	284.2	14.4	18.5	612.6	48.4	14.0	8.3	8.0
11.5	5115.0	328.8	6.6	13.5	568.7	64.0	27.8	9.4	6.0

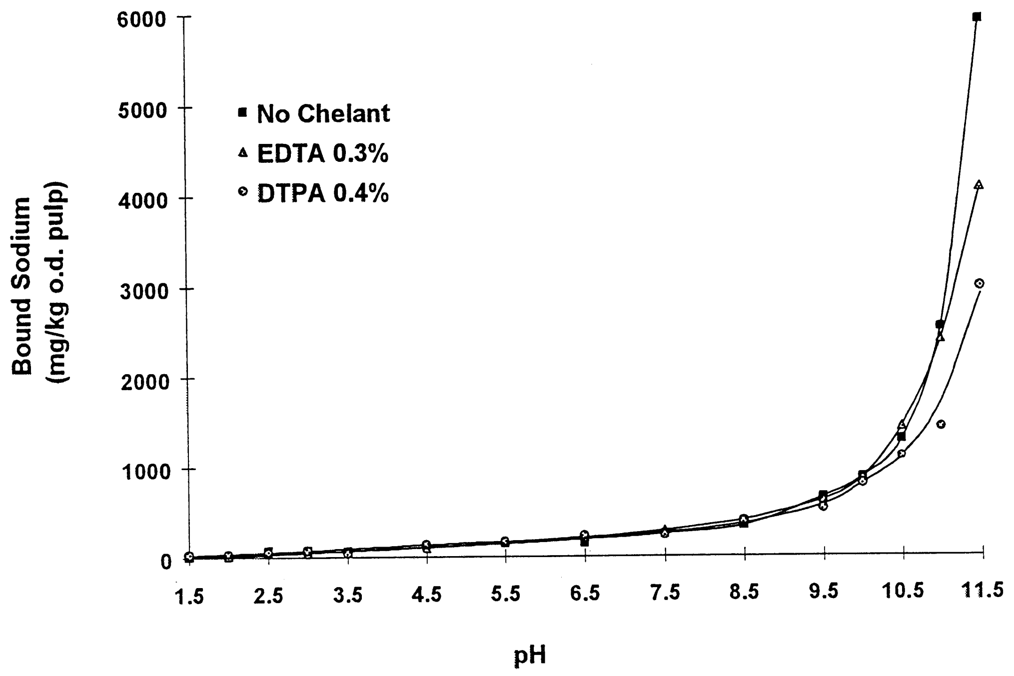

Figure B.1. Fiber-bound sodium as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

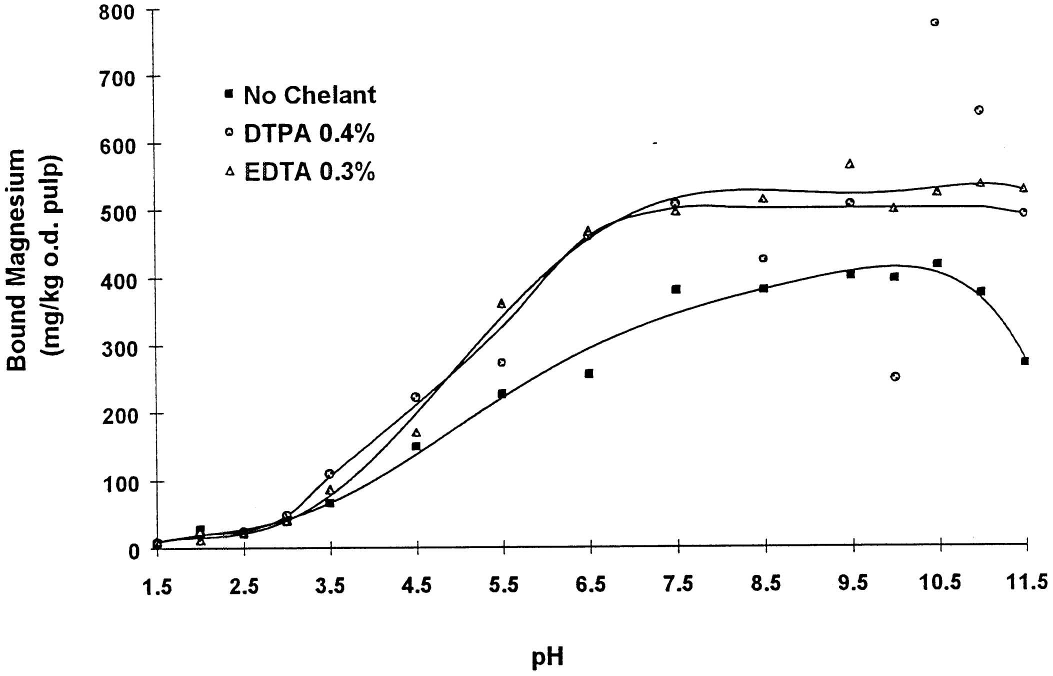

Figure B.2. Fiber-bound magnesium as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

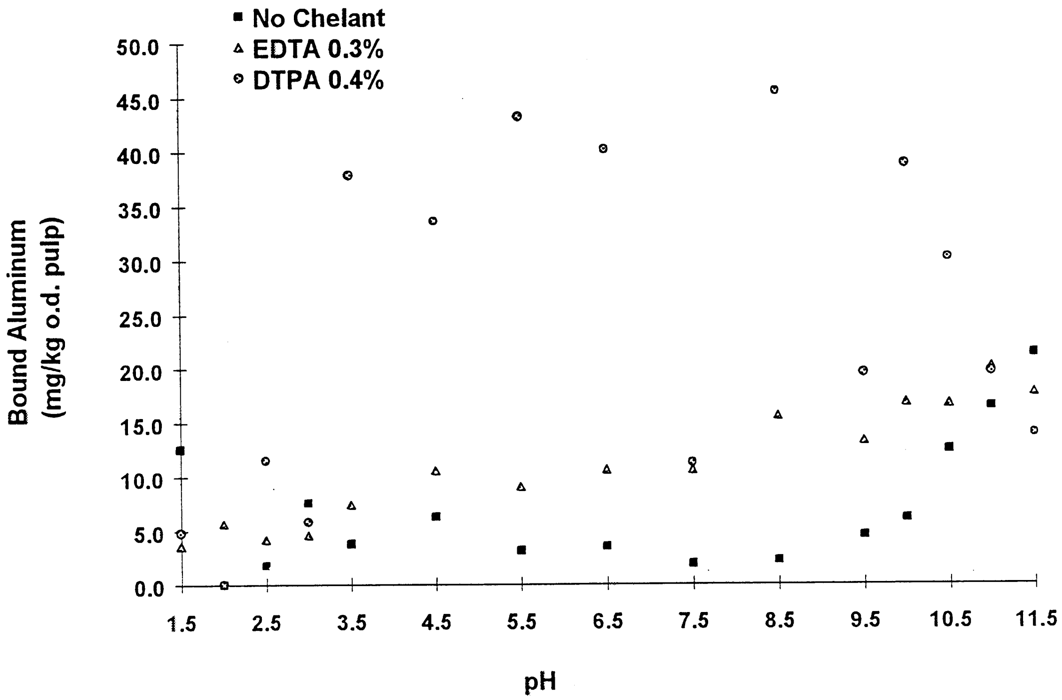

Figure B.3. Fiber-bound aluminum as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

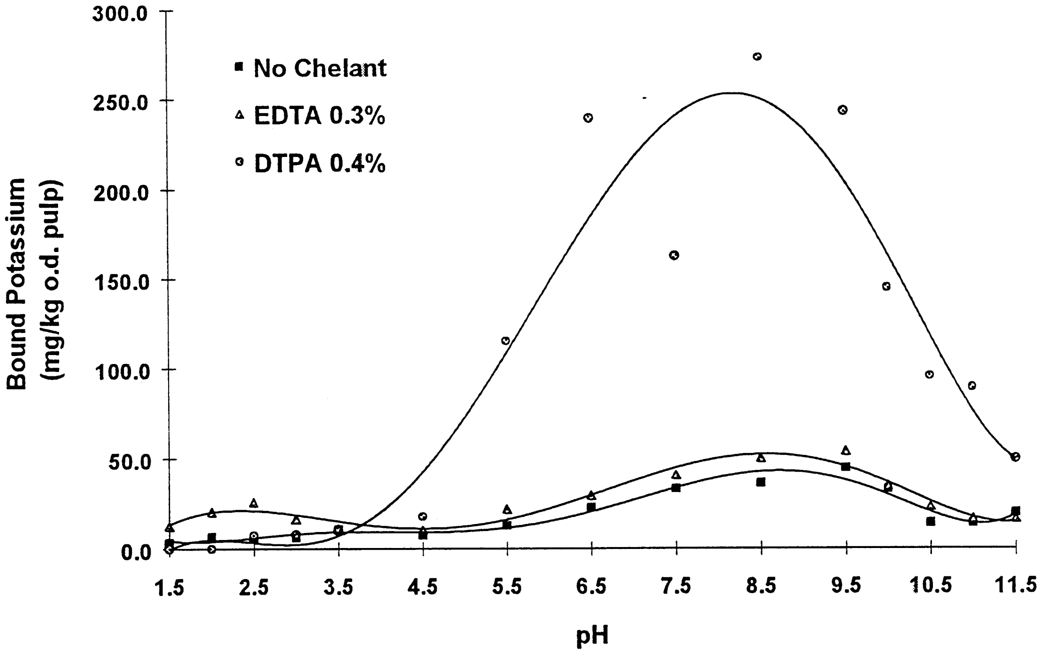

Figure B.4. Fiber-bound potassium as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

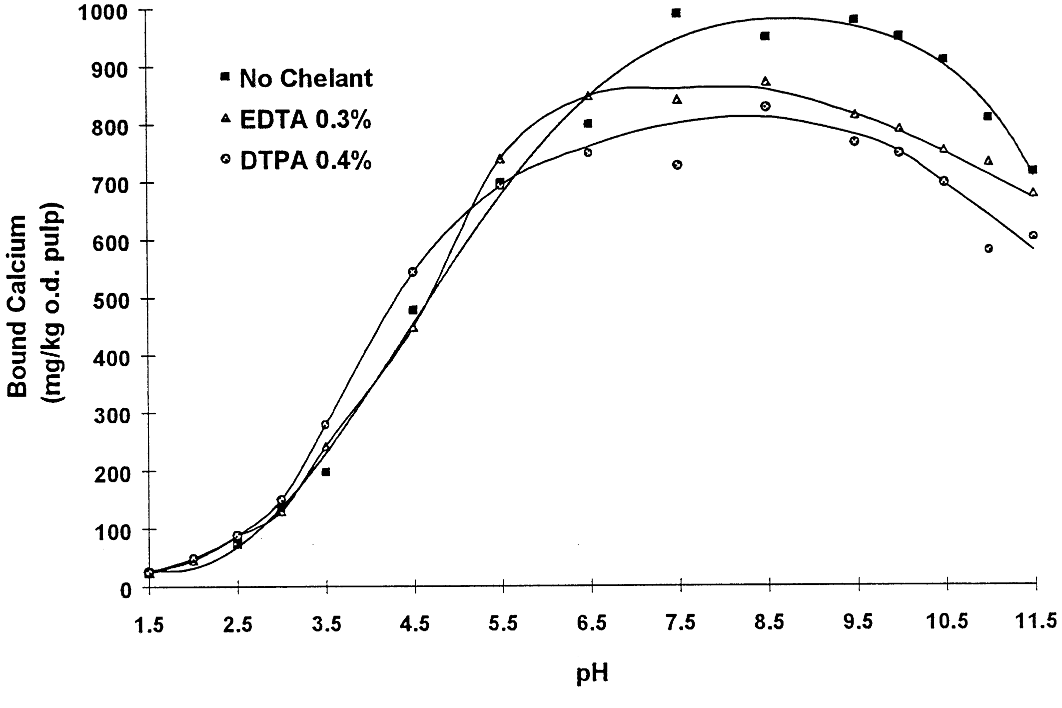

Figure B.5. Fiber-bound calcium as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

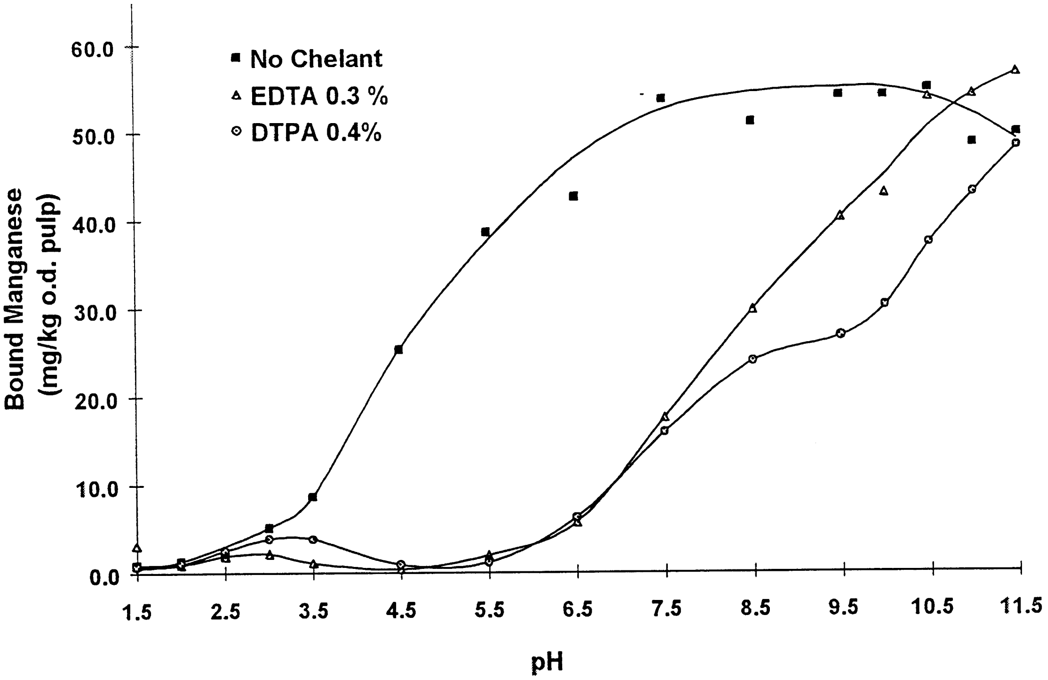

Figure B.6. Fiber bound manganese as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75° C, 1% consistency slurry, 30 minutes mixing.

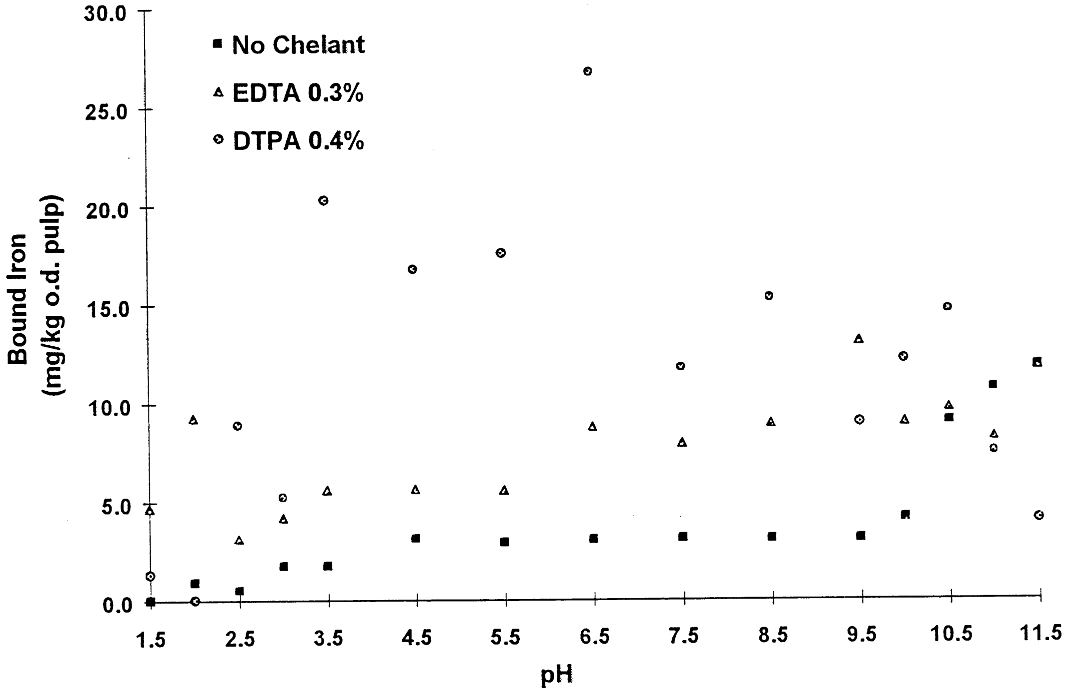

Figure B.7. Fiber-bound iron as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

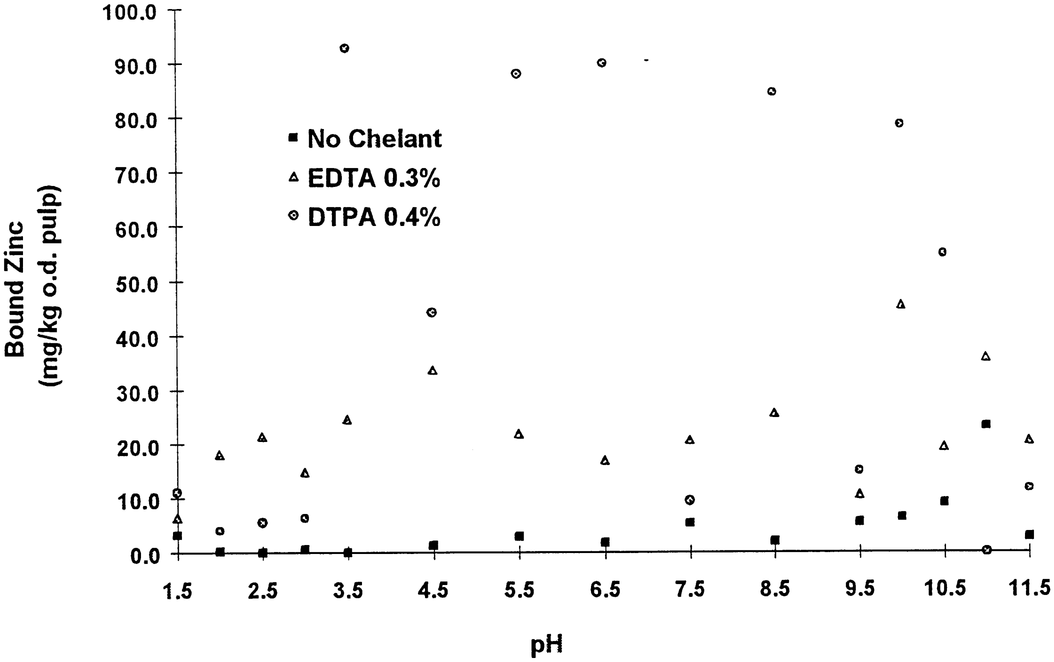

Figure B.8. Fiber-bound zinc as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

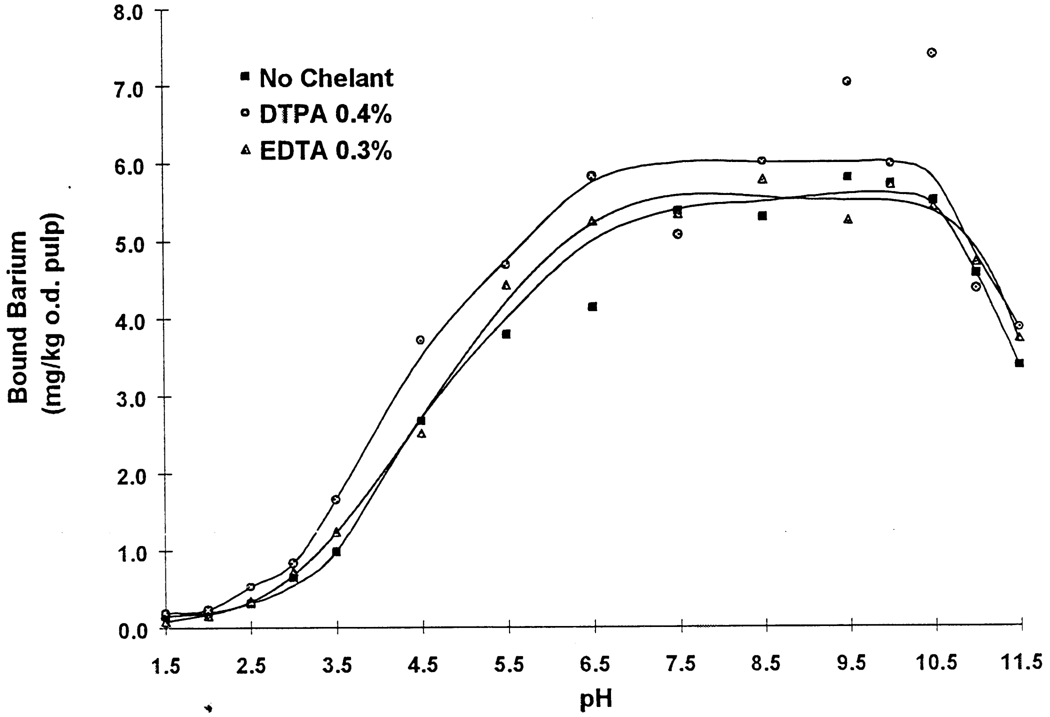

Figure B.9. Fiber-bound barium as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

