

ANNUAL PROGRAM REVIEW

CHEMICAL RECOVERY

Volume II

March 6-7, 2000

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DUES-FUNDED PROJECT SUMMARY

Project Title: Electrolytic Causticizing of Kraft Smelt

Project Code:

Project Number: F034

PAC: Recovery

Project Staff

Principal Investigator: P. Pfromm

Co-Investigators: J. Winnick (Chem. E. Faculty, GIT)

Research Support Staff: R. Wartena (PhD Student, GIT), D. Taylor (IPST, Senior Tech.)

PAC Subcommittee

FY 99-00 Budget: \$97,058

Allocated as Matching Funds: -

Time Allocation:

Principal Investigator: P. Pfromm 15%

Co-Investigators: J. Winnick 0%

Research Support Staff: R. Wartena 100%, D. Taylor 30%

Supporting Research:

Special Students: -

External (Where Matching Is Used): -

RESEARCH LINE/ROADMAP:

8. Develop technologies (compatible with present pulp-mill assets) to allow cost-effective expansion of kraft-pulp-equivalent fiber capacity (hardwood and softwood) by 30% without adding Tomlinson recovery boilers.: Process Improvements outside the Recovery Boiler, Alternate Combustion Technologies (primary)

10. Reduce net energy consumption per ton by 30 percent compared to '97 levels. (secondary)

PROJECT OBJECTIVE: Determine the thermodynamic fundamentals and address the fundamental material issues (electrodes) for a recausticizing process using electrolysis of molten kraft smelt. The smelt will be recausticized beyond the chemical equilibrium limitations of current recausticizing.

PROJECT BACKGROUND: *A joint IPST/GIT patent on the process has been applied for in 1998. This project was new with FY00 (start July 1999) as a follow up to a DOE Agenda 2020 project which closed in October 1998. The DOE project resulted in the construction of a kraft smelt electrolysis laboratory system at IPST. The system was*

successfully concluded the feasibility study that was the goal of the DOE project. The project was funded on recommendation by the recovery PAC for FY00, and an extension for one year (FY01) is pending before PAC.

MILESTONES: *No formal milestone plan was used. The list of deliverables shall serve to clarify the work undertaken here.*

DELIVERABLES:

- 1. Electrochemical studies (cyclic voltammetry, CV) to determine reaction mechanisms. Progress: CV is being used to investigate a number of electrodes, reference electrodes, and smelt compositions.*
- 2. Test electrode materials and materials of construction. Progress: Nickel/nickel oxide is a candidate*
- 3. Test and optimize process conditions and hardware. Progress: hold until thermodynamics are sufficiently clear.*

STATUS OF GOALS FOR FY 99-00: This was a new DFRC project for FY 00. The goals are to achieve the deliverables listed above.

SCHEDULE:

Task Descriptions	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
1. Cyclic Voltammetry	-----	-----	-----X	
2. Test electrode materials	-----X		-----	-----X
3. Test and optimize process conditions	---X		-----	-----X
4. Develop Model		-----	-----X	
5. Write yearly report				-----X

SUMMARY OF RESULTS:

The electroanalytical tool of cyclic voltammetry has allowed us to investigate the electrochemical mechanisms in high temperature molten salts. Various mechanisms leading to the decarbonization of kraft smelt and the production of sodium oxide (the precursor to sodium hydroxide) have been identified.

The electrochemical behavior of three molten salt systems will be presented here. These systems include pure sodium carbonate, and mixtures containing sodium carbonate: sodium sulfate (2:1), and sodium carbonate: sodium sulfide: sodium sulfate (3:2:1). The mechanisms were investigated at ~863°C under an argon atmosphere with a reference electrode with floating electrical potential.

Inert electrodes of platinum and gold were used to determine the electrochemical reactions occurring in the bulk of the kraft smelt. Commercially viable electrode materials have been investigated and the most promising anode material is nickel oxide, as is used in the Molten Carbonate Fuel Cell (MCFC) industry [1]. The oxide formed upon nickel hard and strips almost reversibly as is indicated by approximately equivalent areas of oxidation and reduction peaks in cyclic voltammetry experiments. Stainless

steels have shown corrosion problems in kraft smelts, even under cathodic conditions. Nickel has shown to be a promising cathode material.

