

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

SLIDE MATERIAL

To The
Engineering Project Advisory Committee

October 20-21, 1988
The Institute of Paper Chemistry
Continuing Education Center
Appleton, Wisconsin

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Project 3628
RECOVERY BOILER FIRESIDE CORROSION
David C. Crowe

October 20, 1988

Project 3628
RECOVERY BOILER FIRESIDE CORROSION
David C. Crowe

OBJECTIVE:

Understand the mechanism of high temperature corrosion in the recovery boiler so that corrosion control options may be identified.

Costs of Recovery Boiler Corrosion:

- Possible Explosion: Injuries, Fatalities, Loss of Production.
- Inspection, Repairs and Downtime.
- Increasing Insurance Premiums.

*Boiler used is Stone Container
a is operating at Name Plate Rate.
Suggested we look @ effect
in boilers running @ 120-130% of nameplate, i.e. Port Hudson type boiler
that has the mod made for higher production.*

Lower Furnace Corrosion Problems:

1. Composite Tube at Air Ports
2. Smelt Spouts, Liquid Level
3. Oxidation/ Sulfidation of Waterwall.

Results to Date:

- The technical literature has been surveyed.
- A tube furnace has been refurbished and a second furnace purchased.
- Preliminary tests of 1018 carbon steel and 304 steel have been completed.
- A corrosion probe for use in an air port has been proposed.

Results Since Last Report:

- Installation of a probe access port in a secondary windbox of a recovery boiler.
- Temperatures in deposits on the back sides of air port tubes have been measured.

Progress:

A probe access port was installed in a secondary wind box.

Progress:

Temperatures were measured in deposits on the backside of secondary air port tubes:

200 - 270 °C (390 - 520 °F)

Progress:

- Temperatures, air flow and deposit accumulation varied considerably throughout the day.

Preliminary Result:

- Frequent rodding, even air flow and stable operation may contribute to lower corrosion rates.

Plans:

1. Design & construction of the corrosion probe.
2. Measure temperatures at other places.
3. Obtain smelt and ash samples.
4. Begin laboratory studies.

Future Activities:

1. Sample smelt and flue gas near air ports and smelt spouts.
2. Document smelt spout problems and relevant corrosion mechanisms.
3. Develop an experimental plan for gas phase oxidation/ sulfidation tests.

Other Potential Activities:

1. Devise a test apparatus which will continuously replenish molten smelt at the corroding steel surface.
2. Develop methods for in-situ corrosion testing.

SIGNIFICANCE TO THE INDUSTRY:

An improved knowledge of corrosion mechanisms in recovery boilers will aid in the design of remedial measures which will extend the operating life and improve safety.

Project 3556

FUNDAMENTALS OF KRAFT LIQUOR CORROSIVITY

David C. Crowe

October 20, 1988

Project 3556

FUNDAMENTALS OF KRAFT LIQUOR CORROSIVITY

David C. Crowe

Objective:

Understand causes of corrosion of carbon steel in kraft liquor, as the basis for developing methods for reducing corrosion damage.

PREVIOUS RESULTS

- Qualification of monitoring methods
- Development of microprocessor-based data acquisition system.
- Liquor corrosivity is more important than grade of carbon steel.
- Fluctuation of corrosion rate could not be correlated with liquor composition changes
- Liquor level cycling increased corrosion rates.
- Effects of various white liquor constituents.

More Recent Results:

1. Further investigation of the effect of velocity using the rotating cylinder electrode and flow loop.
2. Bench testing of improvements to the corrosion monitoring system.
3. Completed study of stress corrosion susceptibility of steel in real mill liquor.

LIQUOR VELOCITY EFFECTS

Objective: To relate corrosion rates to hydrodynamic factors, e.g. shear, Reynolds number.

Technique: Measure corrosion rates under controlled conditions.

Current Objective:

Develop the RCE technique for the study of velocity effects in kraft liquor.

Rotating Cylinder Electrode**Experimental Approach:**

1. Measure kinematic viscosity (γ). Calculate Re , τ
2. Measure corrosion rates over a range of potentials.
3. Determine repeatability of tests.
4. Relate corrosion rates to velocity.
5. Compare results with the flow loop.

Fluid Mechanics of the Rotating Cylinder

Three regimes:

Laminar: Very little mass transfer.

Vortex: Intermediate.

Turbulent: $Sh = 0.079 Re^{0.7} Sc^{0.356}$

$$\tau = (f/2) \rho \omega^2 r^2$$

$Re = Vd/\gamma$ A ratio of velocity & viscous forces.

$Sc = \gamma/D$ Diffusion layer thickness.

$Sh = kd/D$ Dimensionless mass transfer.

**Correlation of Rotating Cylinder
and Pipe Loop.**

$$\log Re_{\text{tube}} = 0.67 + 0.833 \log Re_{\text{cyl}}$$

Equate the shear, τ

Equate the mass transfer.

Rotating Cylinder Electrode Advantages

- small quantities of liquor
- better control of conditions
- uniform surface velocity
- established fluid dynamics
- has been demonstrated in corrosion studies

Applications to Corrosion Studies

Problems:

- may not be diffusion controlled.
- erosion

Previous Applications:

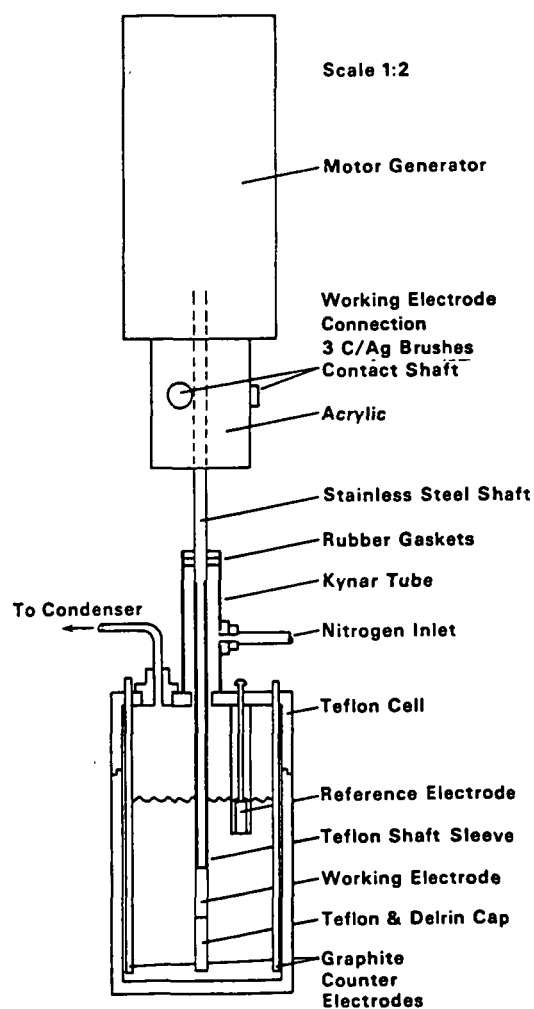
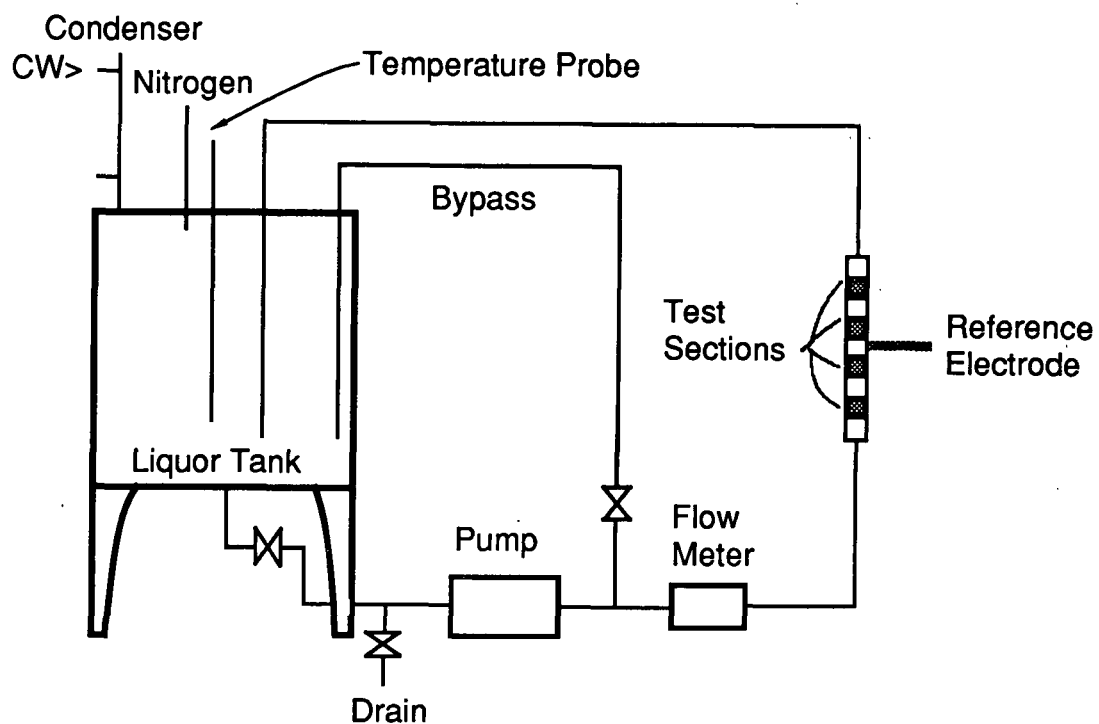
- inhibitors for pipelines
- steels in sulfuric acid
- Cu/Ni in seawater
- corrosion of ships' hulls