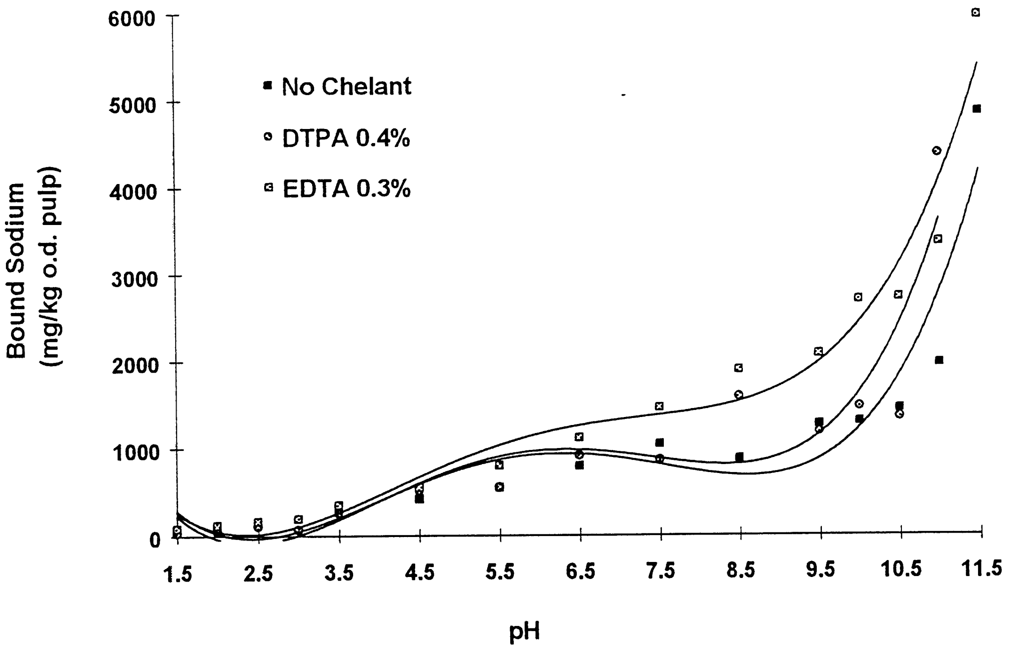

Figure B.10. Fiber-bound sodium as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

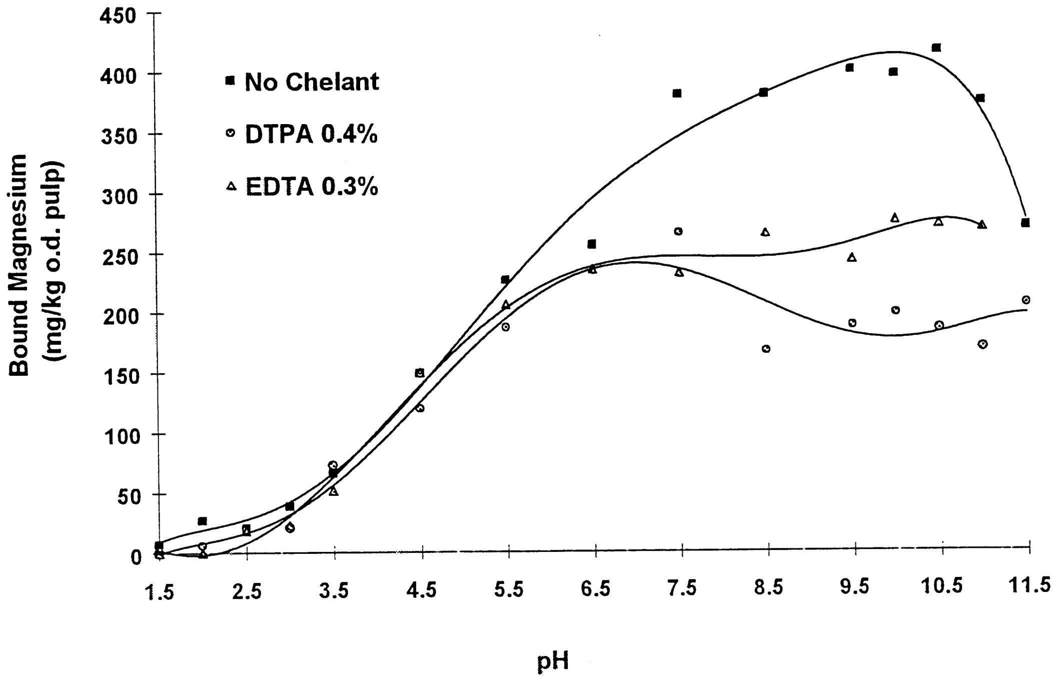

Figure B.11. Fiber-bound magnesium as a function of pH. Pulp B HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

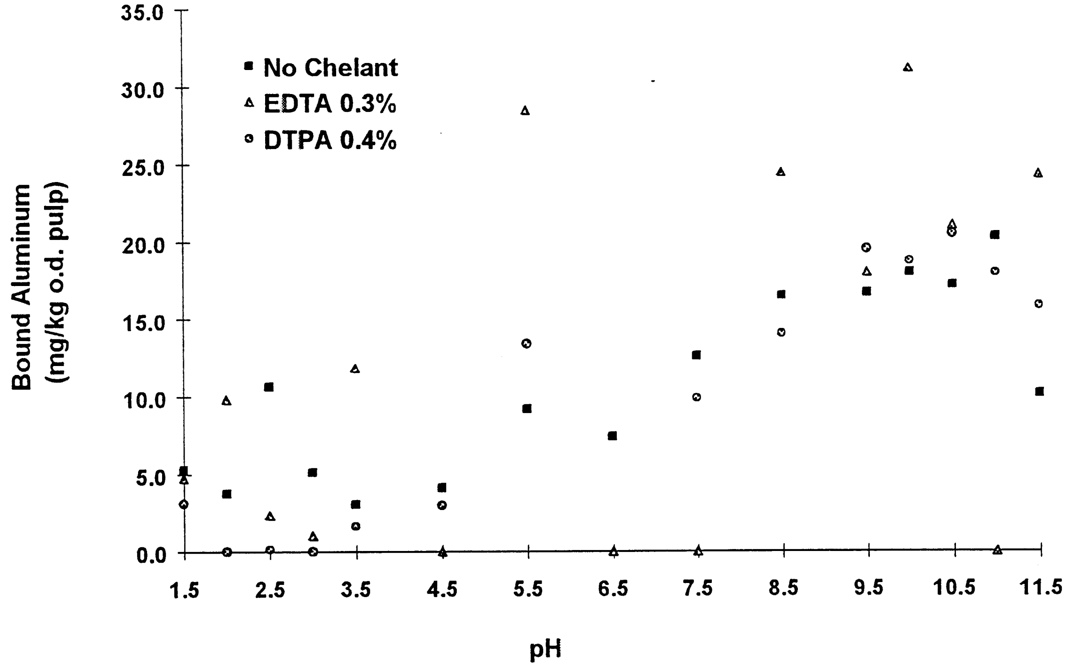

Figure B.12. Fiber-bound aluminum as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

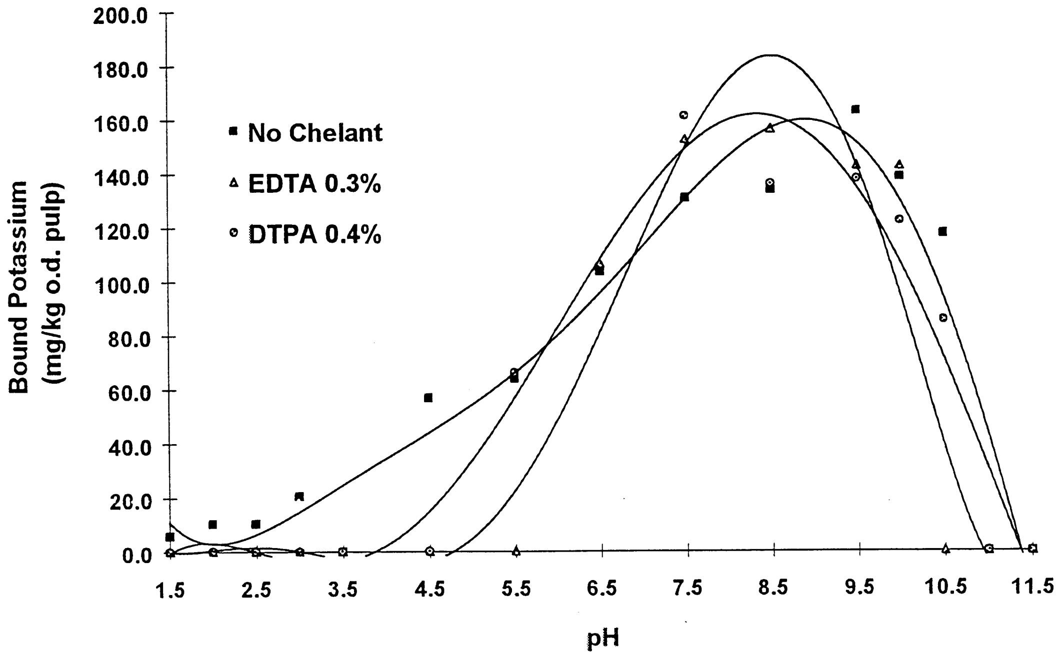

Figure B.13. Fiber-bound potassium as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

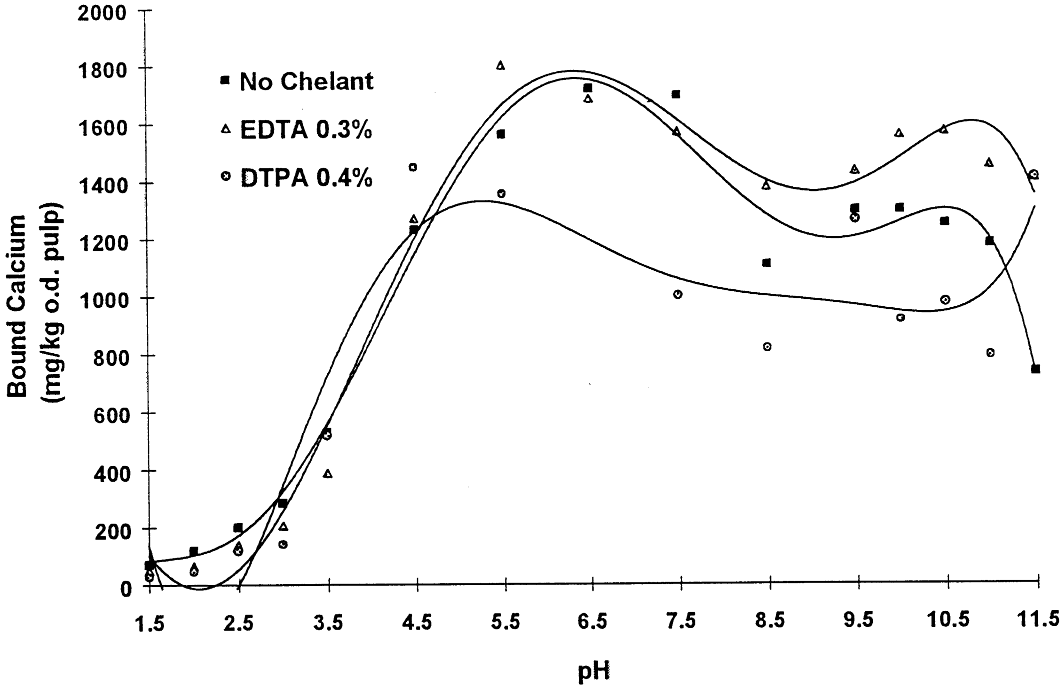

Figure B.14. Fiber-bound calcium as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

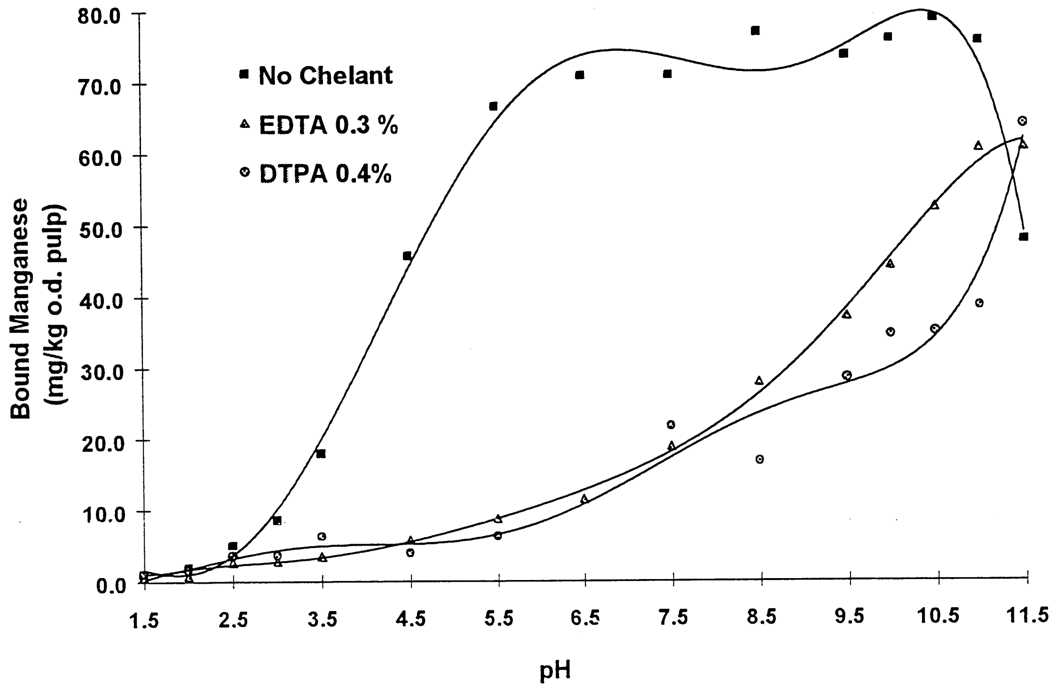

Figure B.15. Fiber bound manganese as a function of pH. Pulp B HW 13 Kappa. Temperature 75° C, 1% consistency slurry, 30 minutes mixing.

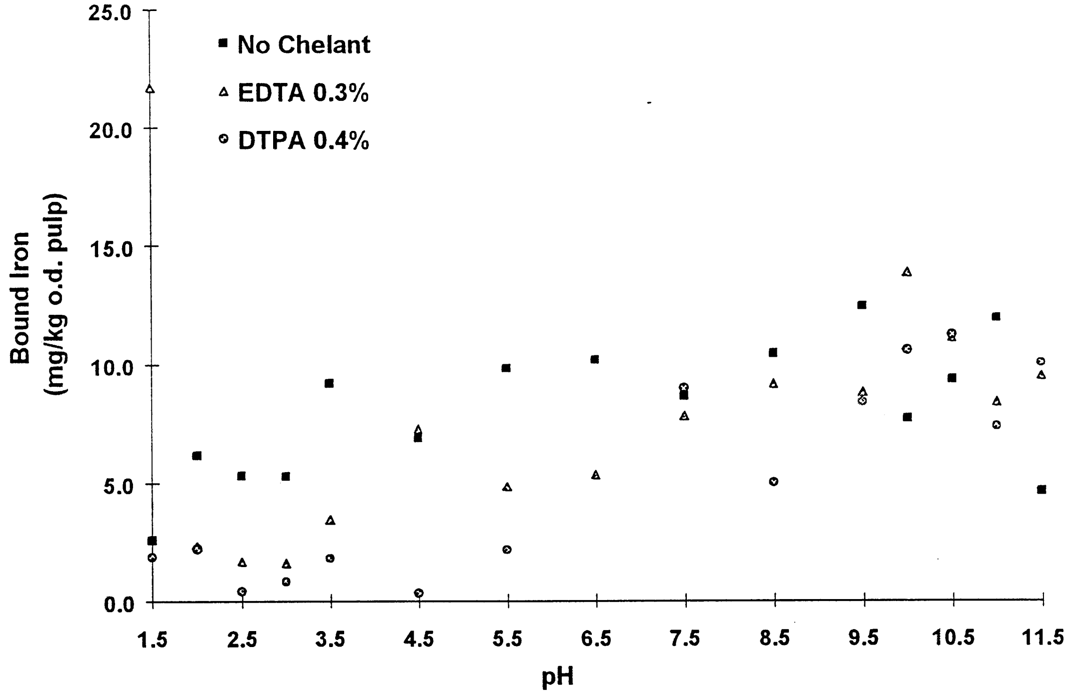

Figure B.16. Fiber-bound iron as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

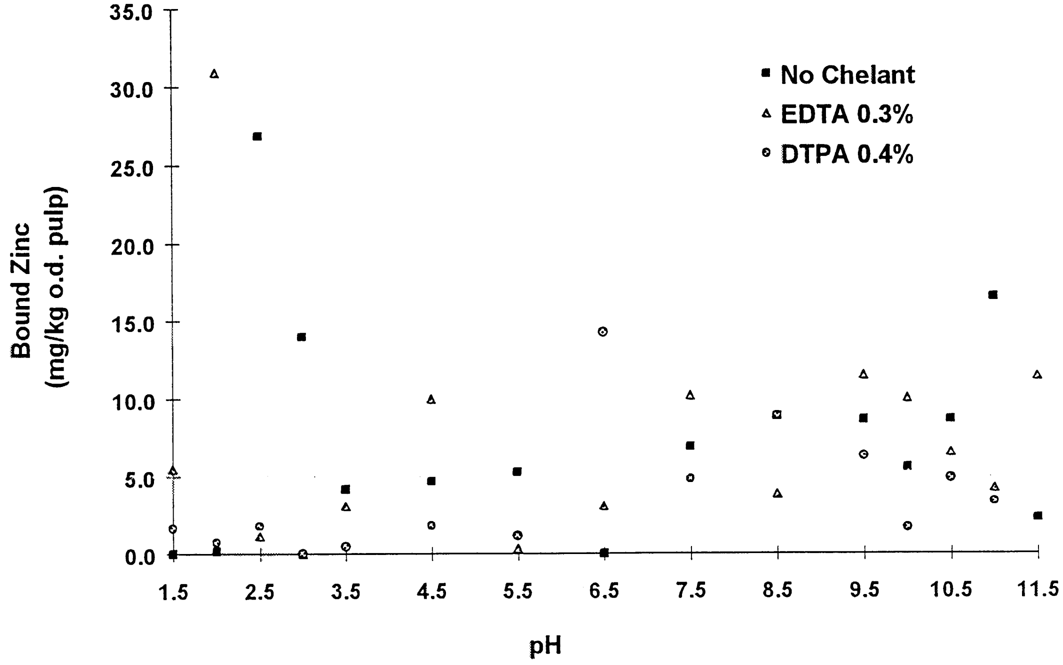

Figure B.17. Fiber-bound zinc as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

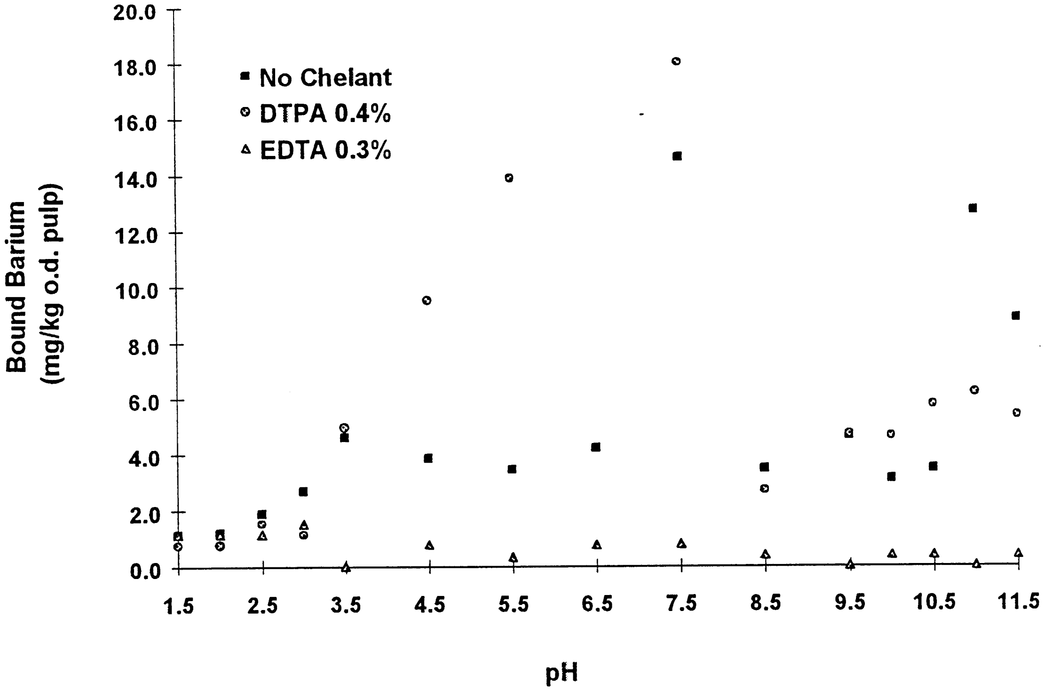

Figure B.18. Fiber-bound barium as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