SUMMARY OF KEY CONCLUSIONS:

The following electrochemical reactions were determined to occur in a synthetic kraft smelt by means of cyclic voltammetry with a floating reference electrode. Viable commercial electrode materials have also been identified.

- Sodium Carbonate
 - Oxidation: $\text{CO}_3^{=}\rightarrow\text{CO}_2+0.5\text{O}_2+2\text{e}^-$ Reaction 1
 - Reduction: $\text{CO}_3^{=} + 2\text{e}^- \rightarrow 2\text{O}^{=} + \text{CO}$ Reaction 2
 - $\text{Na}^+ + 1\text{e}^- \rightarrow \text{Na}$ Reaction 3

- Sodium Carbonate: Sodium Sulfate, (2:1)
 - Oxidation: $\text{CO}_3^{=}\rightarrow\text{CO}_2+0.5\text{O}_2+2\text{e}^-$ Reaction 1
 - Reduction: $\text{SO}_4^{=} + 8\text{e}^- \rightarrow \text{S}^{=} + 4\text{O}^{=}$ Reaction 4

- Sodium Carbonate: Sodium Sulfide: Sodium Sulfate, (3:2:1)
 - Oxidation: $\text{S}^{=} + 4\text{CO}_3^{=} \rightarrow \text{SO}_4^{=} + 4\text{CO}_2 + 8\text{e}^-$ Reaction 5
 - $\text{S}^{=} \rightarrow 0.5\text{S}_2 + 2\text{e}^-$ with $0.5\text{S}_2 + \text{S}^{=} \rightarrow \text{S}_2^{=}$ Reaction 6
 - Reduction: $\text{SO}_4^{=} + 8\text{e}^- \rightarrow \text{S}^{=} + 4\text{O}^{=}$ Reaction 4

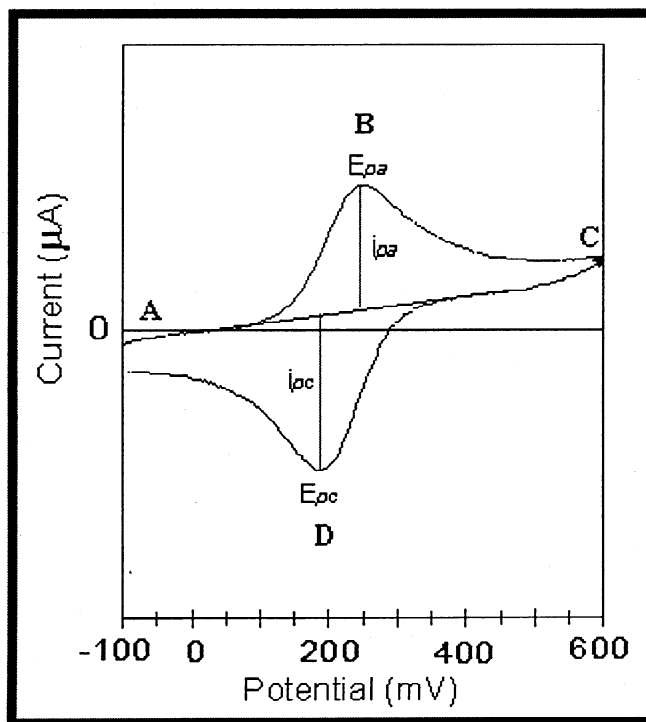
- Electrode Materials
 - Nickel Oxide Anode
 - Nickel Cathode

DISCUSSION: *Mechanism and Electrode Study with Cyclic Voltammetry***Significance**

It is necessary to determine the electrical operating potential of the desired electrochemical reaction mechanisms. The desired reaction mechanisms include any reductions that will form sodium oxide and any reductions or oxidations leading to decarbonization of the kraft melt. In addition to investigating the chemical reactions occurring in the bulk of the molten salts, cyclic voltammetry can also assist in determining the stability of oxide layers on an anode such as nickel oxide.