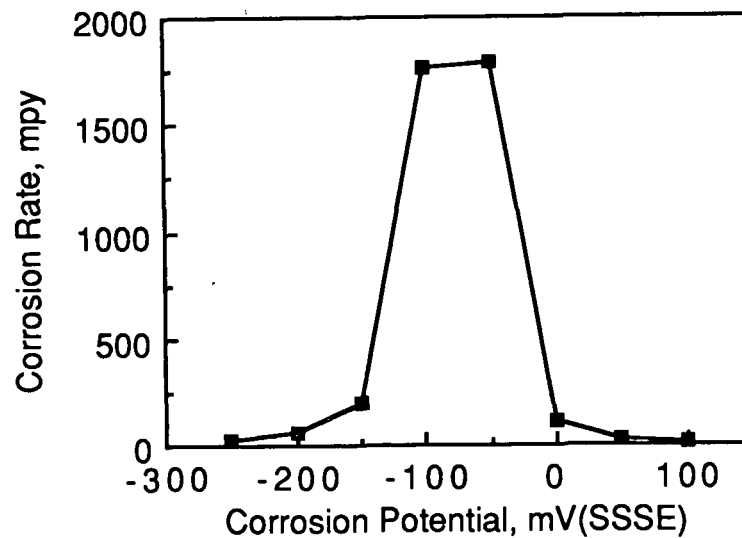
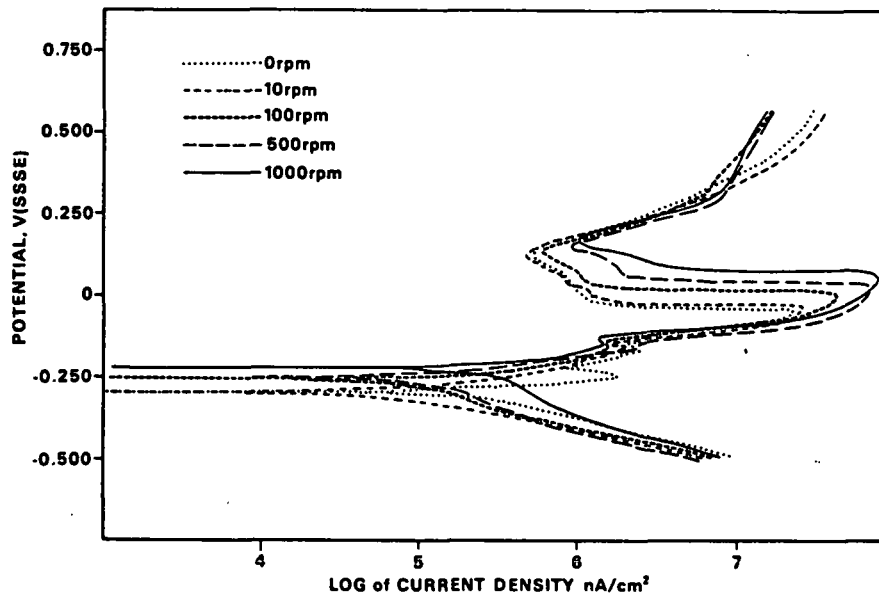
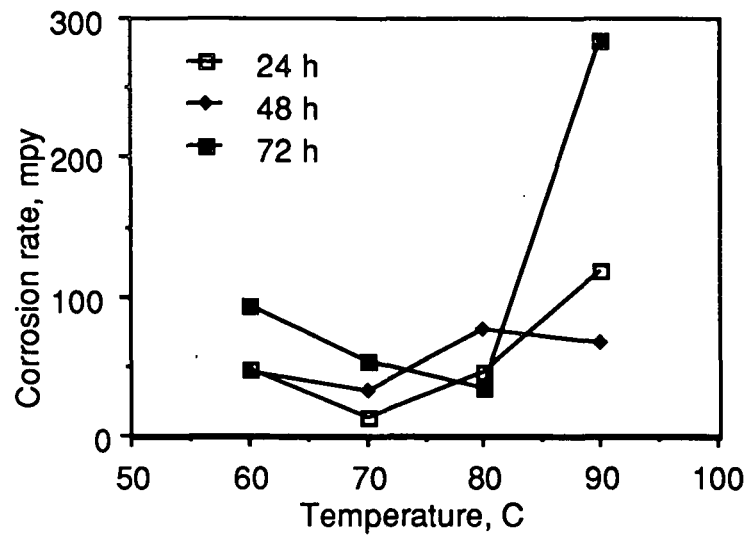
Pipe Flow Loop:

- duplicates flow in mill pipe systems.
- fluid dynamics established.
- must be carefully controlled, cumbersome.

Progress:

A bypass loop was added to the flow loop to attain lower flow rates.





Results Since Last Report:

Further testing with the rotating cylinder electrode and the flow loop showed considerable scatter in measured corrosion rates even when the corrosion potential was controlled.