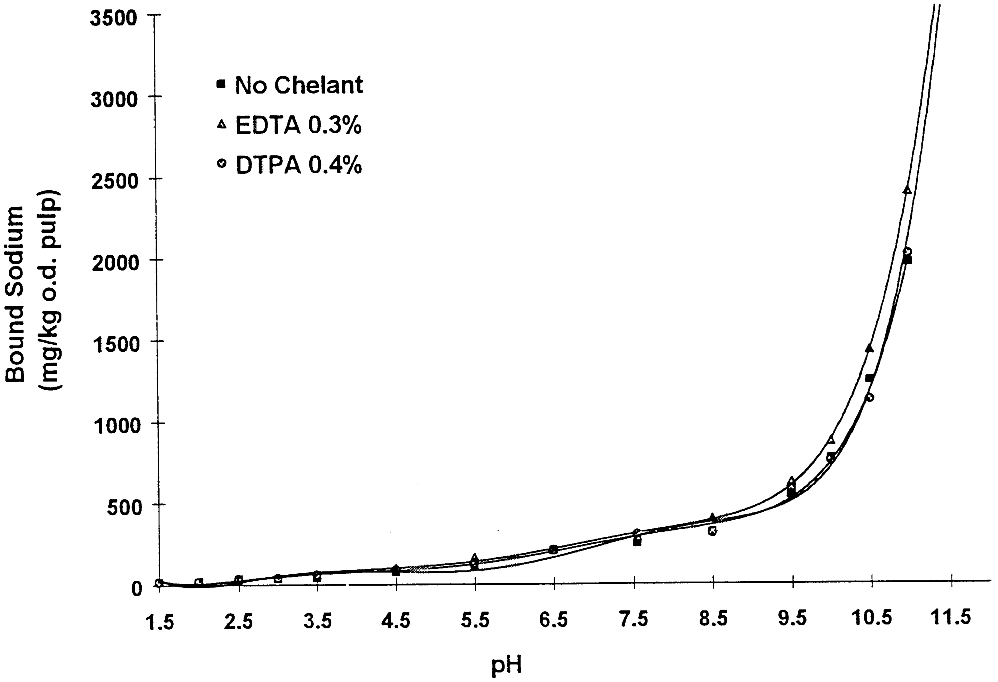

Figure B.19. Fiber-bound sodium as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

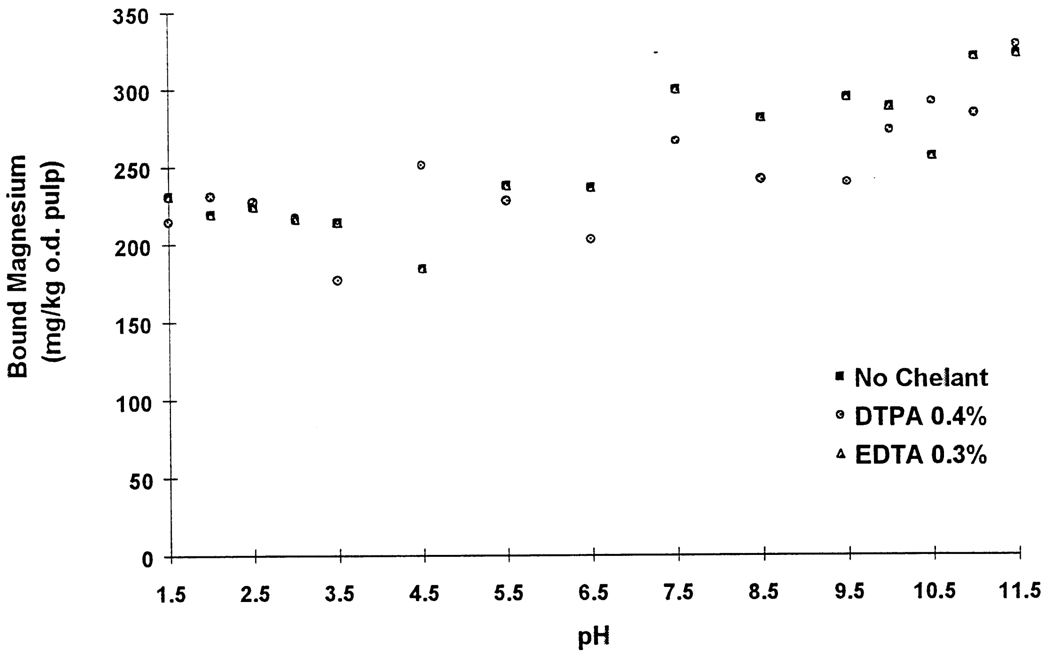

Figure B.20. Fiber-bound magnesium as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

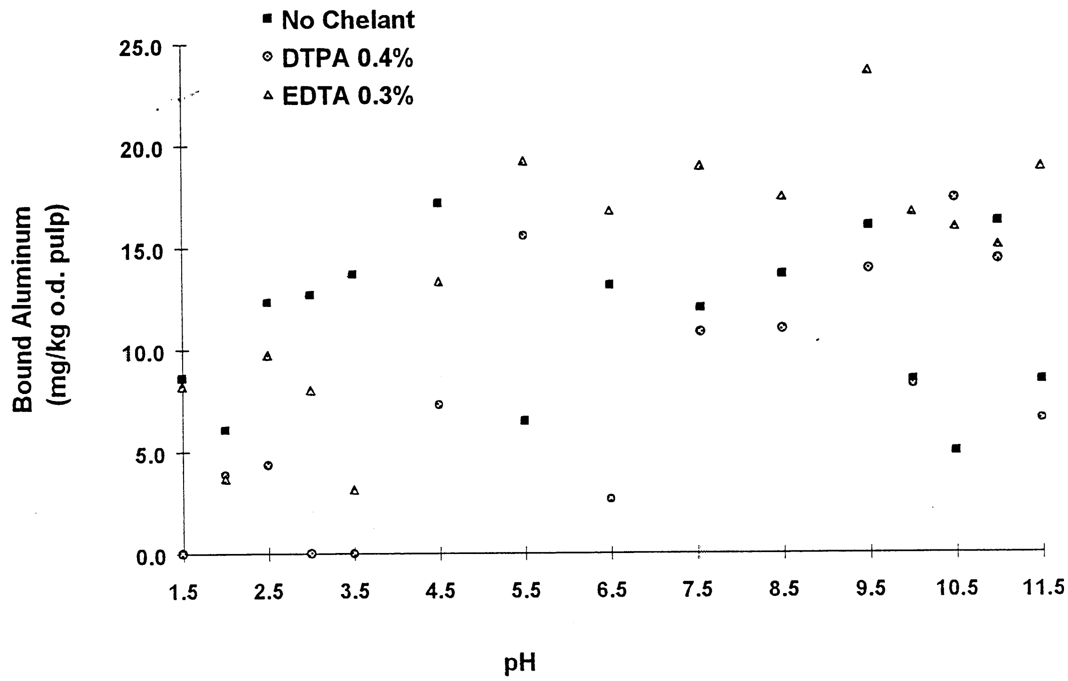

Figure B.21. Fiber-bound aluminum as a function of pH. Pulp C Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

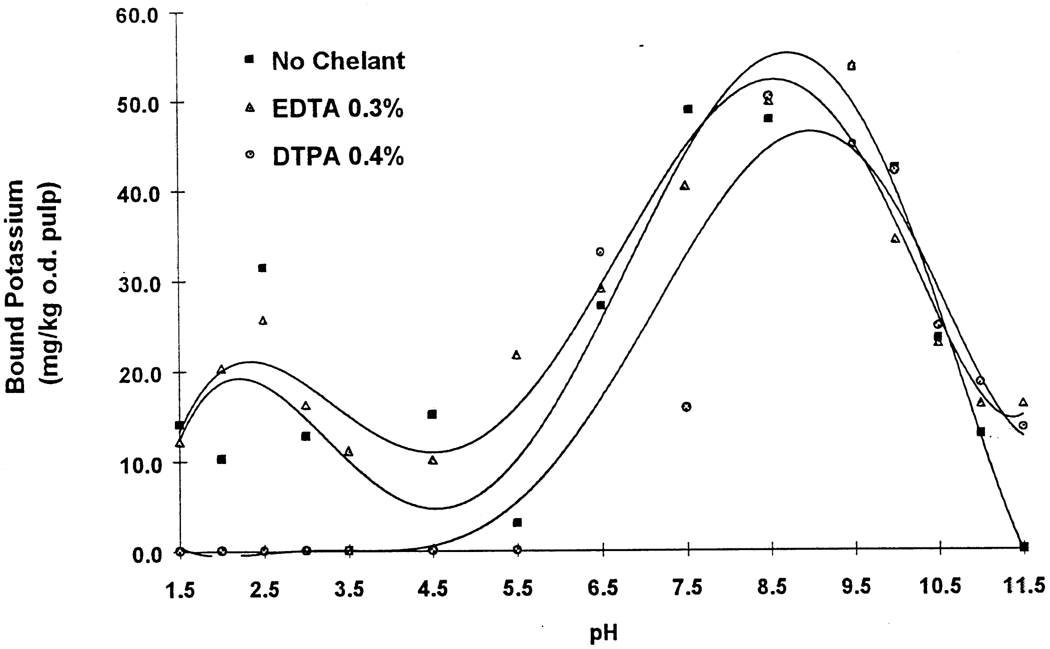

Figure B.22. Fiber-bound potassium as a function of pH. Pulp C Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

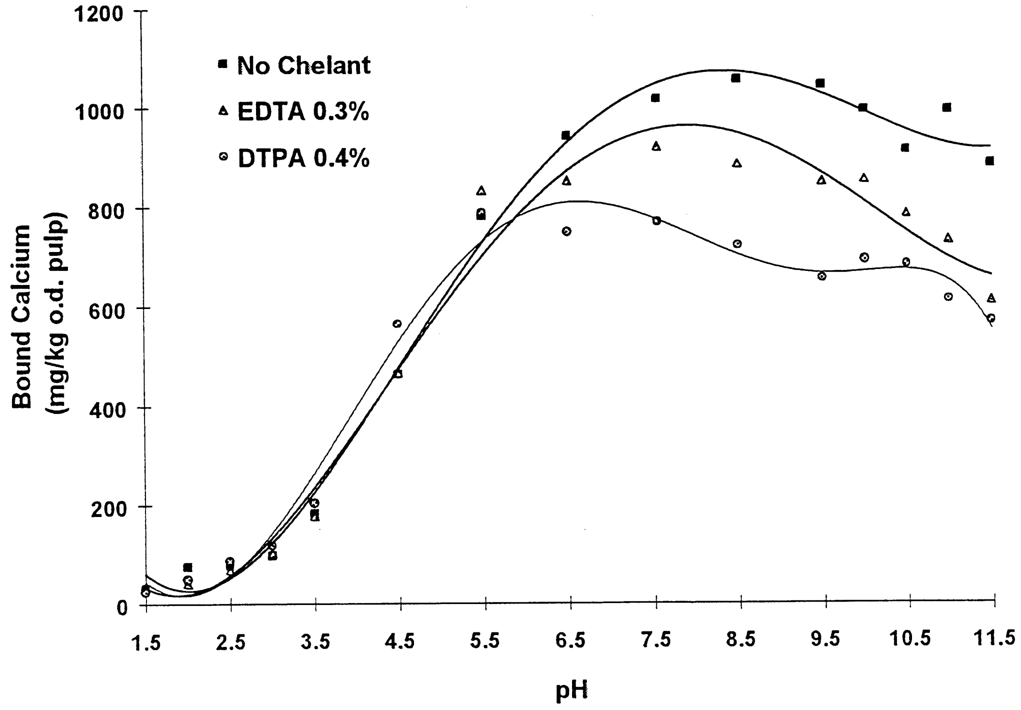

Figure B.23. Fiber-bound calcium as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

Table 12. D2 Stage Bleaching of Conventional and modified Pulps

Unbleached Pulp		D1		D2					
Type	Kappa Number	%ClO2	Brightness	%ClO2	Exit pH	Residual, %	Brightness	Viscosity, mPa.s	Reversion, points
CK	28	0.8	69.7	0.2	4.9	0.02	80.8	21.4	77.9
				0.4	3.8	0.00	84.4	19.1	81.9
				0.8	3.6	0.04	86.7	20.6	84.3
		1.2	82.0	0.2	4.4	0.00	87.4	20.5	85.5
				0.4	4.0	0.04	88.9	20.0	87.0
				0.8	3.8	0.10	89.2	16.4	87.5
		0.8	70.9	0.2	4.3	0.00	80.4	19.3	77.8
				0.4	4.1	0.03	83.6	21.5	80.9
				0.8	4.0	0.04	86.6	20.8	84.2
		1.2	80.8	0.2	3.2	0.00	86.9	21.1	84.3
				0.4	2.8	0.01	88.0	20.1	85.7
				0.8	2.8	0.04	88.8	18.4	86.5
CK	18.5	0.8	71.8	0.2	4.0	0.00	83.2	14.6	80.8
				0.4	3.2	0.01	86.2	13.0	83.7
				0.8	3.1	0.04	87.1	12.1	84.6
		1.2	82.9	0.2	3.7	0.00	88.0	12.8	85.9
				0.4	3.2	0.01	88.1	12.7	86.0
				0.8	3.3	0.05	89.0	12.8	86.9
		0.8	72.3	0.2	4.6	0.01	84.0	12.9	81.5
				0.4	3.9	0.01	86.2	14.1	83.9
				0.8	3.7	0.06	87.4	12.6	85.5
		1.2	82.0	0.2	4.0	0.01	88.2	13.2	86.7
				0.4	4.1	0.03	88.6	12.7	87.1
				0.8	3.7	0.09	88.9	11.6	87.3
EK	29.1	0.8	77.9	0.2	3.6	0.00	85.9	25.2	83.3
				0.4	3.3	0.01	88.0	28.7	85.6
				0.8	3.0	0.05	88.6	27.2	86.5
		1.2	83.6	0.2	3.8	0.01	88.1	24.7	85.8
				0.4	3.4	0.02	88.8	20.9	86.9
				0.8	3.4	0.07	90.0	24.5	87.8
		0.8	73.3	0.2	4.2	0.00	83.2	31.6	80.4
				0.4	3.2	0.00	85.7	20.8	83.5
				0.8	3.1	0.03	88.0	28.2	85.5
		1.2	82.9	0.2	4.3	0.00	88.9	22.2	86.8
				0.4	4.0	0.04	89.4	22.3	87.7
				0.8	3.6	0.08	90.1	22.5	88.2
EK	18.5	0.8	80.1	0.2	3.9	0.00	88.1	21.3	86.1
				0.4	3.5	0.02	89.2	20.2	87.2
				0.8	3.7	0.06	90.0	21.3	88.1
		1.2	83.9	0.2	3.9	0.01	89.3	20.5	87.4
				0.4	3.7	0.03	90.2	20.9	88.3
				0.8	4.0	0.11	90.4	19.8	88.6
		0.8	81.3	0.2	4.0	0.01	88.0	22.0	86.1
				0.4	3.8	0.04	89.1	22.6	87.2
				0.8	4.0	0.12	89.6	21.8	87.8
		1.2	84.1	0.2	4.1	0.01	89.2	24.1	87.5
				0.4	4.0	0.05	89.7	23.4	88.0
				0.8	4.0	0.11	90.0	18.3	88.3
EK	14.5	0.8	84.1	0.2	4.0	0.01	89.5	14.4	87.6
				0.4	3.1	0.05	90.2	14.8	88.6
				0.8	3.0	0.09	90.7	11.6	89.1
		1.2	85.0	0.2	4.0	0.01	90.1	14.3	88.7
				0.4	4.2	0.04	90.7	13.2	89.1
				0.8	4.0	0.10	90.9	12.0	89.3
		0.8	84.1	0.2	3.8	0.03	89.8	14.9	88.3
				0.4	3.8	0.05	90.2	13.8	88.7
				0.8	3.9	0.11	90.6	13.0	89.1
		1.2	84.5	0.2	4.0	0.01	89.7	14.1	88.1
				0.4	3.8	0.04	90.4	13.8	89.0
				0.8	4.0	0.13	90.7	12.6	89.2

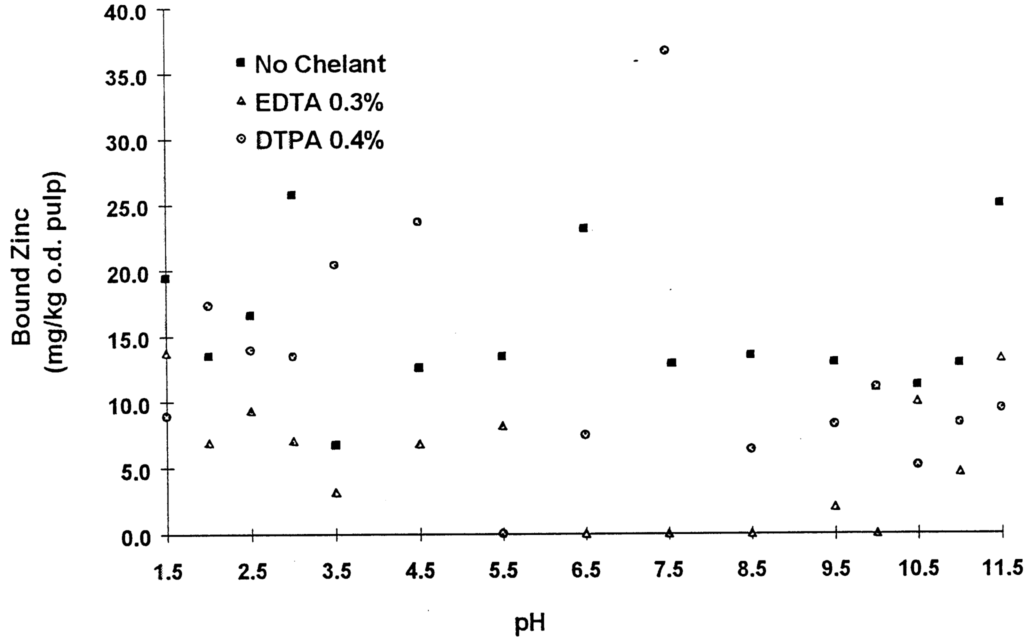

Figure B.26. Fiber-bound zinc as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

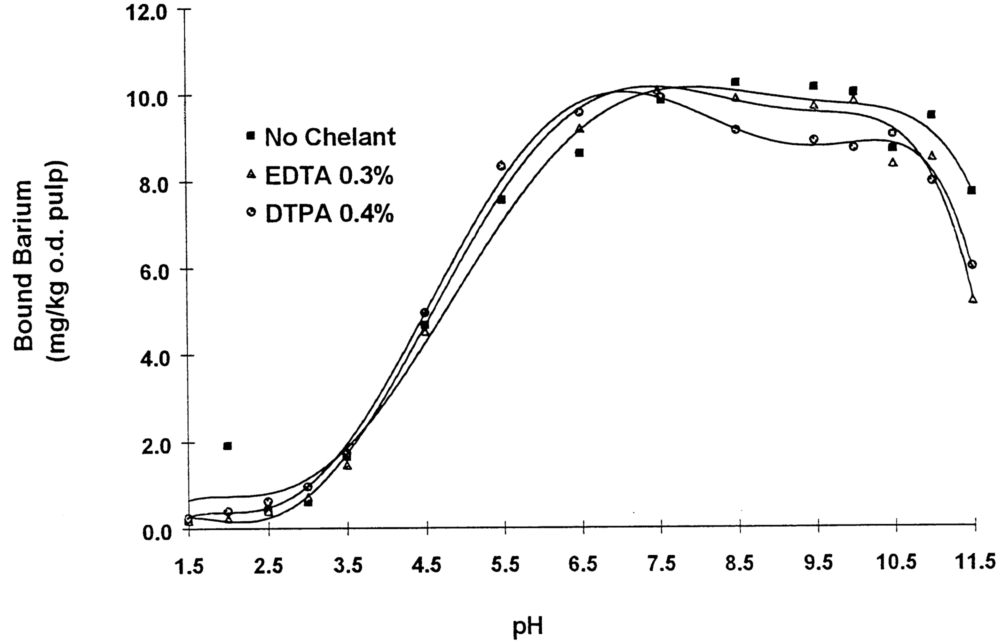

Figure B.27. Fiber-bound barium as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

CLOSED MILL OPERATIONS

Status: Novel Methods of Metals Removal - Iron

Alan Rudie
Fadi Chakar
Giselle Ow Yang

TECHNICAL PROGRAM REVIEW

PROJECT TITLE: CLOSED MILL OPERATIONS

PROJECT STAFF: Alan Rudie
Fadi Chakar (M.S. 1995, Bleach Lab, A-280)
Giselle Ow Yang (M.S. 1996)

BUDGET:

DIVISION: C&BSD

PROJECT NUMBER: F017

OBJECTIVE: Evaluate novel metals removal strategies, with an emphasis on improving the removal efficiency of iron. Determine the nature of "hard to remove" iron in pulp.