A Brief Introduction to Cyclic Voltammetry

Cyclic voltammetry (CV) is an electroanalytical polarographic method used to detect electrochemical and chemical reactions, as well as redox potentials and electron transfer kinetics. In voltammetry the potential of a working electrode is scanned within a set potential range as a continuous function of time. Cyclic voltammetry utilizes a linear sweep function that is reversed at the end of the set potential range. This gives the advantage of investigating the product(s) of the forward electrochemical reaction in the reverse scan since the experiments are performed on the order of seconds to minutes in a quiescent fluid. A measure of reversibility of a redox pair may be obtained by the separation of reduction and oxidation peaks. A sample cyclic voltammetry experiment is discussed below.



The figure above depicts a simple cyclic voltammogram where a species initially in its reduced form is oxidized and then quickly (or reversibly) re-reduced, ideally returning the system to equilibrium. The cyclic voltammetry experiment can be performed with either a two or three electrode configuration where the potential on the working electrode is scanned in a positive (anodic) and then negative (cathodic) direction (or vice versa) while the potential difference is monitored versus a known reference electrode.

The present voltammogram was scanned in a clockwise direction beginning at point "A" with a fixed scan rate measured in millivolts per second (mV/s). The scan is started at the open-circuit potential where no faradic current flows, that is no electrolysis occurs (point "A") and the voltage is increased in the positive direction. As the voltage scan proceeds, the reduced species in the melt begins to become oxidized resulting in a net increase of anodic current, observed by the increasing slope towards "B". The electrochemical reaction continues at an exponential rate towards anodic peak, point "B" since the bulk of the quiescent melt contains the reduced species until significant concentration gradients develop and diffusion of reactants to, and products away from, the electrode surface hinder the electron transfer of the electrochemical oxidation. This effect is observed in the downward slope after point "B" and towards point "C". At point "C" the linear sweep of the potential is reversed in a negative direction to investigate the products of the oxidation, which happen to be the reactants of the present reduction. Between point "C" and point "D" the current delivered by the working electrode changes sign from positive (oxidation current) to negative (reduction current). Since the melt is quiescent (diffusion by concentration gradients only) the oxidation products will be in the vicinity of the working electrode surface and are reduced resulting in a current peak of similar shape to the oxidation (point "D"). The separation of the peaks at points "B" and "D" is a measure of the redox potential. The area under the curves represents the amount of current delivered to each of the electrochemical reactions. If the oxidation peak ("B") has a greater area than the reduction peak ("D") then it may be inferred that irreversibilities occurred due to phase changes (solid/gas production), diffusion effects or other physical phenomena. Further scans of the potential range may assist in determination of additional electroactive species and coupled chemical (thermal) reactions.

Approach

The complex molten kraft smelt to be recycled has been simulated as a ternary mixture of sodium carbonate, sodium sulfate and sodium sulfide. Three different compositions starting with a sodium carbonate only melt, followed by adding the sulfur species of sulfate ($\text{Na}_2\text{CO}_3:\text{Na}_2\text{SO}_4$, 2:1 mass ratio) and finally the representative melt of all three components ($\text{Na}_2\text{CO}_3:\text{Na}_2\text{SO}_4:\text{Na}_2\text{S}$, 3:1:2) were experimented on by cyclic voltammetry. A three-electrode configuration was used consisting of working and counter housed in a double bored alumina tube and a reference in a separate alumina tube three centimeters away. The scan rate for all the experiments was 100 mV/s. All experiments were conducted with an argon purge through the reactor at a flowrate of 1 liter per second

A potentiostat was connected to the working, counter and reference electrodes. The cyclic voltammograms obtained were compensated for the IR drop across the melt and the distances between peaks in the voltammogram were compared to the thermodynamically predicted equilibrium potentials of the possible electrochemical reactions.