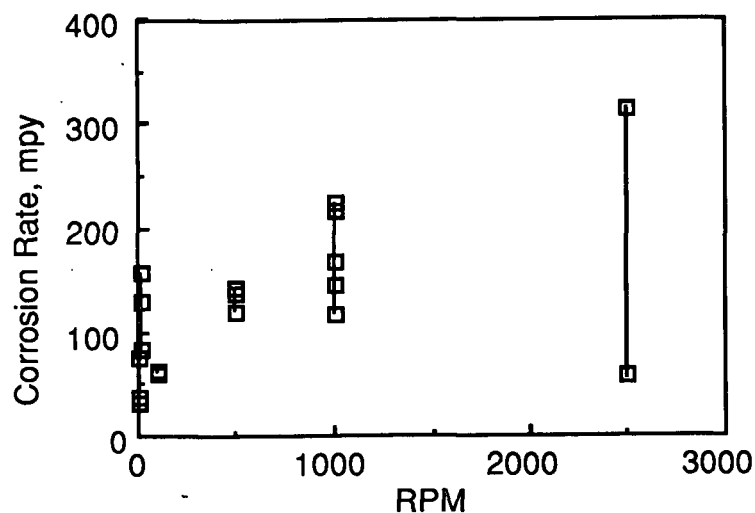
Progress:

RCE tests were performed at a range of rpm at a controlled potential.

There was considerable variation in measured corrosion rates, even when the potential was controlled.

Table 1
Dependence of Corrosion Rate on Rotation Rate

rpm	C.R., mpy	v, m/s	Re	τ , N/m ²
0	33, 76, 39	0	0	0
10	158, 129, 83	4.8×10^{-3}	83	5.3×10^{-4}
100	64, 63, 61	4.8×10^{-2}	832	2.7×10^{-2}
500	143, 121, 137	0.24	4160	0.41
1000	217, 169, 118, 223, 145	0.48	8322	1.34
2500	313, 59	1.20	20805	6.37
3000	-	1.44	24966	8.68



Progress:

Flow loop tests were performed at a controlled potential and at the free corrosion potential.

There was considerable variation in measured corrosion rates, even when the potential was controlled.

Table 2
Flow Loop Results

Electrode	Corrosion rate, mpy			
	5	6	7	8
Potential	-150 mV	-150 mV	E_{corr}	E_{corr}
Run 1	158	138	162	155
Run 2	95	94	271	214
Run 3	346	285	254	304
Run 4	83	79	95	82
			$E = -104/-125 \text{ mV}$	

Why so much scatter ?

- differences in surface roughness ?
- differences in original surface film ?

Tewari & Campbell:

Pyrite (FeS_2) - protective in flow.

Mackinawite ($\text{Fe}_{(1+x)}$) - non-protective.

Plans for Next Period:

1. Compare corrosion rates measured with the rotating cylinder electrode and pipe loop.
2. Begin tests of stainless steels (304, 316).

SIGNIFICANCE TO THE INDUSTRY

Corrosion monitoring methods may be applied reliably in white liquor systems.

Effects of major liquor constituents on corrosivity of white liquor have been determined.

Some operating parameters which increase corrosion rate have been identified.

Project 3309

FUNDAMENTALS OF CORROSION CONTROL IN PAPER MILLS

David C. Crowe

October 20, 1988

Project 3309

FUNDAMENTALS OF CORROSION CONTROL
IN PAPER MILLS

David C. Crowe

Objective:

To extend the life of paper machine suction rolls through corrosion and corrosion fatigue studies to establish mechanisms that limit lifetime.

Results Since Last Report:

Due to staff changes, no results have been obtained in the last period.

Future Plans:

1. Near threshold fatigue testing in a simulated pit environment.
2. Rotating bending fatigue testing and alternating bending testing in a simulated pit environment.
3. Investigate crack path through suction roll microstructures.

Future Plans (continued):

4. Study the microstructure of weld deposits on repaired suction rolls.
5. Test effects of superimposed mean stresses on crack initiation resistance.
6. Determine the effect of surface finish on crack initiation.

Significance to the Industry:

Near threshold crack growth behavior has been shown to agree with service performance provided that residual stress effects are considered.

Project 3607

EVALUATION OF STRUCTURAL COATINGS FOR
PULP AND PAPER MILLS

David C. Crowe

October 20, 1988

Project 3607

EVALUATION OF STRUCTURAL
COATINGS
FOR PULP AND PAPER MILL SERVICE

David C. Crowe

Objective:

To rank commercially available paint systems based on their ability to protect structural steel in the aggressive environments found in the pulp and paper mill, especially if applied under less than optimum conditions.

APPROACH

- Precorrode test coupons in mills.
- Clean and coat the coupons under less than optimum conditions.
- Reinstall in the mill and test to failure.

Progress to Date:

Test coupons were installed, uncoated, at mills to pre-rust. They were returned and have been coated after various surface preparations for reinstallation and exposure until failure in:

- Paper machine wet end
- Bleach plant
- Recovery boiler structure

The Coating Systems:

1. Epoxy Amide Primer/ Epoxy Phenolic Topcoat
2. Inorganic Zinc Epoxy Primer/ Chlorinated Rubber
3. Organic Zinc Primer/ High Build Epoxy/ Gloss Epoxy
4. Epoxy Mastic/ Epoxy Phenolic Topcoat
5. Alkyd Primer/ High Build Epoxy/ Gloss Epoxy

The Coating Systems:

6. Rust Conversion Coating
7. Inorganic Zinc Epoxy/ High Build Epoxy/ Vinyl
8. Vinyl Ester/ Vinyl Ester
9. Inorganic Zinc Epoxy Primer/ High Build Epoxy/
Gloss Epoxy
10. Gloss Epoxy

Surface Preparation:

1. Water Wash
2. Wash + Power Tool Cleaning SSPC-SP3
3. Commercial Blast SSPC-SP6
4. White Metal Blast SSPC-SP5
5. New

Results Since Last Report:

Painted panels were inspected
after six months mill exposure.

Table 1
Frequency of various performance ranks for each coating system in all mill locations.

Performance Rank	Coating System									
	1	2	3	4	5	6	7	8	9	10
Failure		6				15				7
Poor	1	8		2	1	3				5
Fair	9	7	1	7	4		1		12	5
Good	20		5	5	6	1		5	8	2
Excellent	53	3	9	21	19	12	13	9	62	11
No Observ.	4	5	5	1	1	2			5	1

Table 2
Frequency of various performance ranks for each coating system in bleach plants.

[illegible]

Table 3
Frequency of various performance ranks for each coating system in recovery areas.

[illegible]

Table 4
Frequency of various performance ranks for each coating system in paper machine areas.

Performance Rank	1	2	3	4	5	6	7	8	9	10
Failure		6				5				2
Poor		8								1
Fair	2	7	1	3					1	2
Good	7		5	4	4	1			5	1
Excellent	7	3	9	2	2				6	1
No Observ.	4	5	5	1		2			5	1

Results to Date:

The one step rust conversion coating (System 6), the chlorinated rubber (System 2) and a single coat of gloss epoxy (System 10) were inadequate, having failed in less than 6 months.

Plans

Inspect the panels in spring 1989.