GOALS:

- Evaluate acetylacetone and potassium fluoride for improving metals removal efficiencies.
- Determine the oxidation state of "hard to remove" iron.

SUMMARY:

The efficiency of metals removal with Acetylacetone (2,4-pentanedione), and the fluoride ion have been determined. At a pH of 3, Acetylacetone (acac) reduces the pulp iron to the hard to remove residual, equivalent to H_2SO_4 at a pH of 1.5. Acac charges of 0.1% and 0.7% on pulp appear to be equally effective. Acac has little or no effect on removal of Calcium, Manganese, and Magnesium (the efficiency is the same as an acid wash). Addition of fluoride ion (0.45% on pulp as KF) improves the metals removal at a pH of 5 relative to an acid wash at pH 5, but has no incremental benefit at pH below 5.

Two methods are being tried to determine the oxidation state of iron in wood pulp. Cellophane has been doped with Fe(II) and Fe(III) at levels where they can be detected with UV-Visible spectroscopy. The treatment is carried out in a glove bag under nitrogen and the samples are exposed to air prior to the spectroscopy. The predominant state of iron in these samples appears to be Fe(III). Current efforts are attempting to obtain a UV-Visible spectrum of Fe(II) in cellophane, determine the "hard to remove" level of iron in the doped cellophane, and obtain a UV-Visible spectrum of the hard to remove residual. The second method applies X-ray fluorescence using beam line X26A on the National Synchrotron Light Source at Brookhaven National Labs. Beam X26A is an X-ray microprobe system set up to perform trace element studies with a resolution of 8 microns or larger. XANES is capable of detecting most metals down to 10 ppm, and can be used to determine oxidation state and to a limited extent, symmetry and ligand structure. Initial samples indicate that most iron in pulp is Fe(III), but the iron remaining after chelation appears to contain a significant amount of Fe(II).

STATUS REPORT

PROJECT TITLE: Closed Mill Operations PROJECT NUMBER: F017
TASK TITLE: The Nature and Removal of Hard To Remove Iron.

INTRODUCTION:

Metals management in the paper industry has been around for a long time, principally related to control of transition metals in peroxide bleaching of high yield pulps.[1] The recent interest in alternative bleaching chemicals and in eliminating the bleach plant wastewater stream, has added a new dimension to the metals management problem. Although the existing methods of removing metals with chelation and/or acid treatment appear to be adequate, the remaining "hard to remove" iron may become a problem in mills with an acid bleach stage following extraction. Under acid conditions, the bound iron is released slowly by the fiber. A second ozone stage, cairo's acid, peracetic acid, mixed acids and dimethyldioxirane bleaching are all carried out under conditions where this is a problem. If the mill attempts to use a direct counter current wash system to minimize water treatment and evaporation, the metals leached out in the second acid bleach stage will precipitate on the alkaline extraction stage washer creating a secondary metals trap in the bleach plant.

The use of jump stage or split filtrate wash flows both prevent the secondary metals build up, but increase water use. Addition of a second metals removal process will also prevent problems, but adds an additional process, and it's associated capital and manpower. Improving the efficiency of metals removal in the first Q stage can reduce the second stage metals input to a level where it is not an issue. This can potentially be done without significant incremental cost.

Acid leaching, and DTPA chelation have been evaluated under a variety of conditions. They successfully remove over 90% of the manganese, calcium and magnesium, but only about 50% of iron.[2] Increasing the chelant dose, or treatment temperature, and extending the treatment time can improve metals removal efficiency to an extent. On manganese, DTPA doses above 0.2% on pulp, treatment temperatures greater than 75° C and treatment times beyond 30 minutes show little incremental gain.[3] Iron behaves in a similar manner, but the residual level of iron, resistant to removal, is generally much higher. There is little likelihood that significant improvements in the performance of acid wash and aminocarboxylate treatments can be achieved.

Bound iron is not considered to be detrimental to peroxide bleaching.[1,4] On the other hand, soluble iron complexes are well known to activate and/or decompose peroxides and a build up of metal in this form will be detrimental.

Acid treatments work by protonating the acid functional groups on the pulp to release the complexed metals. Ideally, the metal forms a soluble complex with water and the counter ion of the acid and diffuses out of the fiber into solution. With manganese, the metal likely forms the $Mn(OH_2)_6^{2+}$ ion which is water soluble and oxidatively quite stable. For iron, the most common oxidation state is Fe(III). Fe(III) does not readily form monomeric hexaquo complexes.

Instead it hydrolyses and/or polymerizes. In this regard, iron is much like Alum, and under the right conditions, iron can be substituted for Alum in sizing[5] and water treatment. At a pH of 2, Fe(III) is found as a dimer, and it is estimated that a pH near zero is required to force it to the monomeric hexaquo complex.[6] At pH near neutral, Fe(III) begins to precipitate as Fe_2O_3.

Although Fe(III) is the most common oxidation state for iron, Fe II is easily formed in the presence of a reducing agent and under some conditions, can be stable to air oxidation. Given the reducing nature of the Kraft process, Fe(II) is likely to be present at the discharge of the digester and may be stabilized by the sulfides and catechols present in the black liquor and lignin. There is also some evidence that the iron associates more readily with lignin[5] which may help to explain why it continues to leach out of the fiber in the bleach plant. A second effort in this program is directed at determining the oxidation states and coordination environments of iron in unbleached pulps.

The complexes formed by Fe(III) in acid or with carboxylic acids are generally octahedral (six ligands) with a high spin electronic configuration. High spin means that the crystal field splitting (or molecular orbital splitting) caused by the six bonded oxygens is not sufficient to separate the five iron d orbitals enough to overcome the electron pairing resistance. The five electrons exist in five separate d orbitals, two of which are effectively antibonding orbitals to the six water molecules. This generally increases ligand lability and destabilizes the complex. With acids, this lack of stability has to be overwhelmed with protons to maintain a soluble ion. With chelating agents, the stability derives from the increase in entropy when a water molecule or carbohydrate carboxylic acid group is replaced by another of the DTPA amine or carboxylate groups.

One method for increasing complex stability is to use ligands with considerable π-bond character like the ß-diketones or 1,10-phenanthroline. These form complexes with extended π structures that include the otherwise non-bonding d_{xy}, d_{xz}, and d_{yz} orbitals into the molecular orbitals of the molecule. This increases the energy separation of the metal d orbitals and causes the electrons to pair up. Under these conditions Fe(III) has five electrons in three orbitals, all contributing to additional bond strength and complex stability. $Fe(phen)_3^{3+}$ and $Fe(acac)_3$ are both low spin molecules with a single unpaired electron. With acetylacetone, the methylene protons are acidic and the iron complex forms three 6 membered, six electron aromatic ring.

$$Fe(OH_2)_6^{3+} + 3\ C_5H8_8O_2 \text{ --> } Fe(C_5H_7O_2)_3 + 3H_3O^+ + 3H_2O$$

The stepwise formation constants for Fe(III) with acetylacetone are 10^{11}, 10^{11}, and 10^4.[7] In comparison, the formation constants for Fe(III) with acetic acids is about 10^3 and the formation constant for addition of each carboxylic acid group in EDTA or DTPA is on the order of 10^4. The over all formation constant for $Fe(acac)_3$ is 10^{26} and for Fe(DTPA) is on the order of 10^{15} to 10^{24}. For these reasons, acetylacetone was selected as one reagent to evaluate for improving the efficiency of iron removal.

The fluoride ion at 10^5 has one of the strongest formation constants with iron of any of the typical anions. This is three orders of magnitude stronger than complex formation with either sulfates or chlorides. In addition, MgF_2 (130 ppm) and CaF_2 (4.9×10^{-11}) are both sparingly soluble in water. This presents the possibility that fluorides under acidic conditions might improve iron removal while suppressing manganese and calcium removal from the pulp. Although FeF_3 is not particularly soluble in water, at 900 ppm, it is 7 times more soluble than Mg. It was decided to also evaluate fluorides for improving iron removal from pulp.

REVIEW OF RECENT RESULTS
(Fadi Chakar: A-280, Pulping and Bleaching Laboratory as Independent Study)

A 28 kappa kraft pulp was oxygen bleached with 3% NaOH, 109° C, 100 psig oxygen and 30 minutes giving a 10 kappa number and 17. 4 mpa·s viscosity pulp. This pulp was split into four batches for metals control. Sample 1 was treated with 0.6% EDTA on pulp, pH 5 at 50° C for 30 minutes. Sample 2 was treated with sulfuric acid, pH 1.5, 50° C for one hour. Sample 3 was treated with 0.5% KF on pulp, pH 1.5, 50° C for one hour. Sample 4 was treated with 0.5% 2,4-pentanedione (acetylacetone), pH 3.0, 50° C for one hour. All four treatments were carried out at 2% consistency in deionized water and were followed with a thorough wash using deionized water.

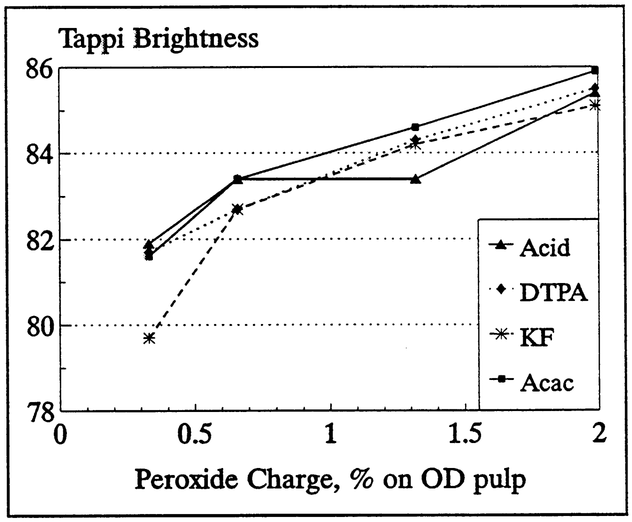

Figure 1. Peroxide bleaching response of pulps from the four metals control treatments.

All samples were ozone bleached with 0.7% ozone on pulp at 35% consistency, and extracted with 2% NaOH at 70° C for one hour. Samples were then bleached with 0.1, 0.2, 0.4 and 0.6% chlorine dioxide on pulp (10% consistency, 70° C and 3 hours) and 0.33, 0.66, 1.32 and 1.99% hydrogen peroxide (10% consistency, 0.05% $MgSO_4$, 70° C and four hours). Results are listed in Table 1 following this report. The brightness response for the peroxide bleaches is shown in figure 1. The highest brightness gain was obtained using acetylacetone for the metals control, but all samples were within 1 point ISO brightness and are considered to be within experimental error. Residual metals analysis on the ozone bleached pulps are given in Table 2. All four metals control methods reduced the manganese content of the pulp below the detection limit. Acetylacetone gave slightly lower iron and copper levels than the other treatments, but again, the differences are probably within the experimental error.

These experiments demonstrated that acetylacetone and potassium fluoride could be used in metals control, but were not sufficient to demonstrate any significant improvement over either EDTA/DTPA or acid treatments. The fluoride did not improve calcium and magnesium retention, and neither KF or acac helped remove the resistant iron.

TABLE 2: Metals Contents of Ozone Bleached Pulps.

Method	Ca	Mg	Fe	Mn	Cu
EDTA	54 ppm	5.9	16	0.4	0.9
Acid	48	4.0	17	0.4	1.3
KF	42	4.5	16	0.4	1.2
Acac	64	5.5	14	0.4	0.5

PROJECT F017

A second series of experiments were carried out under Project F017, to determine the efficiency of the alternate metals control methods relative to conventional chelation and acid treatments. In these experiments, pulp was treated with one of the four metals control methods over a range in pH. The metals removal or residual metals content can then be plotted against pH to evaluate the efficiency of each reagent. In particular, acetylacetone and DTPA should function best at a pH above the pKa for the carboxylic acid groups in DTPA and the methylene protons in the metal complexed acetylacetone.

With manganese, calcium and magnesium, KF, Acid and acetylacetone all show a step change in residual metal concentration between the pH 3 and pH 5 experiments. For example, manganese concentrations for the starting pulp and for the samples treated at pH 7 with H_2SO_4, acetylacetone and KF all fall in the range between 100 and 74 ppm. At pH 5, all fall in a range between 45 to 75 ppm. At pH 3, all fall in the between 0 and 10 ppm. Potassium fluoride and acid treatment were both evaluated at pH 1.5 where the residual manganese was below 1 ppm. There are two distinct differences with the results on iron. First, KF and sulfuric acid do not show the step change loss in iron but rather show a smooth, almost linear drop from about 15 ppm iron in the starting pulp to about 6 ppm iron at a pH of 1.5. Only acetylacetone shows the expected step change with the residual iron dropping from 14 to 15 ppm at pH 5 to about 6 ppm at pH 3. In these experiments, DTPA was evaluated at pH 7 and pH 5. It did not show the expected step decrease in residual metal content around pH 5.

Results of these experiments indicate that the fluoride ion does not help hold the alkali earth metals in the pulp and does not contribute significantly to the metals removal process. Acetylacetone functions like a typical chelating agent but cannot reduce the iron content below the "hard to remove" threshold.

Metal acetylacetonate complexes have a unique attribute. Many of these complexes are neutral and volatile, boiling typically around 200° C. This raises the possibility that metals can be easily removed from the bleach plant filtrates by steam stripping the acetylacetonate complexes from the filtrate. A filtrate sample was generated for this experiment by treating 50 OD grams of pulp with sulfuric acid (pH 2.0) for 30 min at 70° C. Acetylacetone (5 ml) was added to 500 ml of filtrate and the pH adjusted to 4.7. This was distilled in a short path still and the distillate samples collected for analysis. The filtrate contained 2.3 ppm manganese and was below the detectable limit in iron and copper. Distillate samples were recovered after 5 ml (1%), 25 ml (5%) and 50 ml (10%) of the sample had been recovered. These gave iron contents of 0.5, 15 and non detect. This accounts for about 75% of the estimated filtrate iron content. Copper was not detected in the first 5 ml but was found at 0.4 ppm in the second sample and 2.6 ppm in the third sample. This accounts for about 15% of the copper thought to be in the filtrate. Mg, Ca and Mn all remained below the detectable limit in the distillate samples and there was no major change in analysis for these three metals between the initial filtrate and bottoms product from the distillation.

Iron exists in the filtrate as $Fe(H_2O)_6^{3+}$. It forms a tris acac complex which is neutral and monomeric. Manganese exists in solution as Mn(II). It forms $[Mn(C_5H_7O_2)_2 \cdot 2H_2O]$, a bis acac complex with two coordinated waters.[8] The hydrogen bonding of the water molecules raises the boiling point for the complex. Cobalt, nickel and magnesium form hydrates, similar to manganese.

Giselle Ow Yang, A-190: Masters Independent Study Research.

There are a number of reasons why a portion of the iron may be inert towards acids and chelating agents. The metal may be imbedded deep in the fiber wall and unable to diffuse out, bound within a crystallite of cellulose, bound to a structure that provides increased stability, or in a form that is relatively inert. Since manganese, magnesium and calcium are present in much higher concentrations than iron and are almost completely removed by acids and chelating agents, it is unlikely that the resistant iron is due to the metal being inaccessible. For the most part, all metals would have equal probability for this. This suggests the resistant iron is due either to a different oxidation state or aspects of the local environment that are in some other way, uniquely suited to the iron. The task is to determine what is unique about the environment.

Obtaining useful information on iron at natural concentration levels is quite difficult. In wood pulp made from normal wood sources, iron starts around 20 ppm and after conventional bleaching, acid treatment or chelation, ends up at 5 to 10 ppm. At this concentration level, most spectroscopic techniques are unable to even detect iron, let alone provide useful information on the local environment. Two alternative approaches are available:

1. Work with unusual samples with high iron contents either because of wood location, process (sawdust pulp) or intentional doping of metals. The problem with this approach is there is no guarantee that the high metal content pulp is representative of the real metal environment in normal pulps.

2. Use the few spectroscopic resources available that can detect metals at ppm levels. Both methods are being used in this project.

About the only spectroscopic techniques capable of detecting iron in the ppm level are EDXA using the electron microscopes, and X-ray excitation techniques. Most offer very little information other than the approximate concentration and in some cases, the spacial distribution of the metal. Bailey and Reeve have reviewed some of these methods and presented results from secondary ion mass spectroscopy as well.[9] These methods indicate the iron and manganese are concentrated in the middle lamella. Although these methods have been useful for determining the spacial distribution of the metal, they have provided little useful information on how it is bound to the wood.

A spectroscopic technique that is useful at the 10 ppm level is x-ray fluorescence spectroscopy. In this technique, an electron is ejected from a core level. When a valence electron falls down to fill the vacancy, the atom emits a characteristic X-ray. Several techniques are used but the method of most interest in this case is XANES, (X-ray Absorption Near-Edge Structure). This method sweeps the X-ray frequency through the edge or side of the absorption peak for the element of interest. Changes in the oxidation state of the atom result in changes in the energy of the core and valence level electrons, causing a shift in the leading edge of the X-ray absorption.

For iron, the Kα edge is at 6.403 kev. The leading edge of the absorption increases by 6 to 10 ev with changes in oxidation state, so the instrumentation has to be quite sensitive. Synchrotrons have a number of advantages as X-ray sources. The X-ray emission is intense, already collimated and highly polarized. The collimated source allows the X-rays to be focussed with mirrors set at a glancing angle, and the polarization of the X-rays reduces background scatter. Beam size is selected by placing a pin hole aperture in the beam, establishing beams widths of 8, 10 or 20μm. These features can be used to improve sensitivity and/or focus the X-rays into a microprobe that determines elemental abundance on a μm scale. Using a monochromator to select an X-ray wavelength, the spectrometer can be set to sweep the wavelength through the X-ray absorption edge to obtain information on oxidation state.

To date, 4 samples have been analyzed in preliminary testing using beam X26A at the National Synchrotron Light Source in Brookhaven. Working with us on this project are Dr. Paul Bertsch and Dr. Douglas Hunter of the University of Georgia Savannah River Ecology Laboratory.

One sample tested was a bleached sawdust pulp with an expected iron content around 35 ppm of hard to remove iron. The second sample was an unbleached softwood with an iron content of 13 ppm. The third was a mild acid treated sample with 10 ppm iron, the fourth was a DTPA treated sample of the same pulp with the iron content reduced to 11 ppm. The bleached sawdust sample was scanned using the 20 μm microprobe in white light mode (broad spectrum X-ray irradiation). It did not show any significant concentrations of iron, typical of contamination from rust or process metals. However, the metal was not distributed completely uniformly in the sample. All four samples were evaluated using monochromatic irradiation scanning the iron X-ray absorption edge. Both the unbleached pulp and the mild acid treated pulp show predominately iron (III) character; the X-ray absorption edge was between the X-ray edge standards for Fe(II) and Fe(III), suggesting a mixture, but about 90% Fe(III). The sample treated with DTPA in which about 25% of the iron has been removed gives an X-ray Absorption edge suggesting about 40% iron (II) and 60% iron (III). The bleached sawdust pulp sample was similar to the DTPA sample, with the X-ray absorption edge indicating 20 to 30% Fe(II) content.

Unfortunately, there are a number of unsettled issues with these preliminary results. The X-ray iron analysis does not agree with the initial ICP analyses for these samples suggesting they may have been mixed up or contaminated during the sample prep. None of the samples were well chelated or acid washed before the analysis so they are not exclusively hard to remove iron. (We were not able to use the lowest metal content pulps because at 10 ppm, the samples are near the resolution limit of the process and in preliminary testing, NLS is not willing to collect data for extended periods.) The results have demonstrated that iron (II) is present in pulp samples and contributes at least a portion of the hard to remove iron. The results have also indicated that the iron is evenly distributed in the sample and not concentrated as would be expected if the source was rust or other contamination.

REMAINING WORK

1. Evaluate conditions to improve Manganese stripping by acac
2. Evaluation of iron adsorption on lignin and cellulose
3. Evaluation of iron on doped cellulose using UV-Vis spectroscopy.
4. Possibly, evaluation of another set of samples using the synchrotron X-ray source.
5. Prepare a proposal for funding of additional synchrotron work.