Results

Electrochemical reaction mechanisms for decarbonization and sodium oxide production have been identified in the three synthetic kraft smelts.

Sodium Carbonate

Two trials are reported for the sodium carbonate system on gold electrodes at 863°C in an argon atmosphere (Figure 2). The shorter of the potential scans shows the reduction of sodium ions to sodium metal (Reaction 3) and the carbonate oxidation (Reaction 1) with a potential span (2.08 V, IR compensated) that agrees well with thermodynamic calculations based on tabulated potentials of electrochemical reactions (2.16 V). The second scan was taken to an increased potential and evidence of bubbles is observed (bubble nucleation and release causes variable electrode area available for reaction, this effect is observed as significant fluctuations in delivered current). This indicates carbonate reduction (Reaction 2) in addition to reoxidation of reduction products of oxide to peroxide and oxygen. The potential span between peaks of the run with increased potential also agrees with thermodynamics.

Sodium Carbonate and Sodium Sulfate (1:2)

Interaction of sodium sulfate with the carbonate was investigated on both gold and nickel/nickel oxide electrodes at 866 and 865°C, respectively. Sodium sulfate is electrochemically reduced to sodium oxide and sodium sulfide at the cathode (Reaction 4) while the complementary reaction of the sodium carbonate oxidation occurs at the anode (Reaction 1) to produce gaseous products and effectively "cleans" the melt of carbonaceous material. The potential span between bulk reduction and oxidation agrees well with thermodynamics at 1.65 V. At further negative potentials, it is likely that both sodium production and carbonate oxidation also occur and this would explain the observed bubbling in Figure 3. The cyclic voltammograms on the nickel/nickel oxide electrodes were equivalent in the span of the bulk oxidation and reduction. Additional peaks of equivalent areas relating to the reduction and oxidation of the nickel/nickel oxide were found (Figure 4) indicating the formation of a stable oxide layer on the anode

Sodium Carbonate, Sodium Sulfate and Sodium Sulfide (3:1:2)

The representative kraft smelt was investigated on platinum electrodes at 864°C. In Figure 5 the 0.902 V span between the bulk reduction and first oxidation peak corresponds to the thermodynamic prediction of sulfate reduction to sulfide and oxide (Reaction 4) and oxidation of sulfide with carbonate to produce sulfate and carbon dioxide (Reaction 5) at 0.87 V. The bulk reduction is for sulfide going to elemental sulfur that quickly reacts chemically with additional sulfide to produce polysulfides (Reaction 6). This span of 1.028 V also agrees reasonably with the thermodynamic estimation of 0.98 V. The negative current peaks around zero in Figure 6 correspond to the re-reduction of the sodium polysulfides formed just prior in the scan. The experiment consisted of three cyclic scans of fixed potential range, the first scan was started towards reducing potentials and significant increase in reduction current did not start until -0.25 Volts. Reduction current on the order of -0.5A/cm^2 only appeared on the second and third scans meaning that polysulfides were produced by the oxidation reaction then re-reduced to sulfide in the scan reversal.

Conclusions

The electrochemical reaction mechanisms for a small set of compositions have been identified in the synthetic kraft smelts including sodium oxide production and decarbonization reactions. In melts not containing sodium sulfide, the bulk oxidation is carbonate to carbon dioxide and oxygen. In mixtures containing sodium sulfide, a peak oxidation involving carbonate occurs due to production of sulfate and carbon dioxide. The bulk oxidation under these circumstances is sulfide going to elemental sulfur that reacts with additional sulfide to form polysulfide, a desirable component of pulping liquors. In melts not containing sulfur species the reduction of sodium metal is favored over the production of oxide from carbonate. In mixtures containing sodium sulfate the reduction mechanism for sulfate reduction to sulfide and oxide is favored over the sodium metal production.

Nickel oxide appears to be a stable anode material but this requires further investigation. It is necessary to perform cyclic voltammetry with a known reference electrode reaction in order to determine the operating potentials of the desired reactions.