SIGNIFICANCE TO THE INDUSTRY:

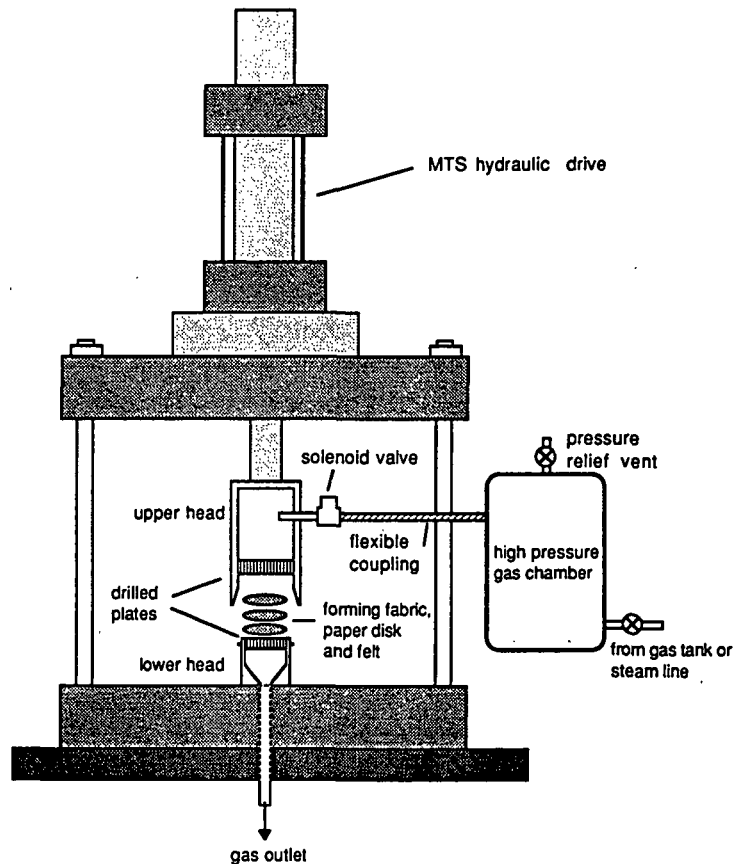
This project will provide mills with an independent assessment of the long-term reliability of structural coatings.

Project 3480

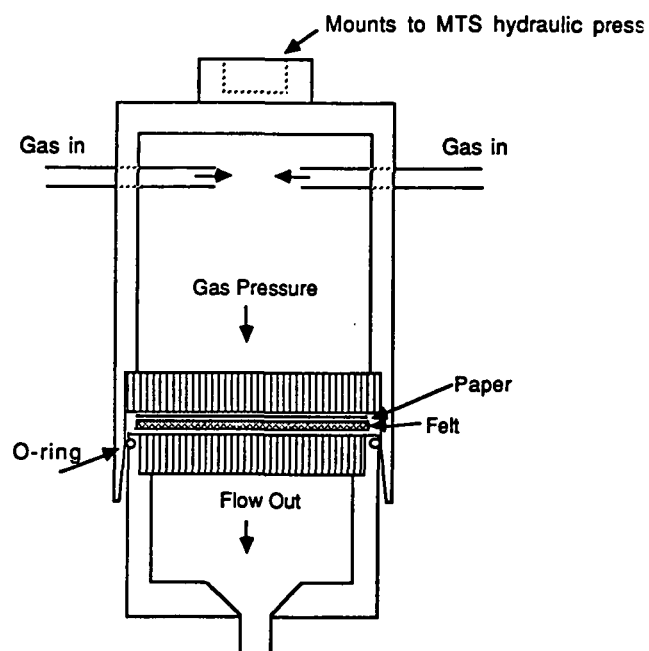
FUNDAMENTALS OF WET PRESSING

Jeff Lindsay
and
Cyrus Aidun

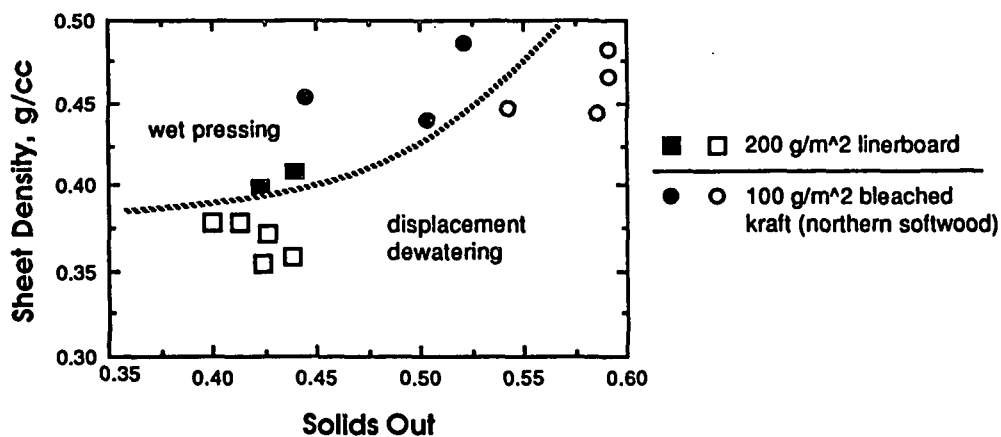
October 20, 1988



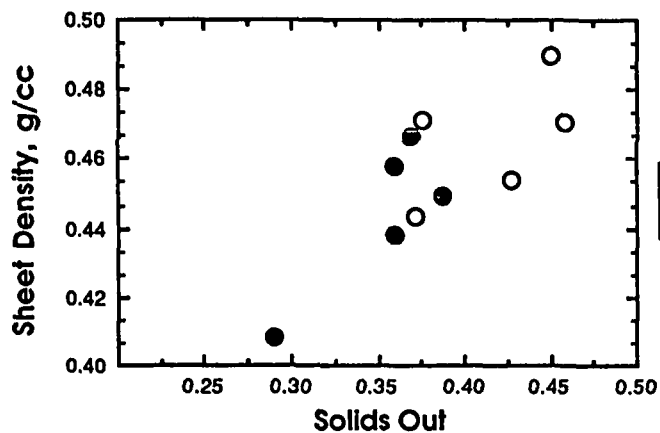
Experimental displacement dewatering device installed in the MTS hydraulic system.



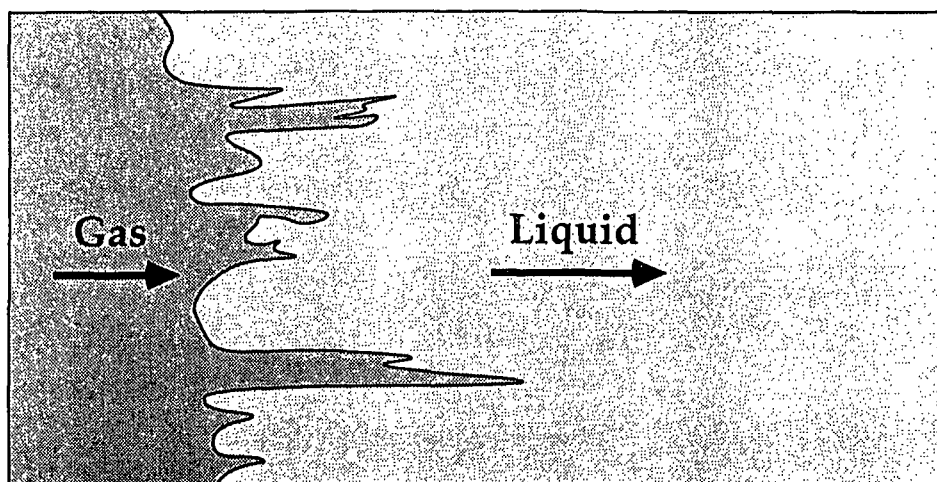
Displacement dewatering equipment (gas supply valves and pressure chamber not shown).