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Table 17. D2 Stage Bleaching of Low-EA, High-EA and Nonuniform Pulps

Unbleached Pulp			D1		D2			
Type	H-Factor	Kappa Number	%ClO2	Brightness	%ClO2	Exit pH	Residual, %	Brightness
LEA	1569	28	0.8	75.1	0.2	4.3	0.00	84.4
					0.4	3.5	0.01	86.8
					0.8	2.8	0.30	87.2
			1.2	77.6	0.2	3.9	0.00	87.7
					0.4	3.3	0.11	88.6
					0.8	2.8	0.29	88.7
			0.8	73.5	0.2	4.3	0.01	85.4
					0.4	3.0	0.03	87.0
					0.8	2.6	0.21	87.0
			1.2	76.9	0.2	4.0	0.01	87.9
					0.4	3.2	0.07	88.3
					0.8	2.7	0.28	88.9
LEA	4000	14.5	0.8	74.8	0.2	4.2	0.00	84.9
					0.4	3.5	0.12	85.4
					0.8	3.2	0.36	84.8
			1.2	76.0	0.2	4.1	0.00	84.9
					0.4	3.5	0.11	85.5
					0.8	2.9	0.28	85.3
			0.8	73.1	0.2	4.2	0.01	84.1
					0.4	3.5	0.08	84.7
					0.8	3.0	0.27	85.0
			1.2	75.4	0.2			
					0.4			
					0.8			
HEA	763	28.8	0.8	69.9	0.2	4.2	0.00	82.6
					0.4	2.8	0.03	84.1
					0.8	2.4	0.23	84.9
			1.2	74.1	0.2	4.2	0.00	85.9
					0.4	3.2	0.05	86.5
					0.8	2.8	0.26	87.1
			0.8	71.6	0.2	4.3	0.01	84.1
					0.4	2.8	0.02	84.4
					0.8	2.2	0.15	85.5
			1.2	75.0	0.2	4.3	0.01	86.5
					0.4	3.1	0.07	87.1
					0.8	2.5	0.22	87.4
HEA	2105	13	0.8	78.0	0.2	4.5	0.02	87.8
					0.4	3.7	0.13	88.0
					0.8	3.1	0.34	88.3
			1.2	78.8	0.2	4.5	0.03	88.5
					0.4	3.8	0.10	88.8
					0.8	3.2	0.35	89.1
			0.8	77.2	0.2			
					0.4			
					0.8			
			1.2	78.2	0.2			
					0.4			
					0.8			
NU	n.a.	27.7	0.8	78.1	0.2	4.5	0.00	85.3
					0.4	3.5	0.08	87.1
					0.8	2.8	0.26	87.2
			1.2	80.0	0.2			
					0.4			
					0.8			
			0.8	76.5	0.2			
					0.4			
					0.8			
			1.2	78.5	0.2			
					0.4			
					0.8			

Table 20.

Measurements after the D_2 stage as functions of KF, D_0 RT and D_2 ClO_2 charge - 1/3

			D_2				
Kappa Factor	D_0 RT (minutes)	% ClO_2 on odp	Final pH	ISO Brightness	ISO Brightness after 24 hours at 105°C	Res. ClO_2 (% on p)	Viscosity (mPa.s)
0.10	1	0.2	6.7	85.8	80.3	0.06	
		0.4	6.9	87.3	81.7	0.11	13.40
		0.8	6.6	88.0	83.1	0.16	
	5	0.2	6.2	87.3	82.8	0.07	
		0.4	6.0	87.8	83.7	0.09	13.80
		0.8	5.6	88.9	84.6	0.13	
	25	0.2	6.3	87.0	82.5	0.10	
		0.4	5.2	88.9	84.8	0.04	13.15
		0.8	5.2	89.3	85.3	0.12	

Note : D_2 NaOH charge (in %) = 1/2 D_2 ClO_2 charge (in %)

Table 3. Metals removal.

% charge	pH	Time, min	Temp °C	Ca	Mg	Mn	Fe	Cu
Starting				1431	309	80.4	13.3	10.6
H_2SO_4	1.53	30	55	90.7	9.6	0	5.3	0.5
	2.05	30	70	100.6				
	3.02	30	55	110.4	32.9	9.0	10.5	5.2
	3.09	120	55	106.3	18.9	1.6	10.2	5.8
	5.03	75	55	1121	237	67.7	12.2	8.2
	7.09	120	55	1554	332	91.0	13.6	7.0
	7.02	120	55	1400	280	73.4	17.8	7.5
DTPA 0.4	5.02	75	55	880	201	33.8	9.9	0.11
0.4	7.03	75	90	1069	262	44.8	11.6	2.1
0.2	7.06	75	90	1348	267	46.7	27.2	0.5
0.7	7.09	120	55	900	239	39.5	11.7	1.6
Acac 0.1	3.05	120	55	203	11.0	0	6.4	1.3
0.7	3.10	30	55	203	17.6	2.8	8.1	5.2
0.4	5.03	75	55	1226	237	73	19.4	16.6
0.4	5.06	75	55	1170	245	74	13.1	6.9
0.4	5.10	75	55	1070	310	63	14.5	10.9
0.7	7.03	120	55	1670	380	101	24.1	4.6
0.1	7.09	30	55	1469	350	86	16.1	10.9

Table 3, continued.

% charge	pH	Time, min	Temp °C	Ca	Mg	Mn	Fe	Cu
Starting				1431	309	80.4	13.3	10.6
KF, 0.25	1.53	120	55	138	11.4	0	6.3	1.7
0.25	1.56	30	55	360	57.8	0	5.8	0.1
0.65	3.00	30	55	209	31.7	0.2	9.8	2.0
0.65	3.00	120	55	215	30.5	0	10.5	6.5
0.45	5.00	75	55	777	149	44.0	8.2	8.2

CLOSED MILL OPERATIONS

Task: Electro-membrane Purge of Chloride

Peter Pfromm
Maribeth Amundsen

SUMMARY

Peter Pfromm and Maribeth Amundsen

Economic evaluation and other tasks

Tests with actual ESP catch and mill water confirmed the great potential for direct dechlorination of dissolved ESP catch by electrodialysis without any pretreatment. For the electrodialysis unit only, investment costs of $210,000 with operating costs of $16,000 per year were estimated for a 1000 ton per day mill. This quotation is from one of the two U.S. suppliers of the needed chloride selective membranes. This estimate does not include dissolving equipment.

In this report period (4-95 to 2-96) the basic feasibility of efficient and selective chloride removal from dissolved ESP catch was shown. A comprehensive report on chloride removal technologies and on recent results at IPST was distributed to the members. Experiments to determine optimized parameters (current density) for chloride removal were initiated, but put on lower priority compared to extended experiments with actual mill ESP catch and water. The potassium selectivity of the process was investigated, but further work was delayed in favor of the tests with actual mill materials.

Tests with mill materials

Two dechlorination runs with actual ESP catch/mill water showed no deterioration of the membranes or any process parameters. A loose brown precipitate was found on the membranes and spacers, but this material washed off easily. The material is most likely lignin-like and is probably carried over from the boiler on the surface of the dust particles. The membranes used were never changed since the start of this project. Based on removing 80% of the chloride from 1000 kg of ESP dust, only 5.5 kg sulfate will be lost through electrodialysis, while 457.2 kg sulfate would be lost if dust was discarded to reach the same chloride removal (See below).

Proposals and contacts

One member company mill reacted positive to hosting pilot trials, if the laboratory results warranted that. The mill samples were supplied by another member company that also expressed direct interest in this work. Contacts with EPRI, Georgia Power, and Southern Company Services (owner of a pilot scale electrodialysis system) were initiated and discussions for pilot test funding continue. Pre-proposals for pilot tests were sent to these entities. A representative from Southern Company will be visiting IPST for discussion of the project. One proposal in cooperation with Argonne National Laboratories was submitted to DOE's Agenda 2020. The proposal deals with removal of NPE's from bleach plant effluent before recycling to recovery. Another proposal on NPE removal from closed-cycle white water systems in cooperation with other faculty at IPST was also submitted to Agenda 2020.

STATUS REPORT

Motivation

RAC recommended area I, as of 11-16-1994, "Minimize the Environmental Impact"
Subgoal: Develop separation technologies for Non Process Elements (NPE's).
Subtask d:Eliminate unwanted chlorine compounds (no end-of-pipe).

The removal of chloride from the kraft pulping operation is necessary due to the negative impact of increased chloride concentrations on recovery boiler operation (sticky deposits), and corrosion. One method of chloride control is to discard large amounts of the ESP catch. On the other hand, if the chloride could be removed selectively, the ESP catch could be recycled, resulting in a direct payback due to savings in chemical makeup. In addition, the inorganics discharged to waste treatment and to the environment would be very significantly reduced.

Currently, crystallization of an ESP catch slurry is being tested by Champion International for chloride and potassium control. The simplicity of the membrane process proposed here, in addition to ease of operation and low energy demand are the motivation to explore this technology.

The chloride purge stream from crystallization will contain organics. That is not the case for electrodialysis, where all organics are recycled with the saltcake to the recovery boiler, and a purely inorganic salt solution is discharged.

The total chloride removal capacity from the ESP catch by any technique may not be sufficient for some bleach plant closure schemes. If proven feasible for actual ESP catch in presence of organics, electrodialysis for chloride control could be used in the bleach plant. This is not directly possible for evaporation/crystallization.

Benefits

The benefits of selective chloride removal from the ESP catch by electrodialysis are:

- Reduced chemical makeup (direct payback)
- Reduced environmental impact
- Reduced washing frequency for the recovery boiler (increased productivity)
- Reduced corrosion

The advantages of electrodialysis vs. alternative processes (evaporation/crystallization, ion exchange) are:

- Continuous process
- No organics entrained in the chloride purge
- No regeneration chemicals needed
- Simple startup/shutdown
- Chloride removal rate is easily adjusted
- Low energy requirements
- Low space requirements

Task 1:Technical Feasibility

Status: Partially complete

Basic Feasibility

The basic feasibility was shown using commercial univalent selective anion and cation exchange membranes in batch experiments. The ESP catch was simulated with pure chemicals. Deionized water was used. The feasibility experiments have been summarized in the Report 1 of Project F017, Subtask Electro-Membrane Processing, "Selective Chloride Removal from the Kraft Process: Review and New Results", issued 11-28-95 to the Member Companies. Please contact P. Pfromm, (404) 894-5305 for additional copies. This is an internal report not available to non-members.

Mill Materials

The goal was to obtain experience with actual mill materials and extended dechlorination runs. It was suspected that the organic components in the ESP catch that are carried over from the recovery boiler could foul the electrodialysis membranes.

ESP catch was obtained from Mill A. This mill has a recovery boiler with an electrostatic precipitator (no direct contact evaporation). A 50 gallon drum of mill water was also obtained. The analysis of the ESP catch sample is shown below.

Cl	CO3	SO4	Na	K	Org. Carbon
weight%	weight%	weight%	weight%	weight%	weight%
3.46	2.35	57.15	25.09	10.74	0.10
mol per 100g	mol per 100g	mol per 100g	mol per 100g	mol per 100g	
0.10	0.04	0.59	1.09	0.27	
mol%	mol%	mol%	mol%	mol%	
4.65	1.87	28.36	52.02	13.10	
electrochem. equivalents anions:		1.37	(assumed as 100%)		
electrochem. equivalents cations:		1.37	mismatch %:	0.03	
Mass balance, total wt% accounted for:		98.89			

Table 1: Analysis of ESP catch sample, Mill A. Organic carbon content was very similar to ESP catch from another mill that was analyzed.

The analysis in Table 1 shows excellent matchup of anions vs. cations, and very good total mass balance. Na and K are analyzed at IPST by atomic absorption. Anions and organic carbon are analyzed by an external laboratory. No further trace analysis for metals and transition metals was conducted, since no difficulties are anticipated from them.

The physical appearance of the ESP catch is a brilliant white fine powder. Upon dissolution at 140 grams per liter of water, a brownish color is first seen. Over night, a brownish precipitate with discrete particles is formed at the bottom of a beaker. The supernatant solution is clear. The high ionic strength will precipitate most organics.

The organic components must be either present as a surface layer on the dry dust particles with a thickness below the wavelength of visible light, or dispersed inside of the particles.

ESP dust dissolved very readily in mill water. Some magnetic particles were found adhering to the stirrbars. This could be iron compounds from the electrostatic precipitator or the conveying system.

The analysis of mill water is shown in Table 2. The significant excess of inorganic anions vs. cations is most likely due to incomplete analysis of all possible cations present.

Ca	**Mg**	**K**	**Na**	**Cl**	**CO3**	**SO4**	**Org. C**
ppm	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
31	**5.1**	**1.74**	**3.29**	**3.95**	**93**	**23.7**	**1.5**
mol/liter	**mol/liter**	**mol/liter**	**mol/liter**	**mol/liter**	**mol/lite**	**mol/liter**	
773.1E-6	**209.9E-6**	**44.5E-6**	**143.0E-6**	**111.3E-6**	**1.6E-3**	**246.6E-6**	
electrochem equiv/liter, anions:			**0.003705**	**(assumed as 100%)**			
electrochem equiv/liter, cations:			**0.002153**		**41.87**	**% mismatch**	
Not all cations were analyzed							

Table 2: Analysis of mill water, Mill A.

Trace metals were not analyzed. This may explain the deficiency in cations, when compared to anions, especially since many cations that were not analyzed are multivalent.

Extended Dechlorination Runs with Mill Materials: Experimental

Temperature:

Runs start at room temperature (~22C). The temperature increases slightly to about 25C, mainly due to heat transfer from the pumps. This is counteracted by a thermostatic bath. The temperature control has recently been improved so that constant temperature can be held. This is important since future experiments may take place at increased temperatures (>40C).

Membranes:

Monovalent selective anion and cation exchange membranes made by Tokuyama Soda, Inc. are used. The same set of four anion- and cation exchange membranes is being used since the start of the program.

ESP catch solution:

The solution is made up by dissolving 140 grams of ESP catch per liter in the mill water at room temperature on a stirrplate with a magnetic stirrbar. The solution forms readily, and is made up directly before starting the experiment. No settling is allowed. About 5 liters of this solution are used for a run.

Purge solution:

As in all previous run, the purge solution is 6 grams/liter Na_2SO_4 in deionized water. The sodium sulfate is added to avoid excessive resistance when the experiment is started and no salt has yet been transported to the purge solution. Deionized water is used to isolate effects of the organics in the ESP catch solution from other potential fouling processes. About 5 liters of this solution is used.

Electrode rinse solution:

Five liters of 6 grams/liter Na_2SO_4 in deionized water is used.

Electrical current:

A constant current density of 10 mA/cm^2 (total current 1 amp through the stack) is applied. The experiments are galvanostatic, with constant current, and a voltage that is automatically adjusted to hold this current. 10 mA/cm^2 is a very conservative current density (see below), but it was chosen for consistency with previous runs.

The complete stack setup is shown in Figure 1. Four monovalent selective anion- and cation exchange membranes are used. The boundary of the membrane stack to the electrode purge solutions is formed by two conventional cation exchange membranes.

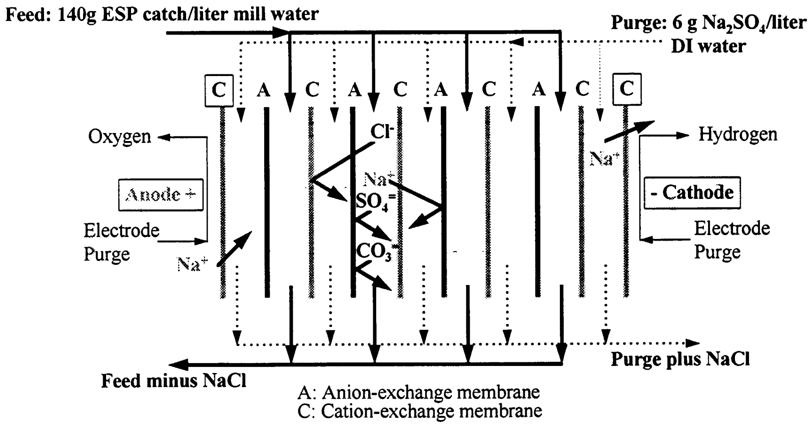

Figure 1: Complete stack setup for dechlorination experiments.

Parameters logged in the batch experiments are temperatures, conductivities, recirculation flow rates, pH, and stack current and voltage. An automatic data acquisition system will be used in the near future.

Extended dechlorination runs with mill materials: Results

A chloride removal current efficiency can be defined for the case of a batch experiment with constant applied electrical current (1 ampere in our experiments) as

$$\phi_{Cl}= 100 * ((m_{Cl}/M_{Cl})/(n\ (I\ t)/F)) \qquad (1)$$

where ϕ_{Cl} is the chloride removal current efficiency in %, m_{Cl} is the total mass of chloride removed during the run in grams, M_{Cl} is the molar mass of chloride in grams per mol, n is the number of diluate cells in the stack (4 in our runs see Figure 1), t is the run time in seconds, I is the current through the stack in ampere, and F is Faraday's constant. This efficiency ϕ_{Cl} accounts for not ideally selective membranes, ohmic losses, and for any bypass of electrical current around the membranes.

On the other hand, the voltage applied needs to be considered, since excessive resistance due to fouling could lead to a sharp voltage increase and thereby decreased energy efficiency. Therefore, the electrical power is integrated over the run time to find the energy that was used. This energy is then normalized by the amount of chloride removed to obtain the energy demand Φ in J/g chloride removed:

$$\Phi = \frac{\int_{t=0}^{t_{end}} U * I dt}{m_{Cl}} \qquad (2)$$

where U is the voltage accross the stack.

Since all flow rates, chloride concentrations, and temperatures are very similar for runs with simulated ESP catch and with the actual material, direct comparisons are shown in Table 3. The voltage is automatically adjusted to maintain an electrical current of 1 amp. The runs are shown in the sequence they were performed. It is important to recall that the membranes have been the same throughout all runs.

	total time [min]	Cl in Feed [g/l]	Cl removed [g]	% Cl removed	Φ [J/g Cl removed]	Current efficiency ϕ [%]
1 Artificial ESP dust (no K, CO_3)	163	6.36	23.4	61	5653	98
2a ESP dust mill A	210	4.84	15.8	56	5866	93
2b ESP dust mill A	195	4.84	16.1	60	5463	98

Table3: Comparison of dechlorination runs.

It is clear form Table 3 that no deterioration is apparent. Several other runs with simulated ESP catch were performed between run 1 and 2 in the Table. After the mill material Run 2 shown in the Table, another identical run was done (not yet analyzed), followed by a mill material run to 90% dechlorination (not yet analyzed). The current/voltage behavior during these two latest runs was virtually identical to the one shown in the table, so that no deterioration is suspected. Overall, the performance of the membranes in actual ESP catch is exceptionally good.

Task 2: Performance Characteristics

Status: Partially complete, delayed due to high priority on actual ESP catch runs

The limiting current density describes the combination of transport parameters where the diffusion of ions in the boundary layer next to a membrane limits the ion removal. Any further increase in current density will lead to splitting of water rather than increased chloride removal. The experiemnts described here were generally run at 10 mA/cm2. The Figure below shows that the current density could be safely increased to twice that amount.

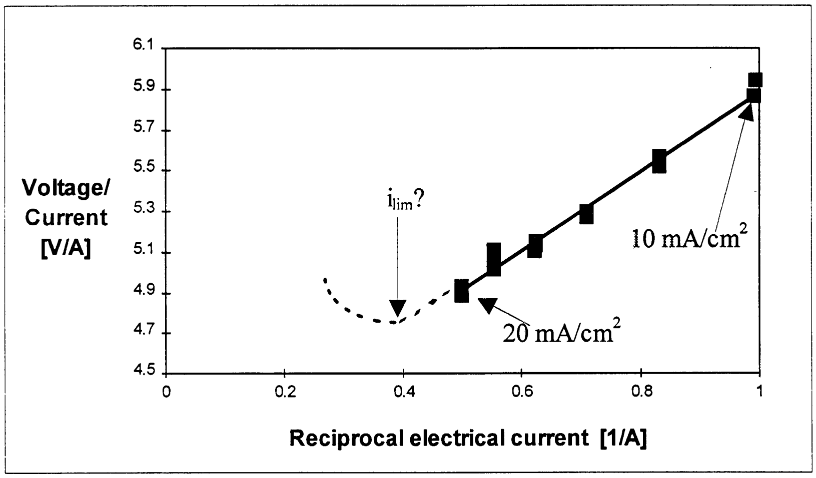

Figure 2: Determination of limiting current density.

The task was temporarily interrupted, since the work with actual mill materials (ESP catch, mill water) was put on higher priority. Further experiments are needed to determine the limiting current density, and the dependence on the solution concentration.

Task 3: Economic Feasibility

Status: Complete

Based on the extremely successful laboratory experiments that showed high selectivity, excellent current efficiency, and no negative impact of organic materials, a quotation was obtained from a supplier of electrodialysis equipment.

Specifications:

- 30,000 gallons per day to be treated (~15.9 metric tons of ESP dust per day, dissolved in water at 140 grams of dust per liter of solution)
- Chloride content: 10 grams of NaCl per liter of solution (Concentration in the solid dust:7.1 weight % of NaCl = 4.3 wt% of Cl)
- Operating Temperature 45C
- 80% of NaCl removed (908.5 kg NaCl removed per day)

The supplier estimated:

Capital Investment Costs (Electrodialysis only, dissolving equipment, plumbing etc. excluded):

$210,000; installed membrane area 220 ft^2 (20.4 m^2)

Operating Costs (Electrodialysis only):

> Membrane replacement: $15,150 (frequency depends on process conditions, see below)
> Power: 22KWhr/Hr ($8,700 per year @ $0.05/KWhr)

If the membrane lifetime is estimated at a minimum of two years, the operating costs are $16,275 per year.