Economics, comparison to the conventional and the borate causticizing processes

The economics and energy demand of traditional causticizing has been compared to the electrochemical causticizing and to the sodium borate process that was described elsewhere [2,3]. There are several very important assumptions that have to be fully appreciated before drawing conclusions from the spreadsheet in Appendices 1 and 2.

1. The borate process will cause a significantly increased recirculating inorganic deadload and water load. The process is therefore possibly prone to capacity reductions in other parts of the process when causticizing capacity is increased. It is estimated that the smelt flow with sodium borate could increase 50 to 100% [2]. With the new developments [3] citing a decrease by half in $\text{NaBO}_2\cdot\text{Na}_2\text{CO}_3$ stoichiometry, the smelt flow would be expected to increase 25 to 50%.
2. The electrolytic causticizing process will likely reduce overall deadload, since no chemical equilibrium limit to causticizing exists in this process, and since more sulfate coming from the recovery boiler may be reduced to sulfide and polysulfides.
3. The energy consumption for the electrolytic causticizing process has been calculated on a two electrons per sodium oxide mechanism (Reaction 4). The electrical energy consumption will be reduced by half if the carbonate reduction is shown to be the dominant electrochemical reaction (Reaction 2) since the ratio of sodium oxide production to electron consumption is 1:1.
4. Increased inorganic deadload through sodium borate and increased water loads can be prohibitive for the borate process if, for example, recovery boiler capacity is not available, or if evaporator or concentrator capacity is not available. Liquors containing borated compounds have a higher viscosity than normal kraft liquors, which would reduce the evaporator capacity. Additionally, the digester throughput may be reduced with increased inorganic deadload and water load.
5. Due to the increased inorganic and water loads, the digester and the evaporator will require additional steam duties, reported as BTUs in the economics spreadsheet.
6. The higher chemical and water loads will have multiple effects on the operation of the recovery boiler and this is realized as a net loss of steam generation. The recovery boiler must provide thermal energy for the endothermic (heat sink) causticizing reaction and heat up the additional water and inorganics resulting in a "redirection" of steam producing energy. The increased loads will tend to lower the combustion temperature leading potentially to combustion instability. Citing from reference [2], "Unstable or marginal combustion could result in a continuing need for auxiliary fuel to sustain combustion and could negate any advantage of eliminating the lime kiln fossil fuel requirement".
7. Sodium borate make-up has been suggested to be added as borax pentahydrate ($\text{Na}_2\text{B}_4\text{O}_7\cdot 5\text{H}_2\text{O}$) at a cost of \$0.188 per pound [4]. The economics spreadsheet (Appendix 1) reflects make-up based on a 98% washing efficiency and a stoichiometry of one molecule sodium borate per molecule sodium hydroxide produced. Recent evidence suggests the sodium borate to sodium hydroxide stoichiometry may be 1:2, effectively decreasing the make-up by half.
8. The analysis for the sodium borate causticizing process was performed for an 80% causticizing efficiency [2] while the electrolytic causticizing process was evaluated at an 85% causticizing efficiency therefore favoring the economic and energy demands of the sodium borate causticizing process.

No attempt was made to take the significant payback due to incremental capacity in account that will result since both borate and electrolytic processing will likely be used at

first for incremental capacity when recausticizing is the bottleneck. Electrolytic causticizing could serve as a complete replacement to conventional causticizing while borate could not. The deadload reduction that can result from electrolytic causticizing was also not specifically highlighted in the operating cost comparison.

Under the assumptions listed above, electrochemical causticizing has an energy savings advantage of 40% and operating cost savings of 11% compared to the conventional process (Appendix 1). The sodium borate process has similar operating cost savings but requires far more energy since the borate causticization chemicals are carried through the entire pulping and chemical recovery cycle. Extra steam is required for the digesters and evaporators due to the increased inorganics content of the liquor. There is also loss of steam generation in the recovery boiler due to the heat sink of the borate decarbonizing reaction and the extra water and inorganic load.