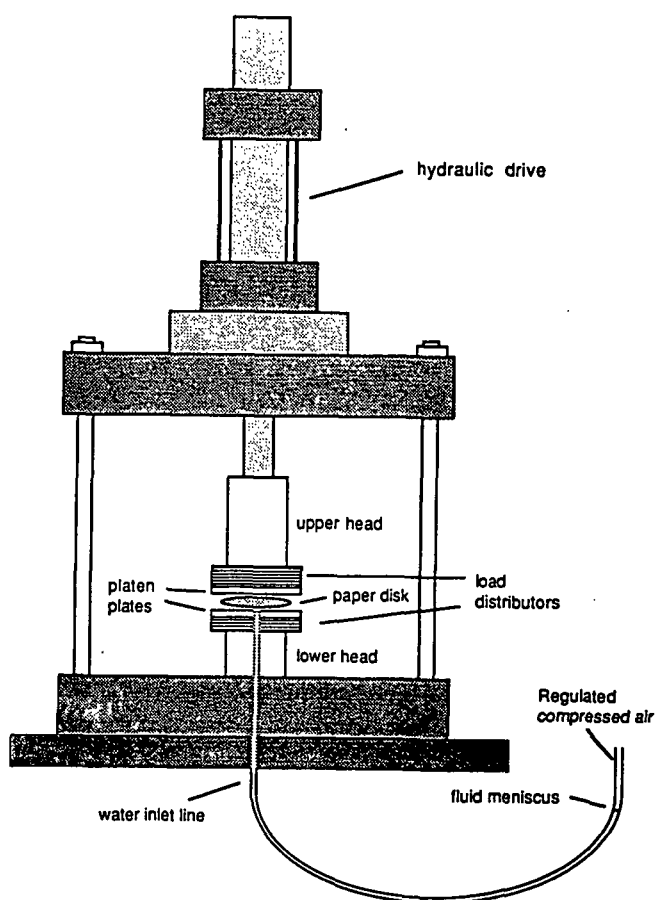
Density-dryness data from displacement dewatering and wet pressing for two furnishes. Nip residence times ranged from 60 to 120 ms, air pressures ranged from 60 to 100 psi, and peak mechanical loads ranged from 200 to 300 psi for the linerboard and from 500 to 650 psi for the bleached kraft handsheets.



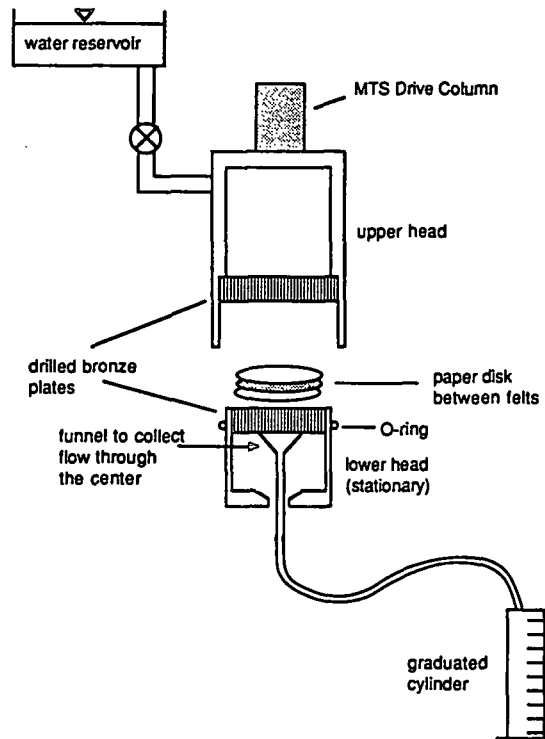
Density-dryness data from displacement dewatering and wet pressing for 125 g/m² linerboard.



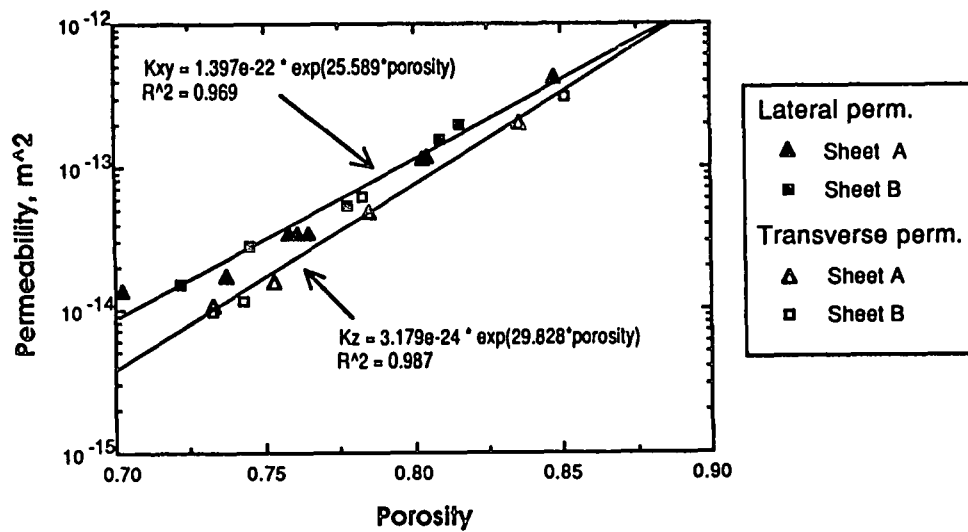
Viscous fingering in a porous medium



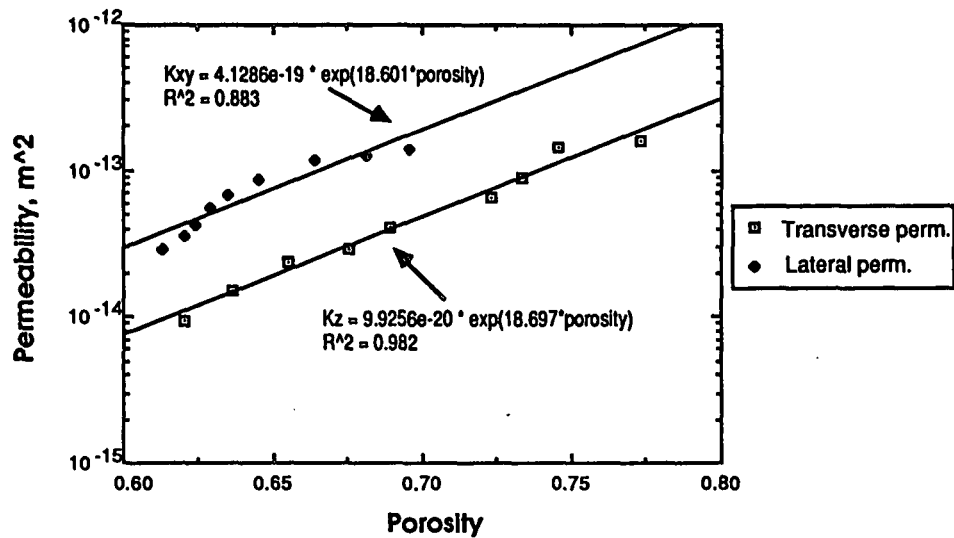
The MTS hydraulic press modified for lateral permeability measurements