The operating and capital investment costs are quite favorable. No comparative data has been published for Champion International's salt removal process.

To prove the value of this process to industry, a pilot scale test is needed. Only actual mill data can lead to successful technology transfer. Interactions with EPRI and Georgia Power are continuing. Pre-proposals for funding of a pilot test are being considered by these entities.

A representative from Southern Company Services will be visiting IPST. Southern Company owns a pilot scale electrodialysis stack that is currently not used. Membranes would have to be installed. Use of this equipment would reduce pilot trial costs.

Additional Tasks Developed by Interaction with PAC:

Task: Write comprehensive report on chloride removal technologies

Status: Complete
The report is available.

Task: Develop preliminary mass balance for the proposed chloride removal process

Status: Complete

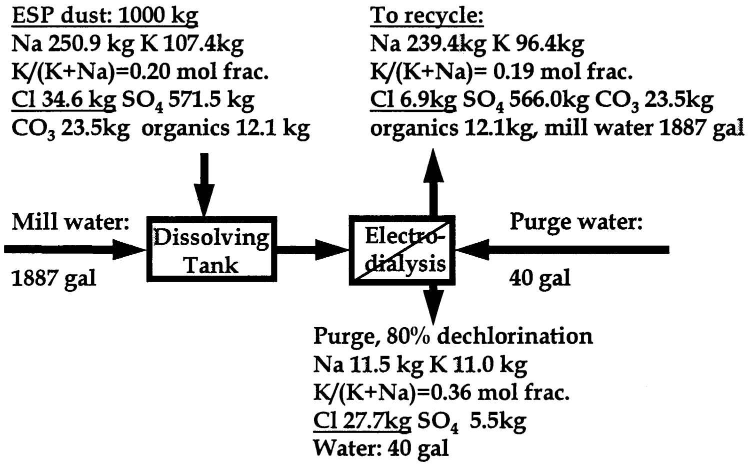

Figure 3: Mass balance for chloride removal from dissolved ESP catch. Basis per metric ton of ESP dust/day. See Table 1 for ESP dust composition. Purge mol fraction K/(K+Na)= 0.36 based on experimental results.

The mass balance above is available as a Microsoft Excel spreadsheet. The critical inout data here is the % dechlotination, the molar ratio K/(K+Na) achieved in the purge, and the amount of sulfate removed with the purge. Derived from the experiments, 0.2 grams of sulfate per gram of chloride removed was used for the above mass balance.

With electrodialysis, 5.5 kg sulfate are lost per 1000 kg of dechlorinated ESP dust. To achieve the same amount of chloride purge by simply discarding dust, 800 kg of dust would have to be discarded, which corresponds to 457.2 kg of sulfate lost.

Suggested tasks for next report period (4-96 to 2-97):

1. Continue limiting current density determination

2. Run at 40C with mill materials, using simulated recycle stream for the concentrate

3. Run with Asahi membranes

4. Continue negotiations for support of pilot scale mill test

5. Consolidate results, issue member report, and prepare for later publication

6. Prepare proposal on direct electrochemical recausticizing (eliminate euilibrium limitations and the lime cycle) with Prof. Jack Winnick (Georgia Tech) to NSF

The basic idea will be explained in the oral PAC presentation. Copies of the proposal would be sent to the PAC members, with a request for consideration of letters of support. A possible mechanism for this could be: PAC (chair) could recommend to NSF to fund, and offer use of certain amount of dues (~$5000) for capital investment or PI time as co-funding, if the proposal is granted. This will significantly increase chances of obtaining the grant (scope: $200-300k over 3 years).

Resources Needed:

Maintain 50% time for 1 technician. If pilot tests are started, reconsideration is necessary.

Associated Student Projects:

PhD: Eric Watkins, Removal of NPE's from the white water cycle by electrodialysis
MS: Manijeh Sadri-Ojeda, Selective removal of potassium from green liquor

CLOSED MILL OPERATIONS

Task: VOC Control in Kraft Mills

Junyong Zhu
Patrick Bryant
Gary Heedick

SUMMARY

This status report summaries the research activities during the last reporting period:

- Developed analytical method for phase equilibrium measurements. Derived an analytical expression for calculating vapor partial pressure using commercial headspace gas chromatography systems: $P_{i\ hs}^{o} = n_{ical} \cdot \frac{A_{ni}}{A_{cal}} \cdot (1 + \frac{V_{hs}}{V_{loop}} \cdot \frac{T_{loop}}{T}) \cdot \frac{RT}{V_{hs}}$
- Evaluated commercial headspace GC systems for the project. Selected Hewlett-Packard HP7695 Headspace and HP 6890 GC for purchase.
- Conducted preliminary measurements of liquid methanol content in several mill black liquor samples using buffer solution method.
- Briefly summarized the work on VOC measurements in Kraft mills by NCASI. Established collaborative relationship with Prof. Amyn Teja of Georgia Tech.
- Submitted a joint proposal for Agenda 2020 funding by DOE.

FUTURE ACTIVITY:

- Continue the current study on the validation of techniques for VOC liquid content measurements in black liquor.
- Obtain more mill stream samples. Samples other than black liquor will also be collected.
- Purchase a headspace GC system and setup the laboratory for this project.
- Validate the headspace GC method for phase equilibrium measurements.
- Conduct preliminary study of phase equilibrium measurements.
- Pursue Georgia Consortium and DOE Agenda 2020 funding.
- Continue work with GA Tech and detail collaboration plan.

STATUS REPORT

JY Zhu and PS Bryant

INTRODUCTION

With the increasingly restrictive environmental regulations posed by the federal agencies, maintaining environmentally sound and technologically competitive in pulp and paper mill operations is a key to the success of the US pulp and paper industry. The new toxic and permit provisions of the 1990 amendments require information on emissions of volatile organic compounds (VOC's) from pulp and paper mill sources. These VOC's are now considered hazardous air pollutants (HAP's). The release of VOC's during mill operations is determined by several factors: (1) the liquid VOC content in mills streams, (2) the fundamental thermodynamic phase equilibrium behavior of the VOC's in mill flow streams, (3) mass transfer associated with specific mill unit operations, and (4) the mill operation conditions, such as wood species and pulping chemicals used, etc. Some of the factors are unit operation and mill specific, such as mass transfer. It is very difficult to generalize all the specific situations. However, the thermodynamic behavior of liquid/vapor phase equilibrium of VOC's is the key factor which controls the VOC release in mill operations. Furthermore, the thermodynamic behavior of the VOC's should not depend on the characteristics of specific unit operations. Therefore, it is important to be able to measure liquid VOC content in mill streams and understand the thermodynamic behavior of liquid/vapor phase equilibrium.

Many data are available on the thermodynamic phase equilibrium of volatile organic compounds, such as methanol and water under various conditions (Ohe, 1989). A series of work on the phase equilibrium and component properties of various pure organic compounds has also been conducted by the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers (Selover, 1990; Cunningham and Jones, 1991) during the last decade. However, all these studies investigated systems with pure species in ideal liquid solutions in which liquid activity coefficients can be derived from existing Gibbs excess energy correlation (Reid et al., 1987, Klotz and Rosenberg, 1994). Then the concentration or the partial pressure of the vapor for a specific species can be calculated using the liquid activity coefficient obtained and species mass balance equations. Little research work has been conducted in the past on the phase equilibrium associated with non-ideal solutions, such as methanol in Kraft pulp mill streams which contain soluble inorganic compounds and dissolved organic solids, such as lignin. The solid content and other minor species such as inorganic components can have a significant impact on the liquid/vapor phase equilibrium (Brusseau and Rao, 1989). Only recently, NCASI initiated a series of work (NCASI, 1994; Crawford et al., 1995) on on-site sampling of VOC's at various mills. These data provided very useful information for a specific mill; however, the data is not conclusive and lacks fundamental understanding about VOC release processes and mechanisms. Therefore, there is a strong demand to understand some fundamentals of thermodynamic phase equilibrium of Kraft mill streams, to provide a tool to quantify VOC release process, and to provide recommendations for minimum VOC emission operations by the pulp and paper industry.

With the basic understanding of the thermodynamic behavior of VOC's, computer model can be developed using VOC liquid activity coefficients obtained from the thermodynamic studies.

REVIEW OF PAST ACTIVITY

Under the recommendation of the spring PAC meeting, the following four tasks have been conducted during this reporting period for the projects.

1. *Development of Experimental Techniques*

Headspace gas chromatography (GC) has been identified as an effective tool for liquid/phase equilibrium studies for multicomponent mixtures (Hachenberg and Schmidt, 1977; Hussam and Carr, 1985). Although other techniques, such as: differential ebulliometry can obtain accurate results, headspace GC method has the advantages of being simple, commercially available, automated, and consistent in measurement results. An ideal headspace GC can give very accurate data as demonstrated by Hussam and Carr (1985). However, the measurement accuracy of commercial headspace GC's and the analytical method for using commercial headspace GC's have not been studied and documented. During this reporting period, we conducted an analytical study on the quantitative analysis of liquid/vapor phase equilibrium using commercial headspace gas chromatography.

THERMODYNAMIC PHASE EQUILIBRIUM PRINCIPLES

Thermodynamic phase equilibrium among N components and 2 phases with uniform temperature and pressure requires the satisfaction of the Gibbs phase rule:

$$\mu_i^V = \mu_i^L \qquad (1)$$

where μ_i denotes the chemical potential of the *ith* component and superscript V and L denote the vapor and the liquid phase, respectively. The chemical potential is an intensive property. It can be expressed in terms of mole fractions of the components involved. For a two phase system involving N components under giving temperature and pressure, there are 2N variables in eqs. (1). The mole fractions add up to unity, therefore, there are only 2(N-1) independent variables. With N equations in (1), the number of free variables of the giving system is therefore:

$$2(N-1) - N = N - 2 \qquad (2)$$

To satisfy eqs (1), we often require the uniformity of the fugacity of each phase for each component:

$$f_i^V = f_i^L \qquad (3)$$

The fugacity of a component in a mixture depends on the temperature, pressure, and composition of that mixture. For vapor phase, the fugacity can be related to the vapor mole fraction by introducing the fugacity coefficient ϕ_i

$$\phi_i = \frac{f_i^V(T,P,\mathbf{y})}{y_i P} \qquad (4)$$

where y_i is the vapor mole fraction of component i and P is the total vapor pressure. For a mixture of ideal gas $\phi_I = 1$.

The calculation of liquid phase fugacity is not trivial. The common approach involves the quantities of standard state fugacity of the activity coefficient. The fugacity of liquid component i can be expressed as:

$$f_i^L(T,P,\mathbf{x}) = x_i \gamma_i(T,\mathbf{x}) f_i^{pureL}(T) \exp\left[\int_{P_i^o}^{P} \left(\frac{\bar{v}_i^L[T,P,\mathbf{x}]}{RT}\right)_{T,\mathbf{x}} dP\right] \qquad (5)$$

where $\bar{v}_i^L$ is molar liquid volume which equals to the ratio of the molecular weight to the density, x_i is the liquid mole fraction, γ_i is the liquid activity coefficient, and the exponential term is the Poynting correction and is only important at high pressures. In equation (5), f_i^{pureL} is the pure liquid fugacity at the "standard state" of T, P_i^s. The standard state is chosen such that a value of $f_i^{pureL}(T)$ can actually be found. A cleaver choice of P_i^s is the saturation (or vapor) pressure of pure liquid i. In this state, the liquid and the saturated vapor is in equilibrium. Therefore,

$$f_i^V(T, P_i^s, y_i = 1) = f_i^{pureL}(T) \qquad (6)$$

Substitute eq. (4) into above equation,

$$P_i^s(T)\phi_i^s(T) = f_i^{pureL}(T) \qquad (7)$$

The liquid fugacity now can be calculated as,

$$f_i^L(T,P,\mathbf{x}) = x_i \gamma_i(T,\mathbf{x}) P_i^s(T)\phi_i^s(T) \exp\left[\int_{P_i^o}^{P} \left(\frac{\bar{v}_i^L[T,P,\mathbf{x}]}{RT}\right)_{T,\mathbf{x}} dP\right] \qquad (8)$$

Substitute eqs. (4) and (8) into eq. (3), we have

$$y_i P = \gamma_i (T, \mathbf{x}) x_i P_i^s \Im_i \qquad (9)$$

where $\Im_i = \frac{\phi_i^s}{\phi_i} \exp\left[\int_{P_i^o}^{P} \left(\frac{\bar{v}_i^L [T, P, \mathbf{x}]}{RT} \right)_{T,\mathbf{x}} dP \right]$ is the Poynting correction factor. For subcritical components, $\Im_i$ is near unity when the total pressure P is not very high. Therefore equation (9) can be simplified as,

$$y_i P = \gamma_i (T, \mathbf{x}) x_i P_i^s \qquad (10)$$

Therefore, the liquid activity coefficient γ_i of component *i* can be found:

$$\gamma_i(T, x) = y_i P / x_i P_{vpi} = P_i / (x_i P_i^s) \qquad (11)$$

HEADSPACE GAS CHROMATOGRAPHY ANALYSIS

The goal of the headspace GC analysis is to obtain the vapor partial pressure P_i of component *i* under equilibrium to calculate the liquid activity coefficient γ_i using eqs. (11). Using ideal gas law the vapor partial P_i is only a function of the molar concentration C_i for a given temperature:

$$P_i = C_i RT \qquad (12)$$

The basic operation principle of an headspace GC is very simple. Put a sample in a temperature well controlled vial and let it equilibrate. Fill the GC sample loop with the equilibrated vapor. Then inject the sample in the loop into the GC column for analysis. However, several issues need to be clearly understood in using headspace GC for thermodynamic phase equilibrium analysis.

A. Effect of Mass Transfer on the Liquid/Vapor Interface on Phase Equilibrium

The mass transfer between the liquid/vapor phase on the liquid/vapor interface reaches a dynamic equilibrium after a liquid/vapor phase equilibrium is established within the headspace of a sample vial. This equilibrium can be disturbed by any external physical phenomenon, such as connecting the headspace to the GC sample loop for sample collection. Sample collected to the sample loop could contain vapor generated after the disturbance of previously established phase equilibrium. The present author calls the sample being contaminated as it contains the newly generated vapor other than the pure vapor before the disturbance. Thus, the accuracy of the phase equilibrium analysis can be affected. It needs to give special considerations in selecting a sample filling method in headspace gas chromatography.

Commercial headspace GC's use pressurization and venting technique to fill the sample loop. During an experiment, the sample vial is pressurized to certain pressure by a supplier gas flow when valve S1 is open as shown in Fig. 1. Vapor sample is collected by venting the loop to atmosphere by opening valve S2. The venting process induces a flow from the sample vial to the sample loop. The magnitude of the flow velocity near the liquid/vapor interface depends on the pressure, the volume, and the geometry of the headspace, as well as the venting time period and the volume vented. The induced flow creates two mass diffusion processes near the liquid/vapor interface. The first is mass diffusion of the component *i* from the liquid phase into the gas phase which generates new vapor and causes the breakdown of the phase equilibrium at the interface. The second is the mass diffusion of newly generated vapor outward into the headspace which could contaminate the sample to be collected. In most commercial headspace GC applications, the volume of the vapor sample collected is about 5-15% of the volume of the headspace. If pure plug flow can be assumed from the headspace to the sample loop during sample collection, the contamination of collected vapor sample by the disturbance of the induced flow is only dependent on the mass diffusion of newly generated vapor near the liquid/vapor interface into the headspace. The mass diffusion length can be approximately calculated:

$$l = \sqrt{\alpha \cdot t} \qquad (13)$$

where α is the vapor mass diffusivity of the component into the headspace and t is the time period of venting. For most VOC's the binary mass diffusivity $\alpha = 0.25 \mathrm{X} 10^{-4}$ m^2/s, typical venting time $t = 4$ seconds, then the diffusion length $l = 1$ cm. Depending on the depth of the headspace, mass diffusion could contaminate the sample collected.

To study the mass transfer effect, a set of experiments needs to be carried out using various depth of headspace for a given known sample (such as methanol/water mixture) under same sampling conditions, such as temperature, pressure, sample loop volume, venting time period, and GC column.

B. Quantitative Analysis

Ideal Headspace

An ideal headspace GC has three features: (1) the volume of the sample loop is infinitively small and negligible comparing to the volume of the headspace , (2) vacuum is used to aspirate the equilibrated vapor sample into the sample loop, and (3) only an infinitively small amount of the sample is aspirated to the sample loop. These features give the ideal headspace GC some advantages: the aspiration time is infinitively short because a infinitively small sample is needed, therefore both disturbance on phase equilibrium and effect of mass transfer on sample contamination will be virtually none; The sample loop is vacuum and the volume is negligible compare to the volume of the headspace, therefore the molar concentration and the component partial pressure in the sample loop after it is filled will be equal to those in the headspace before the aspiration process, which can ease the quantitative data analysis significantly (Hussam and Carr, 1985).

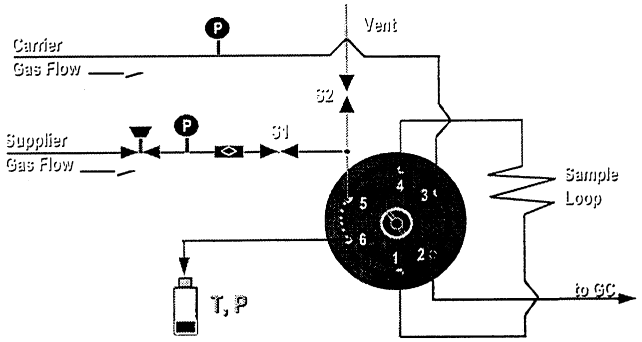

Fig.1 Schematic diagram of a headspace method for phase equilibrium analysis

Commercial Headspace

Method A

In commercial headspace GC's, the sample loop volume is about 5-15% of the headspace volume, the component molar concentration and pressure is not equal to those in the headspace even when pure plug flow during venting is assumed. The initial vapor partial pressure of component *i*, $P_{i\,hs}^{o}$, and total vapor pressure $P_{t\,hs}^{o}$, within the headspace under equilibrium before sample collection can be expressed using the ideal gas law:

$$P_{i\,hs}^{o} = C_{i\,hs}^{o} RT \qquad (14a)$$

$$P_{T\,hs}^{o} = C_{T\,hs}^{o} RT \qquad (14b)$$

At the end of the sample loop filling, the partial and the total pressure within the headspace are $P^f_{i\,hs}$ and $P^f_{T\,hs}$, respectively. Apply the ideal gas law to the remaining vapor in the headspace:

$$P^f_{i\,hs} = C^f_{i\,hs} RT \qquad (15a)$$

$$P^f_{T\,hs} = C^f_{T\,hs} RT \qquad (15b)$$

Assume all the sample left the headspace is filled in the sample loop and injected to the GC column, then the number of moles injected to the GC column can be calculated from eqs. (14a) and (15a):

$$n_{iloop} = n^o_{i\,hs} - n^f_{i\,hs} = V_{hs}(C^o_{i\,hs} - C^f_{i\,hs}) = \frac{V_{hs}}{RT}(P^o_{i\,hs} - P^f_{i\,hs}) \qquad (16)$$

where T is the temperature within the headspace. The final partial pressure of component i, $P^f_{i\,hs}$, within the headspace is a unknown in the above equation. The initial and final total pressure P_{Ths} and $P^f_{T\,hs}$ can be measured by the headspace.