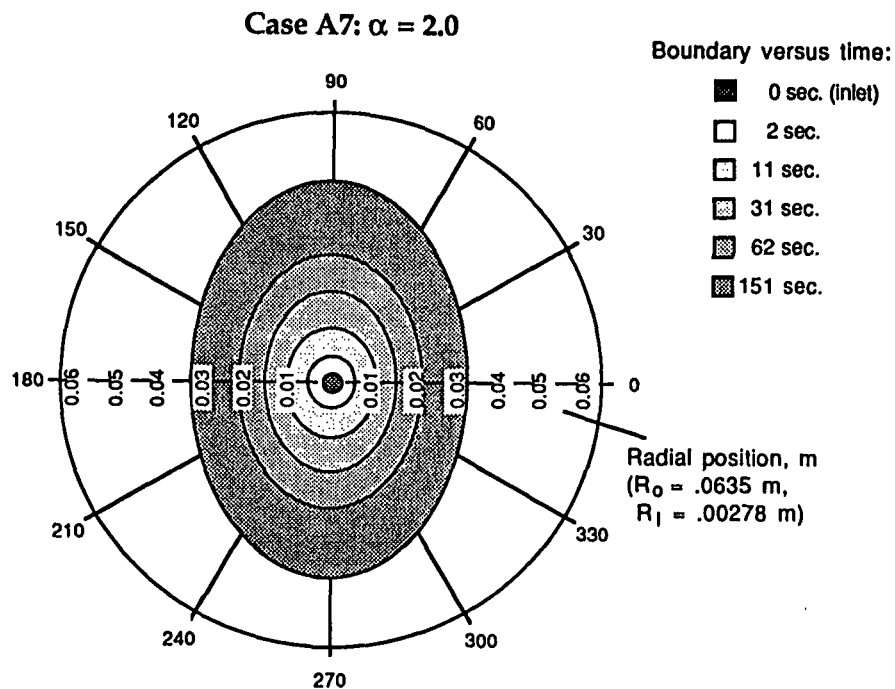
Detail of modifications to the MTS heads for transverse permeability measurements



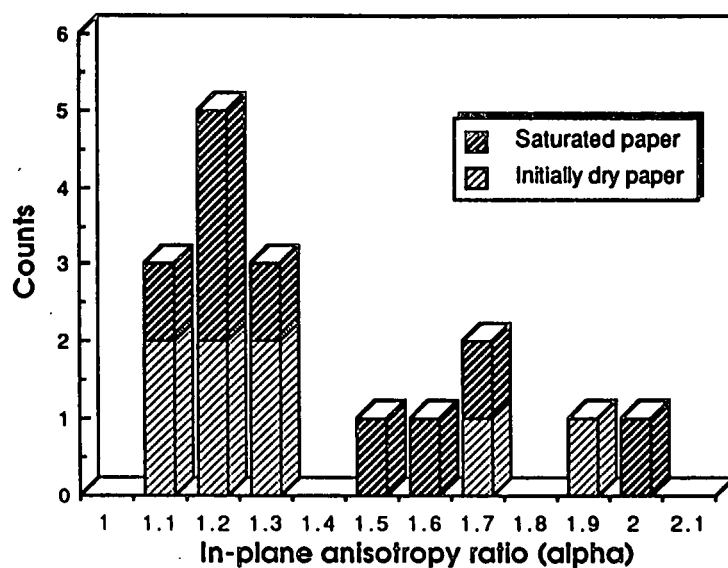
Comparison of lateral and transverse permeabilities in similar linerboard handsheets.



Comparison of lateral and transverse permeabilities in a single sheet of saturated blotter paper. (There is the possibility of a systematic error in measured porosity for the lateral permeability data.)



Predictions of dye boundary growth resulting from lateral injection into a saturated sheet with an in-plane anisotropy ratio of 2.0.
 $K_x = 1.0 \times 10^{-13} \text{ m}^2$, $K_y = 2.0 \times 10^{-13} \text{ m}^2$, viscosity = $1.0 \times 10^{-3} \text{ Pa-s}$, and $\Delta P = 1.0 \times 10^5 \text{ Pa}$.



Distribution of α values in multiple blotter paper samples. Results from initially dry and saturated sheets are shown.

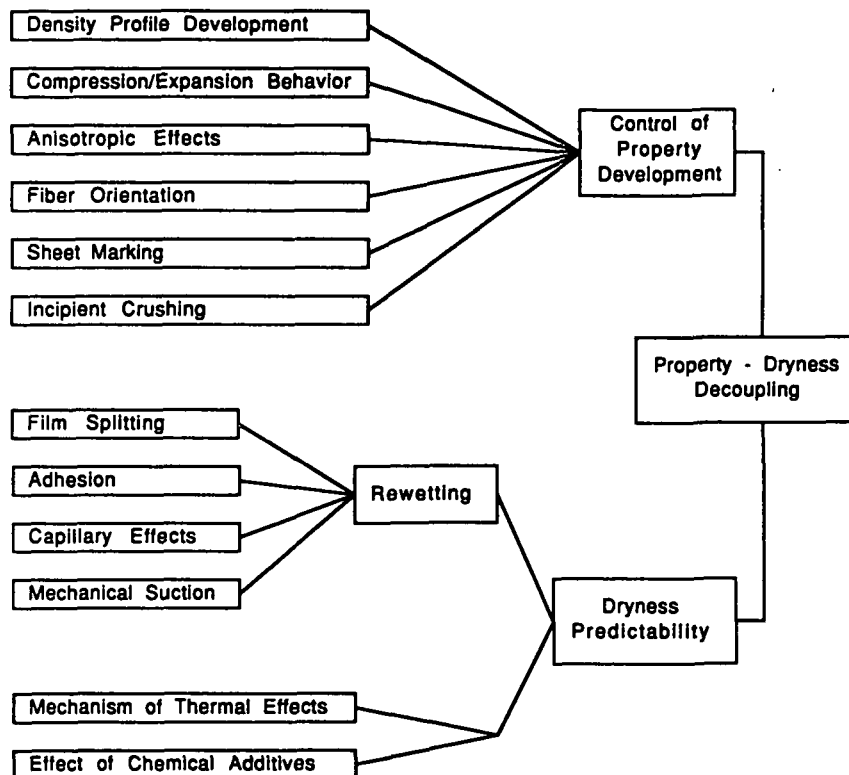
STATUS REPORT
ON
FUNDAMENTALS OF WET PRESSING
TO THE
ENGINEERING PROJECT ADVISORY COMMITTEE

Cyrus K. Aldun
October 20, 1988

OBJECTIVE

To Improve the Performance of Wet Pressing :

Water Removal
Property Development

FUNDAMENTAL ISSUES**APPROACH**

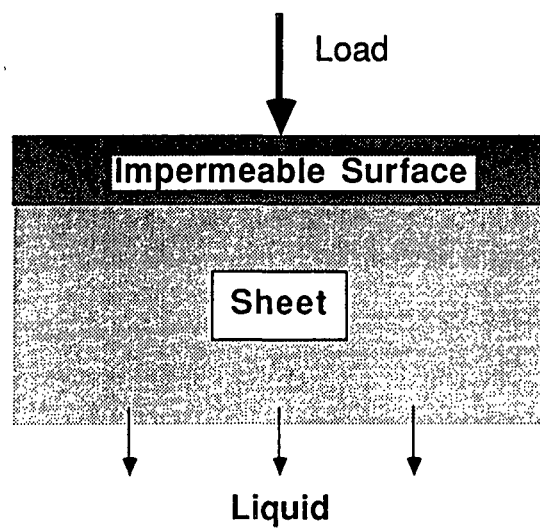
Fundamental understanding of web consolidation through direct measurement and observation.

Development of realistic models for detailed understanding and explanation of experimental observations.

Application of fundamentals to understand and improve the commercial wet pressing processes.

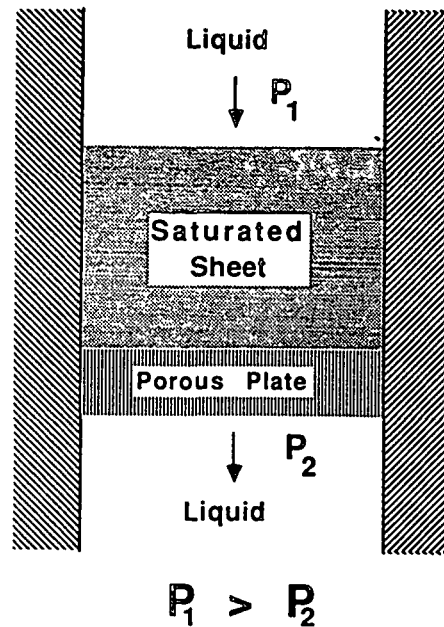
CRITICAL ASPECTS OF WET PRESSING:

**PROPERTY DEVELOPMENT
OR
DEWATERING ?**



Hypothesis :

**Larger density at the lower portion is attributed
to the larger fluid velocity in that region**

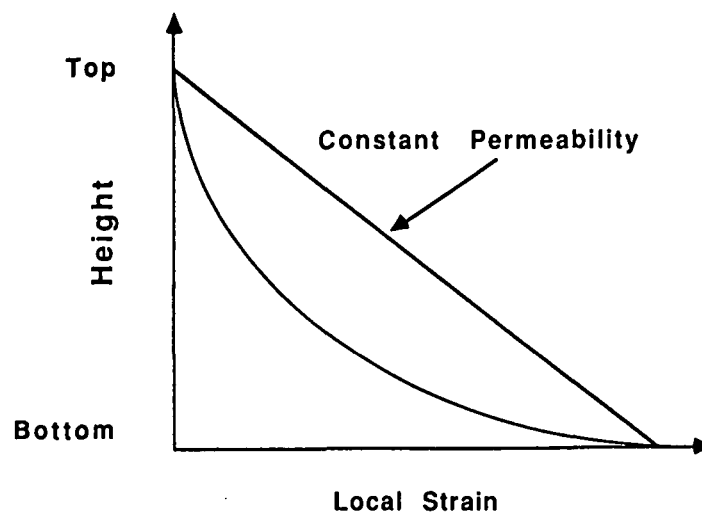


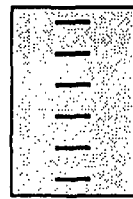
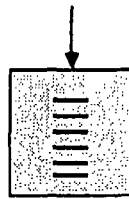
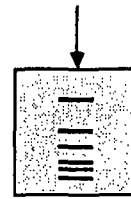
MODEL

Poroelastic constitutive relations (Biot, 1941).

Equilibrium relations for solid and fluid displacement :

- momentum and mass balance



DENSITY DISTRIBUTION IN A DEFORMABLE POROELASTIC MATRIX**No Load****Mechanical
Compression
(No Liquid)****Mechanical
Compression
(With Liquid)**

(After Caro et al., 1984)

CONCLUSIONS

The Velocity gradient is not responsible for the density profile development.

Fluid flow in a deformable porous matrix results in nonuniform (nonlinear) strain distribution, which in turn result in a nonuniform density profile.

Local strain increases in the flow direction.

PLANS FOR THE NEXT PERIOD :

1. Design and construction of an experimental roll press.
2. Study the compression/expansion behavior of a partially saturated fiber bed.
3. Measure the stress-strain response of a saturated fiber bed in presence of fluid flow.
4. Formulate a constitutive relation and a model for consolidation of an anisotropic saturated fiber bed layer.

Project 3576

FIBER AND PAPER PERFORMANCE ATTRIBUTES IN
PROCESS SIMULATION (MAPPS)

Gary Jones

October 20, 1988

Process Simulation

- Addresses some industry needs
- Traditional approach using material and energy balances
 - great for overall design
 - lacks detail on product performance
- MAPPS Performance Attribute System
 - Predicts development of fiber and sheet properties throughout process
 - Incorporates more fundamental process knowledge
 - Better representation of what process units do
 - Supplements mass and energy balances

Paper Industry Goals

- Improved Quality (End-Use Performance)
- Lower Costs (Capital and Production)

New Products and Technology

- Papermachine design, coaters, impulse drying
polymers, wet end chemistry, calendering techniques
- New pulping and bleaching technology

New Sensor Development

Industry Needs

- Better Understanding of Fundamentals
- Predictive tools - models and simulators
 - process design and improvement
 - new process development
- Better process control
 - utilize new sensors
 - provide logic linking sensors to process

Examples

Chemical Pulping and Bleaching

Conventional Simulation

*Process
Performance
#1 attribute*
PAT Simulation

dissolves lignin and

cellulose, consumes

chemicals

reduces kappa

consumes energy

reduces absorption coefficient

increases fiber flexibility

increases fiber bonding

affects fiber strength and density

affects fiber composition

sheet properties

Refiner**Conventional Simulation****PAT Simulation****converts components****also****consumes energy****changes fiber length and width distribution****increases surface area and flexibility****may reduce fiber tensile strength****handsheet properties changed****dissolved extractives reduces absorption****Paper Machine****Screening and Cleaning****Conventional****PAT's****mixing and splitting****detailed particle retention****fiber and water****fiber distributions changed****surface area and CSF changed****handsheet properties changed****Stock Tank****Conventional****PAT's****mixes components****mixes attributes****surface area, length, width****density, strength, modulus**

Drying**Conventional****PAT's****Removes water****Creates hydrogen bonds****Consumes steam****Increases sheet tensile and modulus****Collapse fibrils****Wet Pressing****Conventional****PAT's****Removes water****Increases potential****bonded area****(densifies sheet when dry)****Calendering****Conventional****PAT's**

Bulk densification**Surface densification****Break "bonds"****Reduce tensile and modulus****Affects scattering and brightness****Reduces density variations**