Assume that the venting process will not cause the generation of new vapor within the headspace, the molar fraction of component i within the headspace before and after the venting process will be the same. From eqs. (14) and (15), we have:

$$\frac{P^o_{i\,hs}}{P^o_{T\,hs}} = \frac{P^f_{i\,hs}}{P^f_{T\,hs}} \qquad (17)$$

Substitute eq. (17) into eq. (16), we have:

$$P^o_{i\,hs} = \frac{1}{P^o_{T\,hs}\left(1 - \frac{P^f_{T\,hs}}{P^o_{T\,hs}}\right)} \cdot \frac{n_{iloop}RT}{V_{hs}} \qquad (18)$$

Calibration

The calibration of headspace measurements can be done as it is for conventional GC analysis since equation (16) gives the absolute moles of the measured component. Either a known amount of gas or liquid sample can be injected directly into the GC column. Assuming the detector response is linear, the absolute moles injected can be related the peak area measured by the GC detector:

$$A_{ncal} = k \cdot n_{cal} \qquad (19)$$

For the same reason, we have

$$A_{ni} = k\cdot n_{iloop} \tag{20}$$

Therefore, we have

$$n_{iloop} = \frac{A_{ni}}{A_{ncal}} n_{cal} \tag{21}$$

Combine eqs. (18) and (21), we have the initial vapor partial pressure od component *i*:

$$P^{o}_{i\,hs} = n_{cal} \cdot \frac{A_{ni}}{A_{ncal}} \cdot \frac{1}{P^{o}_{T\,hs}(1-\frac{P^{f}_{T\,hs}}{P^{o}_{T\,hs}})} \cdot \frac{RT}{V_{hs}} \tag{22}$$

Method B

After the sample is collected to the sample loop, the vapor volume is expanded. Assume plug flow and the sample loop and the headspace achieve a pressure equilibrium. Further assume that no vapor is escaped to the atmosphere, mass conservation of the vapor gives the following expressions:

$$P^{o}_{i\,hs} V_{hs} = n^{o}_{i\,hs} RT \tag{23}$$

$$P^{f}_{i\,hs} V_{hs} = n^{f}_{i\,hs} RT \tag{24}$$

$$P_{iloop} V_{loop} = n_{iloop} RT_{loop} \tag{25}$$

$$n^{o}_{i\,hs} = n^{f}_{i\,hs} + n_{iloop} \tag{26}$$

where V_{hs} and V_{loop} are the volumes of the headspace and the sample loop respectively. Substitute eqs. (23) -(25) into eq. (26), we have

$$\frac{P^{o}_{i\,hs} \cdot V_{hs}}{T} = \frac{V_{hs} \cdot P^{f}_{i\,hs}}{T} + \frac{V_{loop} \cdot P_{iloop}}{T_{loop}} \tag{27}$$

The loop final partial pressure P_{iloop} is equal to the headspace final partial pressure $P^{f}_{i\,hs}$ as we assumed previously:

$$\left(\frac{V_{hs}}{T} + \frac{V_{loop}}{T_{loop}}\right) \cdot P_{iloop} = \frac{P^{o}_{i\,hs} \cdot V_{hs}}{T} \tag{28}$$

Substitute eq. (25) into eq.(28), we have

$$P^o_{i\ hs} = \frac{n_{iloop}RT}{V_{hs}}(1 + \frac{V_{hs}}{V_{loop}} \cdot \frac{T_{loop}}{T}) \qquad (29)$$

Use the same calibration procedure discussed above, substitute eq. (14) into eq. (29), we have:

$$P^o_{i\ hs} = n_{ical} \cdot \frac{A_{ni}}{A_{cal}} \cdot (1 + \frac{V_{hs}}{V_{loop}} \cdot \frac{T_{loop}}{T}) \cdot \frac{RT}{V_{hs}} \qquad (30)$$

Both Eq. (22) and (30) can be used for quantitative thermodynamic phase equilibrium analysis using commercial headspace GC's. Eq. (30) has the advantage of not requiring to know the initial and final total pressure within the headspace. Both equations are valid based on the assumptions of plug flow and negligible mass transfer on the liquid/vapor interface or the sample volume is much smaller compared the vapor volume in the headspace. Therefore, a smaller sample loop volume is preferred for headspace GC analysis to obtained accurate measurements.

The liquid activity coefficient now can be calculated by substitution of $P^o_{i\ hs}$ into equation (11) where the pure vapor pressure of component *i*, P_{vpi}, is given and is a function of temperature only. The molar fraction of component *i* in the liquid phase can be measured in a separate set of experiments as discussed below.

VOC LIQUID CONTENT MEASUREMENTS

A known VOC liquid molar fraction under liquid/vapor phase equilibrium is a prior to calculate VOC liquid activity coefficient γ_i of component *i* using equation (11). Most of the mill stream samples, such as black liquor, contain various solid components. The identification and measurements of all of the components within a sample are not trivial. For streams such as weak black liquor and white water which contain more than 80% water, it will be convenient and a good approximation to treat the sample as a mixture of water and VOC to calculate the liquid molar fraction. With this assumption, the liquid VOC molar fraction can be calculated by measuring the liquid VOC contents.

The measurements of liquid VOC content is not trivial. Limited techniques are available to quantify the liquid VOC content in mill streams, particularly in black liquors. Recently, NCASI (Gunshefski and Cloutier, 1994) developed a method for measurement of liquid methanol in black liquor. The method uses buffer solution to precipitate corrosive materials in liquor samples and then inject the solution into a GC for methanol analysis. For other mill streams, a precolumn may be sufficient to filter the undesirable materials which could damage a GC column. Purge and trap method may be used to characterize the liquid VOC content in samples, however, limited studies have been reported. Electrochemical method using memebrane separation technique may also be applied to measure liquid methanol concentration in a sample. A major concern of all these methods is the accuracy and the unknown conditions under which they will be valid. It is one of the task of the project to verify the accuracy and validity of these methods for liquid VOC measurements in mill streams.

Water is the main component in most of the mill streams, in particular in weak black liquor. Therefore, the molar fraction of liquid VOC in mill streams can be calculated using the following expression once the number of moles of liquid VOC is determined.

$$x_i = \frac{n_i^l}{n_i^l + n_w} \cong \frac{n_i^l}{V \cdot \rho_w / M_w} \qquad (31)$$

where n_i^l is the moles of liquid VOC measured in a sample volume, n_w is the moles of water in the sample volume. V is the volume of the sample, ρ_w is the density of water under the testing temperature, and M_w=18 is the molecular weight of water.

*A. **Buffer Solution Method***

This method is developed by NCASI (Gunshefski and Cloutier, 1994). H_2KPO_4 and KOH buffer solution is added into weak black liquor to precipitate the solid. The precipitated solution is injected into a GC column for analysis. A separate calibration test is conducted to calibrate the absolute quantity of methanol injected. The data is then converted to ppm of solid mass.

Preliminary experiments have been conducted using this method to determine liquid methanol content in weak black liquor samples. Two hard wood samples from two mills are tested. Measurements were conducted under various temperatures as shown in Fig. 2. The results show that liquid methanol content is generally in the range of 1000-2000 ppm solid mass. For liquor sample from mill B, a clear decrease of liquid methanol with temperature is observed, indicating the vaporization of methanol when heated. This behavior is not observed for liquor from mill A.

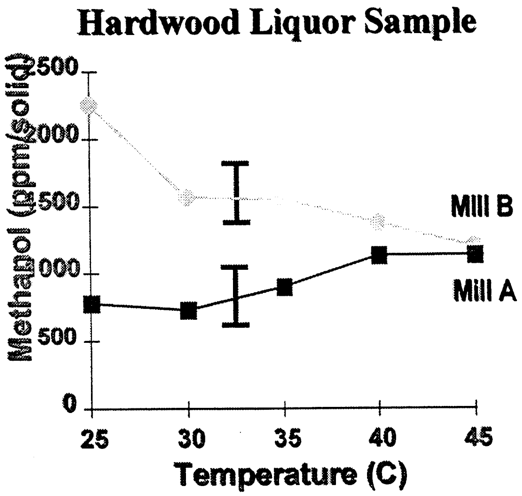

Fig. 2 Measured liquid methanol content in two hardwood weak black liquors

Liquid methanol mole fraction can be easily calculated from above measurements. Future study will be conducted under a wide temperature range and using other method discussed above. More mill samples will be tested.

B. Purge and Trap Method

This task has not been completed. The objectives of this study are to find whether the method can give reliable data comparing to the buffer solution method discussed above and to find the optimum purge time if the method is proved to be viable.

In this method, the liquid methanol molar fraction can be calculated as:

$$x_i = \frac{n_i^l}{n_i^l + n_w} \cong \frac{n_i^l}{(1-S)\cdot m / M_w} \qquad (32)$$

where n_i^l is the moles of liquid methanol measured in a sample volume, S is the solid content of the sample, m is the mass of the sample tested.

C. Membrane Method

This task is underway. No data have been obtained.

2. Summary of NCASI Work on VOC Measurements in Mills

NCASI conducted a series of studies at several Kraft mills to characterize the emissions of volatile HAP's and VOC's from chemical pulp mills in 1993 and 1994. The results of their studies were published in a series of 9 NCASI Technical Bulletins (NCASI, 1994). The results as summaries by Jain (1996) show: (1) paper machines, brownstock washers, Oxygen delignification systems, smelt dissolving tanks, bleach plants were the major contributors to VOC emissions from Kraft mills, (2) Methanol constituted the major fraction of HAP's from most sources, (3) water reuse practice will significantly contribute the VOC emissions in Kraft mills. As a summary of the NCASI study can be found in a paper presented by Jain in the TAPPI Minimum Effluent Mills Symposium (Jain, 1996). This report will not repeat the NCASI data.

3. Evaluation of Commercial Headspace GC for Purchasing

Two commercial headspace gas chromatography systems have been evaluated. The first system is made by Hewlett-Packard (HP 7695 headspace with HP 6890 GC) and the other is by Varian (Varian Genesis Headspace with Varian 3400 GC). Initial demonstration tests were conducted by both of the two systems. The purpose of the tests is to assess if the systems are able to detect the vapor phase VOC's in laboratory experiments. Fig. 2 shows a typical chromatography obtainbed by the Hewlett-Packard system. GC/Mass Spectrometry done at HP research laboratory shows the detected species as listed in Table 1. The laboratory tests indicate that commercial GC's are capable of detecting vapor phase VOC's under experimental conditions comparable to those proposed in this research project and commercial headspace GC's are viable for this project. Because of the complexity of the system to be dealt with in this project, the measurement accuracy of commercial systems is unknown. The validation of commercial headspace GC method will be conducted in the next reporting period. We will work with Georgia Tech. on this task. Simple mixture systems will be used.

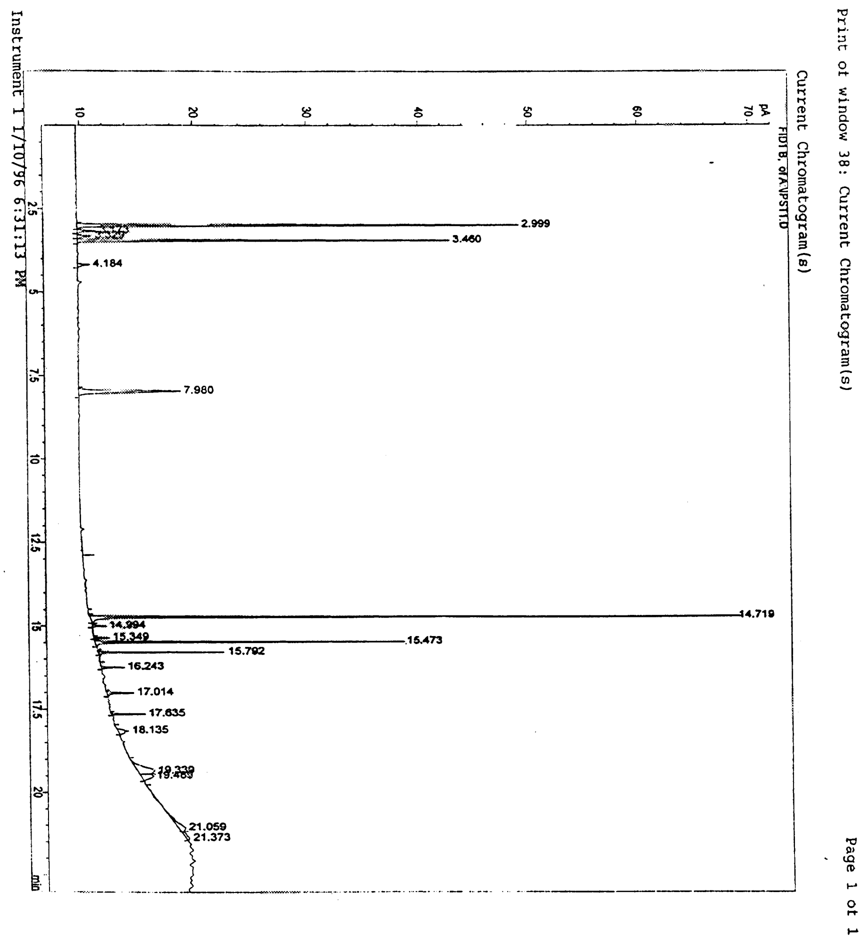

Fig. 3 Gas chromatography of the vapor phase in a black liquor sample measured by HP 7695 headspace with HP 6890 GC.

Table I Major species observed in black liquor vapor sample

SPECIES (Formular)	BP (°C)	Density (s.g.)	GC AREA (%)	SPECIES (Formular)	BP (°C)	Density (s.g.)	GC AREA (%)
Methanol (CH_3OH)	65	0.79	31.69	Ethanol (CH_3CH_2OH)	78.5	0.79	1.62
α - Pinene	155	0.86	28.20	α - Terpinol	220	0.93	1.15
β - Pinene	166	0.86	13.47	Acetone (CH_3COCH_3)	56.2	0.79	0.78
Dimethyl Sulfide (CH_3SCH_3)	37.3	0.85	10.48	Dimethyl Disulfide	146	1.124	0.77
Methyl Sulfide (CH_3SH)	6.2	0.79	1.91	MEK ($CH_3CH_2COCH_3$)	79.6	0.81	0.68
β - Phellandrene	171	0.85	1.75	α - Fenchene	155	0.86	0.67

4. *Establishing Collaboration with Georgia Tech.*

We have established collaboration with Georgia Tech. Dr. Amyn Teja, Regent's professor of chemical engineering will work with us on VOC phase equilibrium. Dr. Teja has very strong credentials in the area of liquid/vapor phase equilibrium. He is the Director of the Fluid Properties Research Institute (FPRI), a university-industry cooperative organization dedicated to the measurement of phase equilibria and thermophysical properties of fluids of interest to the petroleum and chemical industries.

The initial collaborative work will be validation the measurement techniques for this project. Dr. Teja will also be responsible for study phase equilibrium of synthetic mill streams to get fundamental understanding of the subject. While IPST will be responsible for study of phase equilibrium of mill stream samples. A joint proposal has been prepared to Agenda 2020 for DOE funding as discussed in the next section.

5. *Proposal for DOE2020 Funding*

A joint research proposal with Georgia Institute of Technology, University of Idaho, North Carolina State University, and NCASI has bee submitted to PPERA for inclusion in the PPERA's Cooperative Research Program for Agenda 2020 funding by DOE. One of the major collaborator on this proposal, Dr. Amyn Teja, Regent's Professor of Chemical Engineering in Georgia Tech. will be particularly helpful to this project. The proposal is a three cooperative effort among the proposing institutions. The first year budget proposed by IPST is $175,000. The DOE funding will leverage member due's fund in this research program. It will also enable close collaboration between IPST and Georgia Tech. A copy of the proposal is available by request.

CONCLUSION/RECOMMENDATIONS

- Commercial GC's are capable of detecting vapor phase VOC's under experimental conditions comparable to those proposed in this research project and commercial headspace GC's are viable for this project.

- Preliminary measurements of liquid methanol in weak black liuqor sample using buffer solution method has been conducted.
- Measurements method validation for both vapor phase and liquid phase will be the main effort in the next reporting period.
- Mill streams other than black liquor will also be collected and tested.
- Detailed mill VOC emission data can be found in NCASI reports and a summary is presented by Jain (1996) recently in the TAPPI Minimum Effluent Mills Symposium.

FUTURE ACTIVITY

In the next reporting period, the following tasks will be performed:

- Continue the current study on the validation of techniques for VOC liquid content measurements in black liquor.
- Obtain more mill stream samples. Samples other than black liquor will also be collected.
- Purchase a headspace GC system and setup the laboratory for this project.
- Validate the headspace GC method for phase equilibrium measurements.
- Conduct preliminary study of phase equilibrium measurements

The results of these studies will be reported in the Fall PAC meeting.

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CLOSED MILL OPERATIONS

Task: Fundamental of Dregs Removal

H. Jeff Empie
Maribeth Amundsen

FUNDAMENTALS OF DREGS REMOVAL

H. Jeff Empie
Maribeth Amundsen

SUMMARY

It is evident that one of the key unit operations in the liquor cycle for controlling NPE build-up is dregs removal. A reduction in the purge rate of green liquor dregs, brought about by a change in physical/chemical properties or increase in production rate, will increase the levels of Mg and Mn in the lime cycle and increase the levels of Al, Fe, and Si in both the liquor and lime cycles. Hence, a detailed study of the effect of increased levels of NPE's on dregs removal, and therefore purge of NPE's, is mandatory.

Because actual mill smelt composition varies from shift to shift, as well as within a given shift, this study will start with a known, synthetic smelt composition (including dregs), and add a fixed amount of specified non-process element chemicals. These will be heated to typical smelt bed temperatures and held in a nitrogen atmosphere for a period of time to allow the chemicals to equilibrate. The cooled reaction products will then be added to hot water to form a synthetic green liquor. The insolubles will be filtered out and washed with hot water.

These washed insolubles represent the dregs for the simulated process and will be sampled for chemical analysis. The remainder will be contacted with room temperature water and filtration and settling rates determined. Comparisons can then be made with the base condition of synthetic smelt treated at the same conditions with no NPE's added.

To ultimately validate the results, the procedure will then be repeated starting with kraft smelt and green liquor obtained from an operating pulp mill.

A one-liter stirred batch reactor has been designed to carry out these reactions at smelt bed temperatures in the laboratory. All parts which are contacted by molten smelt have been fabricated out of alumina to avoid corrosion phenomena and contamination of the reaction products. Installation is nearly complete.

Samples of green liquor clarifier underflows have been obtained from four member company mills. These have been analyzed chemically, and, along with available published data on dregs composition, have been used to calculate the baseline smelt composition for the study.

STATUS REPORT

PROJECT TITLE: Fundamentals of Dregs Removal

INTRODUCTION:

For kraft pulping the elements Na and S are the principal process elements. The non-process elements include Cl, Al, Si, K, Fe, Cu, Mn, Mg, P, and V. These enter the pulping process with the wood, water, other processing chemicals, and make-up chemicals. They can increase in concentration unless purge mechanisms are provided; presently, these purges are mill solid, liquid, and gaseous effluent streams. Tighter "mill closure" implies a reduction in these effluent discharges in order to decrease both water use and the environmental impact of the pulp manufacturing process.

Although the NPE's tend to be present in low levels, they may have a disproportionate effect on the operation of the mill. Some NPE's (viz. Al, Fe, Mg) are sparingly soluble in green liquor, but more soluble in white liquor. If they are not removed with the dregs, they can carry through to the digester and subsequently cause fouling in the evaporators. Aluminum can trigger evaporator scaling when its concentration exceeds 50-100 mg/L in the white liquor. Aluminum can be precipitated from green liquor by the addition of magnesium to form hydrotalcite. Since there is some Mg naturally in the liquor cycle, entering with bleach plant effluent and make-up lime, some Al is being removed by this mechanism in present mill caustic plants.

Magnesium causes problems when it is allowed to accumulate in the lime mud because it calcines in the lime kiln, consuming fuel. The magnesium hydrates in the slaker, but it has no causticizing power, making it a heat consuming dead load. Magnesium also causes serious problems in the settling and filtration of lime mud. The finely divided particles of magnesium hydroxide in the dregs cause poor settling rates and a tendancy to plug filter cakes. Therefore, it is important to minimize Mg input and control its build-up throughout the caustic plant.

Fe, Cu, and Mn are other trace elements which can cause problems. The only outlet for these elements is the dregs system. Iron build-up is believed to be the cause of dusting from the lime kiln. The concentration of manganese in the lime cycle is quite low because green liquor clarification is effective in removing Mn.

Some NPE's (viz. Si, P) are soluble in green liquor, but less so in white liquor. Hence, if these are not removed from the green liquor, they can accumulate in the lime mud circuit, lowering lime availability and increasing kiln fuel cost. In the presence of lime, phosphorous is precipitated as apatite, $Ca_5OH(PO_4)_3$. In the lime kiln, apatite converts to calcium phosphate, $Ca(PO_4)_2$. Some, but probably not all, of the calcium phosphate converts back to apatite in the causticizing process. P does not precipitate in the green liquor circuit, even when lime is added as a settling or filtration aid. Therefore, its build-up can only be controlled by a purge of lime mud, which is best done at the dregs filter. The recommended bleed is in line with the amount of mud precoat required for optimum operation of the dregs filter.

One other NPE that needs to be addressed is chloride. Its removal is difficult because it is soluble and remains with the aqueous liquor streams. Three methods have been practiced commercially in recent years. In the recovery boiler flue gas, SO_2 can react with NaCl, H_2O, and O_2 to form Na_2SO_4 and HCl gas. The HCl can be either scrubbed out of the flue gas by known methods or allowed to escape to the atmosphere. An alternative method for chloride removal is to purge NaCl by leaching precipitator dust. This method has been developed by Champion International, however it appears cumbersome and expensive. Chloride can also be removed by white liquor evaporation-crystallization. This was practiced as part of the closed mill operation at Thunder Bay, Ontario. It has since been discontinued.

REVIEW OF PAST ACTIVITY:

A one-liter stirred batch reactor has been designed to carry out these reactions at smelt bed temperatures in the laboratory. All parts which are contacted by molten smelt have been fabricated out of alumina to avoid corrosion phenomena and contamination of the reaction products. Installation is nearly complete.