PAT System Process Flow

Wood	Pulping	Bleaching	Stock	Sheet	Pressing	Drying	Calender
Yard			Prep	Forming			

chlorine

kraft ---> ClO2 screen

species alkaline clean headbox wet can multi-

data --> generic--> generic ---> -> four --> press drier nip

base refine drinier or calender

 mechan- hydrogen mix or generic stack

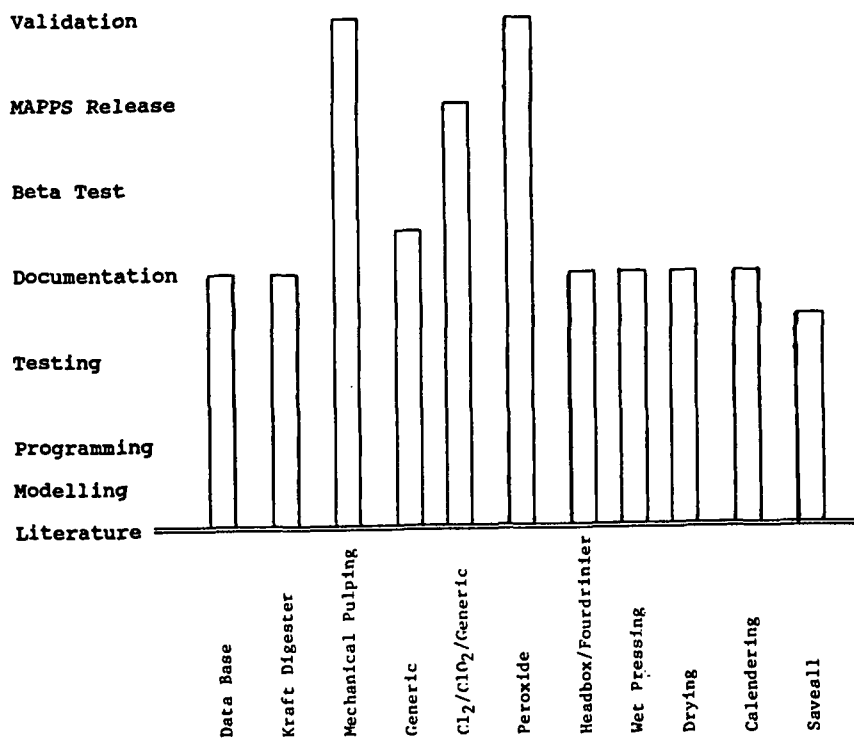
 ical --> peroxide broke generic

 recycle

 repulp

chips -----> fibers -----> network -----> paper

Status of PAT System Development



Performance Attributes

- . New Modules Developed**
- . Significant number of modules modified**
- . Attribute list expanded**
- . Flowsheets developed**
- . Limited testing**
- . Validation underway**

New Modules Using PAT's

- . Head Box and Fourdrinier Wire
Section (FOUR01)**
- . Single Wet Press Nip (WPRESS)**
- . Calendering Nip or Stack (CALEND)**
- . Stream Initialization Block (WOOD02)**
 - Pulping, Bleaching**
 - Paper Streams**

New Modules (cont'd)

- **Property Block (PROPS)**
- **PAT Initialization Block (PAPSIM)**
- **Separator Block (SEPAR3)**

New Property Models

- **Fiber Basic Data**
- **Computes fiber length and width distributions
from statistical parameters**
- **K-factor model**
- **Hydrodynamic Specific Surface Area**
- **Canadian Standard Freeness**
- **Potential Bonded Area before wet pressing**

New Property Models (cont'd)

- . Potential Bonded Area after wet pressing**
- . Actual bonded area**
- . Light Absorption Coefficient**
- . Change in absorption coefficient**
- . Brightness**
- . Anisotropy ratio**
- . Formation (bond density variation)**
- . Directional Properties**
 - Elastic moduli C_{11}, C_{22}, C_{33} (MD, CD, ZD)**
 - Directional tensiles ZX, ZY, ZZ**
 - Directional compressive strength**
 - Edgewise compressive strength**

Property Models (cont'd)

- Surface Properties (gloss and roughness)

Special Utility Routines

- Computes length and width statistics from paper stream composition
- Computes distribution statistics given correlation matrix and distribution type
- Added Weibull fiber length distribution option

Summary of New Module Features

Wet Press Module

- Single nip continuous wet pressing operation
- Calculates rate of water removal from web
- Uses dynamic compressibility model
- treats compressible mat as a Kelvin body responding to a compressive stress

$$M_{out} = M_{in} - M_{in} * (P/C) (1 - e^{-(t/\tau)})$$

P = maximum nip pressure

C = wet web compressive modulus

t = nip residence time

τ = dewatering time constant

τ = function of web flow resistance and initial moisture content

- web flow resistance is a function of CSF, basis weight and moisture content

C = exponential function of initial moisture content and independent of species and freeness

C also a function of basis weight for machine-made webs

PAT's:

Potential Bonded Area S_b increases through compressibility model

Thermodynamics:

Adiabatic, outlet pressures are atmospheric

Wet Press Model based on

- Caulfield, Wegner, Young (main dewatering model)
 - water removal is dominated by transfer from the cell wall
- Wahlström and Sweet (introduce basis weight dependence)

Calendering Module

- . Multiple-nip calender stack**
- . Determines the following:**
 - bulk reduction through nip intensity factor**
 - surface densification through heat penetration**
 - change in bond area and bulk properties depends on relative extent of heat penetration**
 - surface properties based on "surface" densification**

. Contributors

- Ron Crotogino - bulk reduction as a function of nip intensity factor, NIF**

NIF = function of calendering speed, nip load, roll radius and paper moisture and temperature

*** nip temperature depends on approach to equilibrium**

*** approach depends on roll temps, wrap arrangement, speed and sheet properties and basis weight**

. Contributors (cont'd)

- Charles and Waterhouse

Bulk properties such as modulus, tensile and burst

increase with increasing densification to a maximum

then decrease with increasing densification

- Gradient calendering involves short time, high temperature

treatment which has little effect on bulk properties

but influences surface properties significantly

Surface Properties

. Sheffield roughness increases from 10 to 350 as surface

bulk increases from 1 to 2.3

. Gloss decreases exponentially with surface bulk

. Brightness depends on absorption and scattering coefficients

- scattering increases with increasing surface bulk

Headbox and Fourdrinier Module

. Headbox

- Based on Kerekes equations in Tappi J.
- Potential flow theory

Given:

Calculates:

- | | |
|-----------------|---------------------------|
| . Pressure | |
| . Slice height | . Deflection Angle |
| . Pond height | . Contraction coefficient |
| . Machine speed | . Jet velocity |
| . Lip extent | . Drag ratio |
| . Slice angle | . Initial slurry head |

. Wire Section

Input data:

- Machine dimensions
- Forming section length
- Number of each drainage element
 - table rolls, foils, wet vacuum boxes, dry vacuum boxes
 - dandy roll not yet implemented
- Foil length and angle
- Table roll diameter
- Wet vacuum pressure
- Dry vacuum pressure

Input data:

- Wire diagonal length
- Trim fraction
- Orientation angle
- Stretch in open draws, %

Optional data:

- wire resistance
- first pass particle retention
- diameter of suspended material
- density of suspended material

Model Output:

- Basis Weight Profile
- Drainage rate profile
- White water consistency profile
 - after forming board
 - after foil section
 - after table roll section
 - vacuum foil or wet box section
 - high vacuum dry box section

Model Output:

- . Web
 - fiber and moisture content
 - surface area, CSF and PAT's
- . White water
 - fiber content and consistency
 - surface area, CSF and other PAT's
- . Sheet anisotropy ratio
- . Formation parameter

Model Basis:

- . Elaborate filtration and particle separation process
 - controlled by local pressure drop and flow resistance
- * entering slurry split internally into three substreams
 - slurry above (inlet consistency and fiber content)
 - mat (retained fibers and suspended particles)
 - * mat consistency remains constant
 - * gains fibers from slurry
 - * losses fibers to white water
- white water

Retention:

- based on extension of Estridge model
- depends on each particle (component) in slurry
- computed at each drainage element

Local drainage rate

- In forming section based on Victory model
- Remainder based on model of Pires and Springer
- Uses Darcy and Taylor filtration equation with maximum pressure constraint (iterative solution)
- Local filtration resistance is a function of
 - * pressure drop
 - * mixture consistency
 - * turbulence level

Model Verification and testing

- . Debugging, robustness
- . Paper machine model – literature data (Springer, Pires)
- . Calendering model – Crotogino data

Model Testing and Verification

- . Full mill system – newsprint mill data
 - * stone groundwood mill
 - * kraft mill
 - * two different papermachines
- . Flowsheet development
- . Beta test version