Samples of green liquor clarifier underflows have been obtained from four member company mills. These have been analyzed chemically, and, along with available published data on dregs composition, have been used to calculate the baseline smelt composition (assuming 95% reduction efficiency) for the study; namely:

Component	wt.%
Na_2CO_3	74
Na_2S	20
Na_2SO_4	2
NaCl	2
Dregs	2

and the baseline dregs composition:

Component	wt.%
$CaCO_3$	60
Fe_2O_3	3
$Mg(OH)_2$	10
MnO_2	5
SiO_2	1
Al_2O_3	1
C	20

CONCLUSIONS/RECOMMENDATIONS: None

FUTURE ACTIVITY:

1. Base Case (no NPE's added)

A synthetic smelt will be made using purchased chemicals and equilibrated at 850°C under N_2 for 60 minutes. The equilibrated smelt is then cooled, crushed, and dissolved in 90°C dilute aqueous caustic. Filtration at 90°C, followed by washing of the insolubles (dregs) at 75°C, and filtration/settling rate determinations at 25°C will be carried out. Chemical analyses of the green liquors and dregs will be obtained.

2. Non-Process Element Buildup (NPE's added)

The above procedure will be repeated with NPE's added at four different concentration levels to give an indication of solubility effects. The cations to be included are: Al, Si, Fe, Cu, Mn, Mg, K, P, and V. The corresponding anions will include sulfate, carbonate, hydroxide, and oxide.

3. Kraft Smelt

Steps 1 and 2 above will be repeated using actual kraft smelt instead of purchased chemicals. Results for the base case with no NPE's added will be validated by comparing to untreated mill smelt and green liquor analyses.

NEW RECOVERY TECHNOLOGY

NEW RECOVERY TECHNOLOGY

Black Liquor Gasification

Junyong Zhu

TECHNICAL PROGRAM REVIEW

PROJECT SUMMARY

PROJECT TITLE:	**Closed Mill - Black Liquor Gasification**
PROJECT STAFF:	**JY Zhu**
BUDGET:	**$60,000 (Subtask Budget)**
DIVISION:	**CBSD**
PROJECT NUMBER:	**F017**

OBJECTIVE:

The objectives of the subtask are to: (1) describe the problems of hot gas clean-up for integrated black liquor gasification combined cycle applications, (2) provide a thorough review of available technologies for hot gas clean-up and future research needs, and (3) determine the future research direction.

GOAL:

Present future research direction to PAC for review.

SUMMARY:

A report has been completed and sent to PAC members under Project F017, Report 1, entitled "Hot Gas Cleanup for Black Liquor Gasification: A Brief Review of Available Technologies". The report contains the following conclusions:

- Identified a key to the problem - Alkali particle removal.
- Completed technology review and analysis.
- Reviewed available technologies on submicron particle removal.
- Recognized that commercially available technologies cannot meet the requirement for alkali removal in black liquor gasification.
- Indicated that increasing the size of alkali particles or modification of the particle size distribution is an effective way to increase small particle collection with subsequent particle removal process using conventional technologies.
- Indicated that using multiple stages of particle size enlargement and subsequent particle removal can achieve the goal of alkali content less than 50 ppb.
- Presented a literature review on particle agglomeration and future research direction.

FUTURE ACTIVITY:

- Project is on hold.
- Pursue further discussion with PAC.

NEW RECOVERY TECHNOLOGY

Combined Gasification and Autocausticizing

H. Jeff Empie
Gary Heedick

ANNUAL PROGRAM REVIEW

February, 1995 - February, 1996

EXTERNAL CONTRACT (NSF)

PROJECT TITLE:	INCREMENTAL KRAFT RECOVERY CAPACITY USING MIXTURES OF BLACK LIQUOR AND BLEACH PLANT EFFLUENTS
PROJECT STAFF:	Jeff Empie, Garry Heedick
PROJECT BUDGET:	$156,000
PROJECT NO.:	4122

OBJECTIVE:

Demonstrate technical feasibility of gasifying mixtures of kraft black liquor and bleach plant effluents in the presence of certain multi-valent metal compounds (Fe_2O_3, MnO_2, or TiO_2; M_xO_y) to generate a fuel gas and sulfur-free solid amphoteric salt (sodium ferrite, manganate, or titanate), which when hydrolyzed, forms sodium hydroxide and the original metal oxide.

IPST GOAL:

The work proposed will develop a process concept based upon gasification and autocausticization for recovering the chemical and energy values of mixtures of kraft black liquor and bleach plant effluents produced in the manufacture of kraft pulp. The process must be installable in existing kraft mills such that it provides incremental recovery capacity that is economically attractive and environmentally acceptable to the mill.

SUMMARY:

Funding by the National Science Foundation (through MIT) has been obtained for technology development, which if successful, will enable kraft pulp mills to obtain incremental kraft recovery capacity and move toward environmentally mandated closed-cycle operation. This will be done by developing a chemical recovery process based upon gasification technology that will combine bleach plant effluents with black liquor and recover the chemical and energy values contained in them in an economical, safe, and environmentally acceptable manner. Fluidized bed gasification, combined with autocaustization using an amphoteric salt, will provide incremental recovery capacity to mills which typically are production limited by present recovery equipment.

The proposed process will convert the feed liquor to kraft white liquor and process steam to be used elsewhere in the mill.

Autocausticization of the sodium carbonate produced by black liquor combustion has been demonstrated in sulfur-free systems, but not for the kraft liquors that dominate world paper production. Sulfur may combine with the bi-valent metals to put them in a stable sulfide (e.g. FeS) form and renders them useless for autocausticizing. Research on gasification will show how to temporarily remove the sulfur from the sodium chemicals prior to carrying out the autocausticizing reaction.

Research on electrodialysis will be needed to provide a route for separation of carbonate from hydroxide in solution prior to recovering the sulfur by scrubbing with the separated carbonate solution; this will be done after separate funding has been found.

Specific technical milestones are:

* Development of preliminary reaction rate and conversion data to be used as a basis for designing a larger scale reactor. Also, the higher heating value of the fuel gas produced will be determined.

* Determination of the rate of hydrolysis of the amphoteric salt product, and the chemical and physical properties of the metal oxide that is regenerated during hydrolysis.

The initial crucial experiment is to demonstrate, at typical gasification temperatures, the desired chemistry; i.e., formation of solid sodium metallite and H_2S gas, with some unconverted Na_2CO_3, but negligible metal sulfides. This will be done by a relatively simple and inexpensive method patterned after one developed for coal hydrogenation and subsequently used for black liquor. The key feature is a rapid initial liquor heating rate of about 500°C/sec, followed by extended time at the final reaction temperature of 700°C, all in an atmosphere of flowing steam. The time-temperature history of the reactants should closely simulate what would occur in a commercial fluidized bed gasifier under typical process conditions.

The procedure involves rapid electrical heating of several thin pieces of metal screen, upon which rests a small amount of black liquor/bleach plant effluent mixture, intimately mixed with finely divided metal oxide. The electrically heated "sandwich" of reactants and metal screens is enclosed in a small chamber, effectively making a high temperature packed bed reactor through which steam can be continuously passed. The product gas can be analyzed for CO, CO_2, H_2, and H_2S. At the end of the reaction period, cool-down can be made rapid simply by turning off the current and purging with nitrogen. Analysis of the solids left on the screens should yield Na_2CO_3, $Na_2M_xO_{y+1}$, Na_2S, Na_2SO_4, MS_x, and M_xO_y. These data, along with feed rate information, will yield the necessary rate and conversion results needed to establish feasibility and to design a commercial scale process. The bench scale reactor has been designed and is being fabricated.

Hydrolysis of the product solids is straightforward and will yield critical information on the chemical and physical nature of the regenerated M_xO_y. Of primary concern are the filtration characteristics and the extent of metal sulfide formation.

The separation of unreacted Na_2CO_3 from the product NaOH also represents a formidable technical hurdle, the Na_2CO_3 being needed to scrub the H_2S out of the fuel gas. The literature has reported separating KOH from a KOH-K_2CO_3-LiOH solution using electrodialysis with monovalent anion-permeable membranes. Application to our Na_2CO_3-NaOH solution should make the separation problem straightforward. A laboratory scale electrodialysis cell can be used to evaluate commercially available membranes for effectiveness in carrying out the desired separation of carbonate from hydroxide (and chloride).

PROJECT STATUS

New project. Work initiated in the first quarter of 1996.

A KINETIC AND MASS TRANSFER CHARACTERIZATION OF LIMESTONE SORPTION OF HYDROCHLORIC ACID IN AN ACOUSTIC FIELD

James Boerner
Ph.D. Candidate

ABSTRACT

Results indicate an improvement in reaction conversion of CaO and HCl to $CaCl_2$ in an intense acoustic field of 160 dB. Experimental cases presented include temperatures at 200 and 350 °C, and sorbent particle sizes of 20, 75 and 125 µm. Conversion is enhanced more at 350 °C and with the 20 µm sorbent fraction. This is in agreement with steady reaction conditions by other investigators where conversion increases with reaction temperature and decreasing sorbent particle size.

Additional experiments at the above conditions must be run to better establish experimental error. Further experiments include analysis of sound pressure level on reaction conversion and further residence time study with a longer sorbent injection tube. Future results will be correlated with kinetic equations to elucidate possible mechanisms to reaction conversion enhancement. Conversion enhancement seems to be due to a 30-50% increase in particle residence time in the reactor, or improved gas film diffusion around the particles.

HYPOTHESIS AND THESIS OBJECTIVES

It is hypothesized that in an acoustic field, similar to those characteristic of pulse combustor tailpipes, conversion from CaO to $CaCl_2$ will be enhanced. It is expected that mass transfer in an acoustic field will be greater than in steady flow. The reaction enhancement should correlate with particle slip velocity. The primary objective of this research is to characterize the HCl and CaO gas - solid reaction in an acoustic field. This information may lead to improvements in acidic gas removal from combustion processes. Several tasks must be accomplished to reach this objective.

1. Characterize optimum limestone sorbent parameters for the system.
2. Obtain kinetic conversion data for steady and oscillating flow.
3. Measure particle slip velocities for calculation of the particle Reynolds number for steady and oscillating flow. This will help in presenting data in nondimensional correlations.
4. Compare kinetic reaction rates and product conversions among experimental trials to determine degree of mass transfer enhancements.

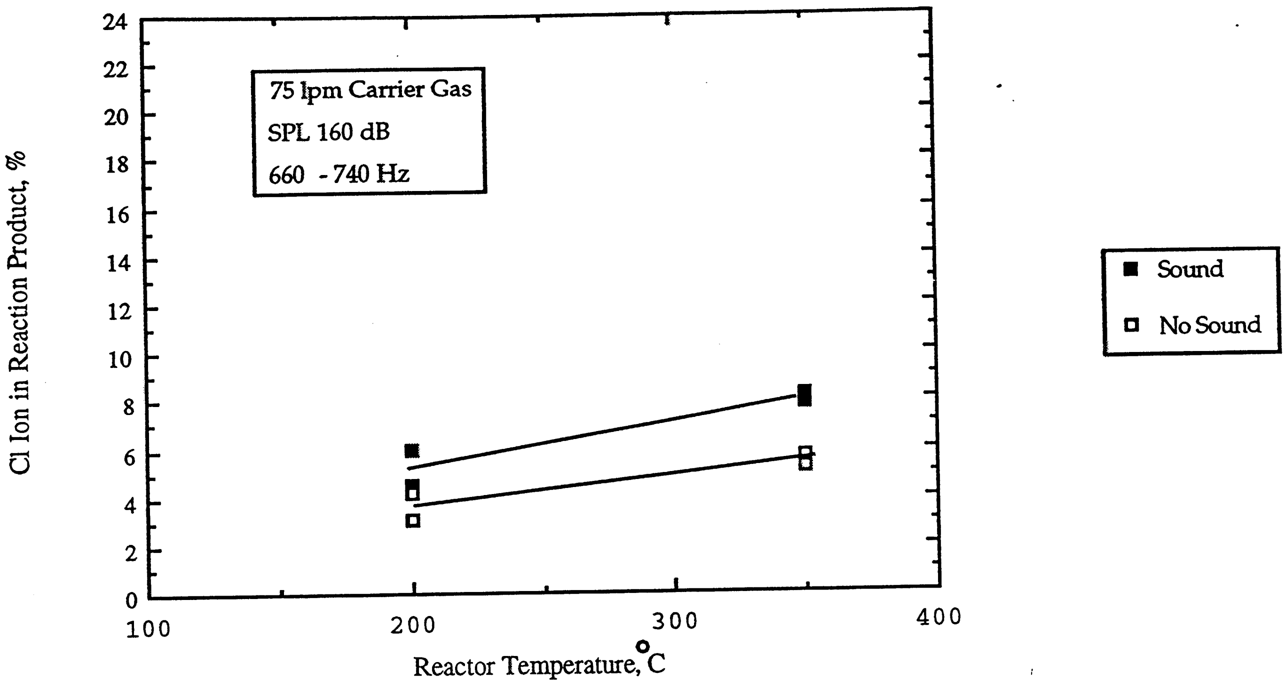

Figure 6 Reaction conversion for 125 μm sorbent particles with and without acoustics.

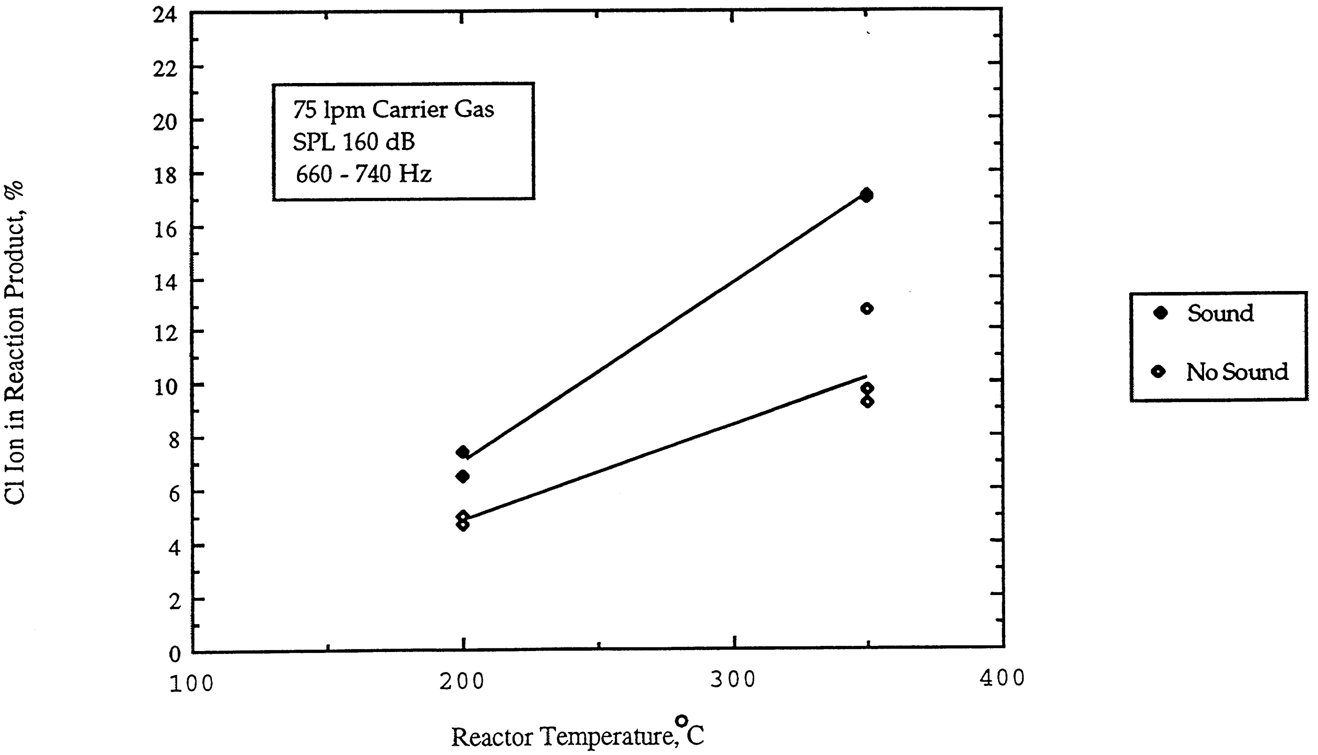

Figure 7 Reaction conversion for 75 μm sorbent particles with and without acoustics.

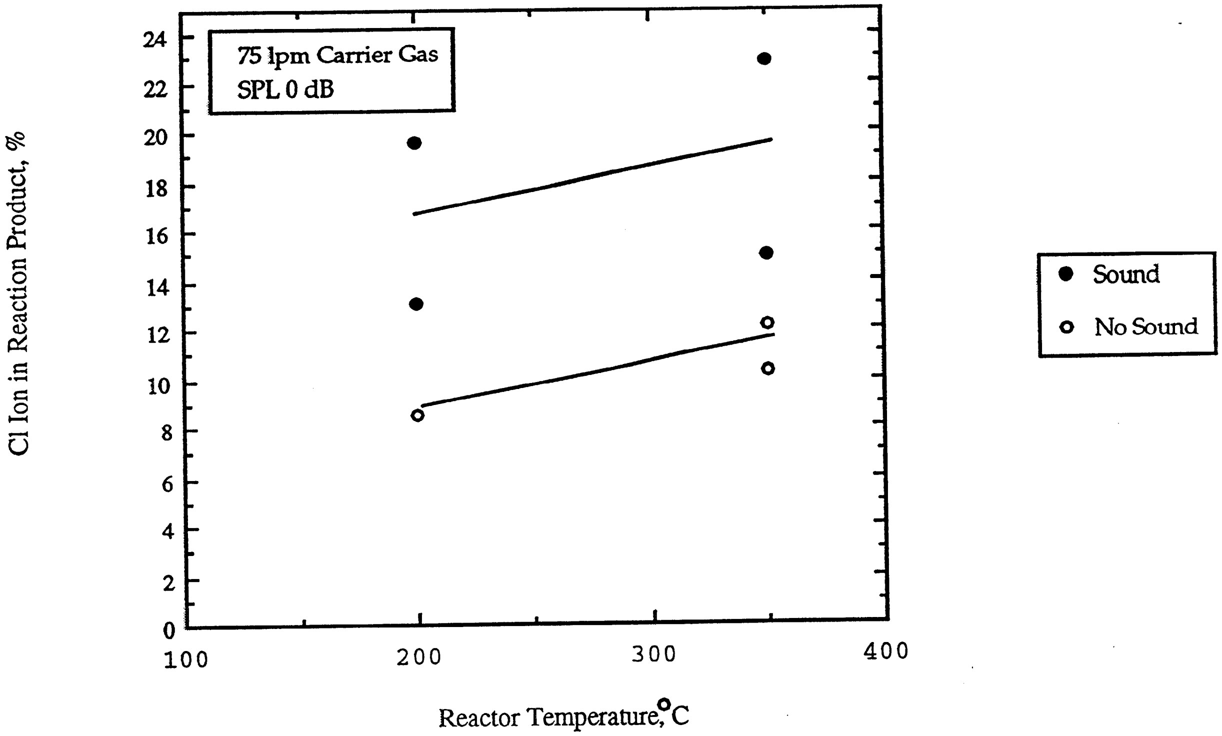

Figure 8 Reaction conversion for 20 μm sorbent particles with and without acoustics.

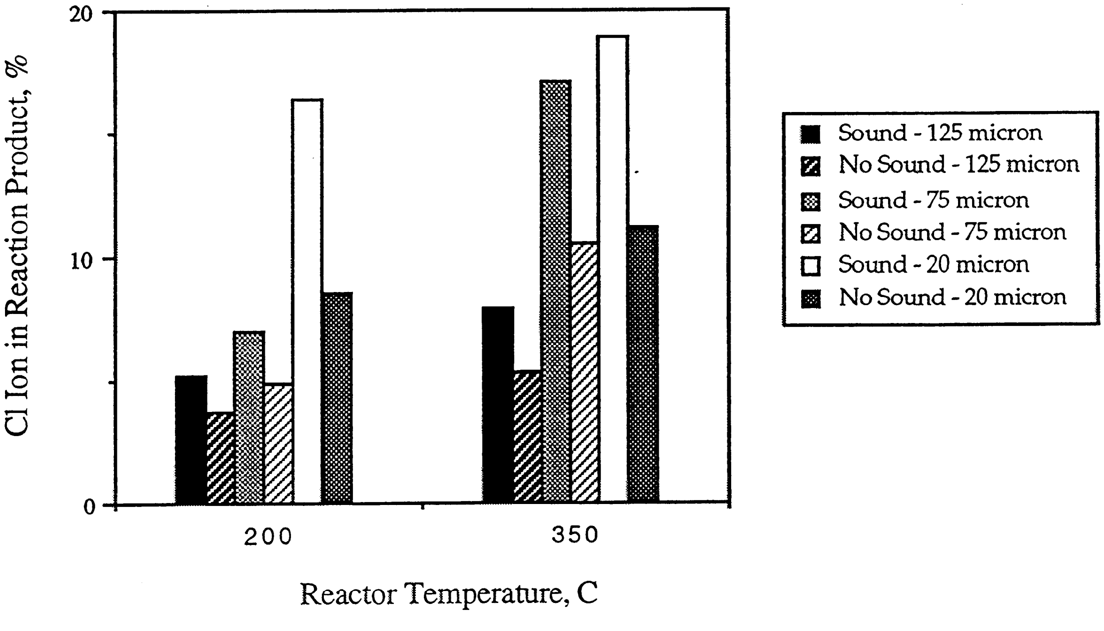

Figure 9 Reaction conversion by sorbent particle size with and without acoustics.