Both non-conventional systems would be beneficial in respect to reducing the levels of Non-Process Elements (NPEs) that are introduced into the chemical loop from impure lime additions.

Deliverables

Progress is reported on two of the deliverables. Electrochemical mechanisms leading toward decarbonization and sodium oxide production have been identified in three melts (Deliverable 1). Various electrode materials have been investigated and the nickel oxide anode and nickel cathode are the most promising commercially viable electrode materials (Deliverable 2).

References

1. ORFIELD, M.L. and SHORES, D.A., "Solubility of NiO in Molten Li_2CO_3 , Na_2CO_3 , K_2CO_3 and Rb_2CO_3 at 910°C ", *J. Electrochem. Soc.*, 135(7): 1662 (1988).
2. GRACE, T.M., "An Evaluation of Non-Conventional Causticizing Technology for Kraft Chemical Recovery", *Report One, Project 3473-3, A Progress Report to Members of the Institute of Paper Chemistry*, January 30, 1981.
3. TRAN, H., et. al., "Autocausticizing of Smelt with Sodium Borates", *International Chemical Recovery Conference, Volume Two*, Tappi Press, June 1-4, 1998.
4. *The Chemical Market Reporter*, Schnell Pub. Co., New York, September 9, 1999.

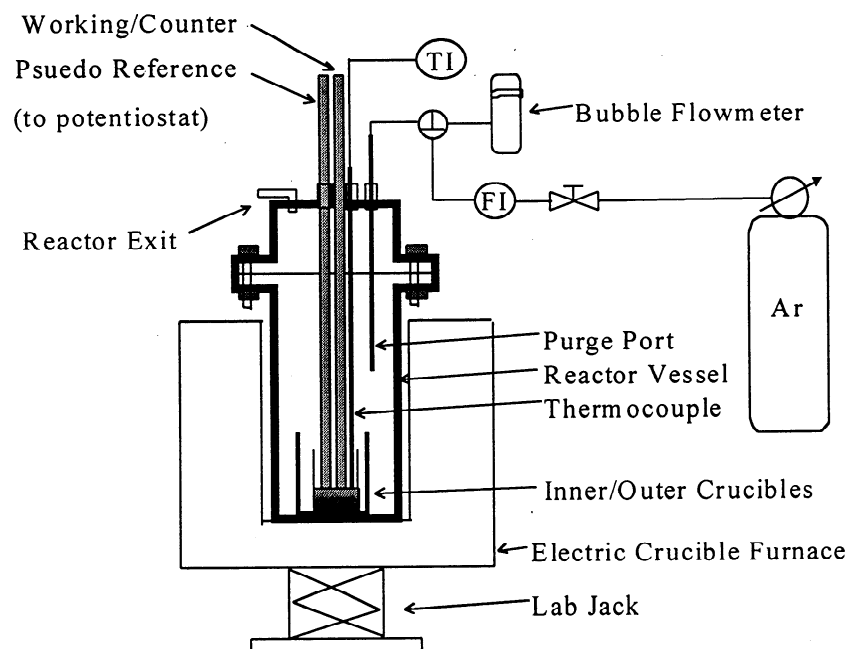


Figure 1: Electrochemical molten salt apparatus

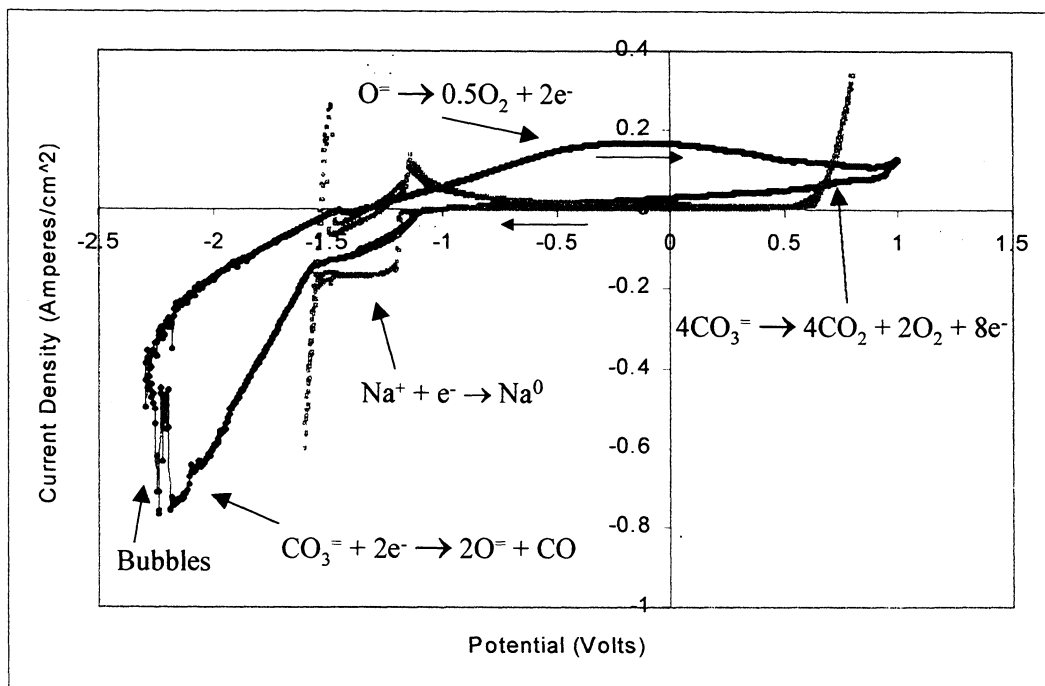


Figure 2: Sodium carbonate on gold at 863°C in an argon atmosphere.

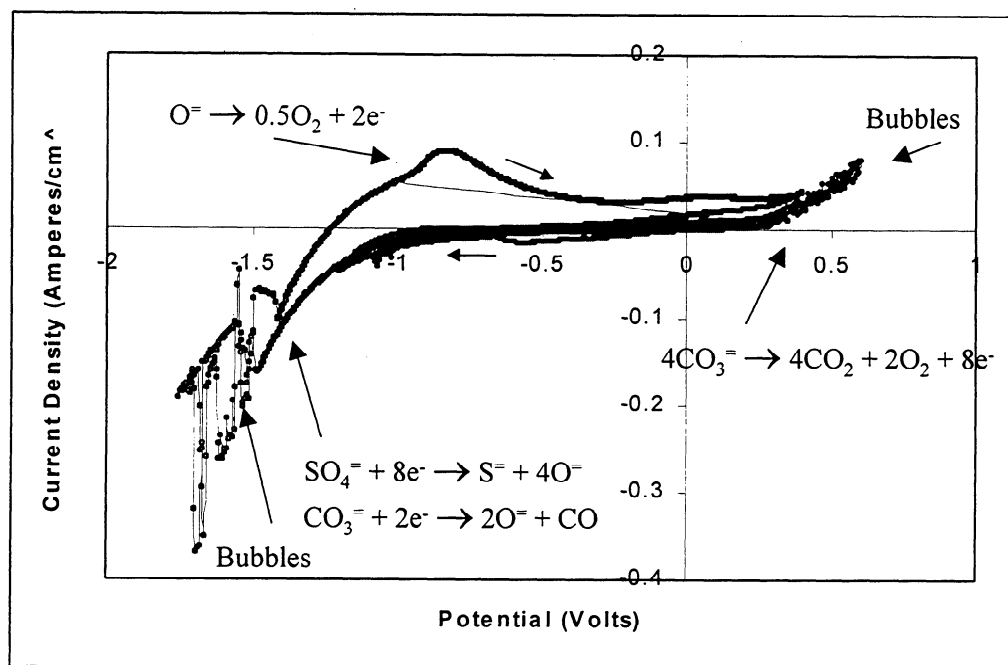


Figure 3: Sodium carbonate and sodium sulfate on gold at 866°C in an argon atmosphere.

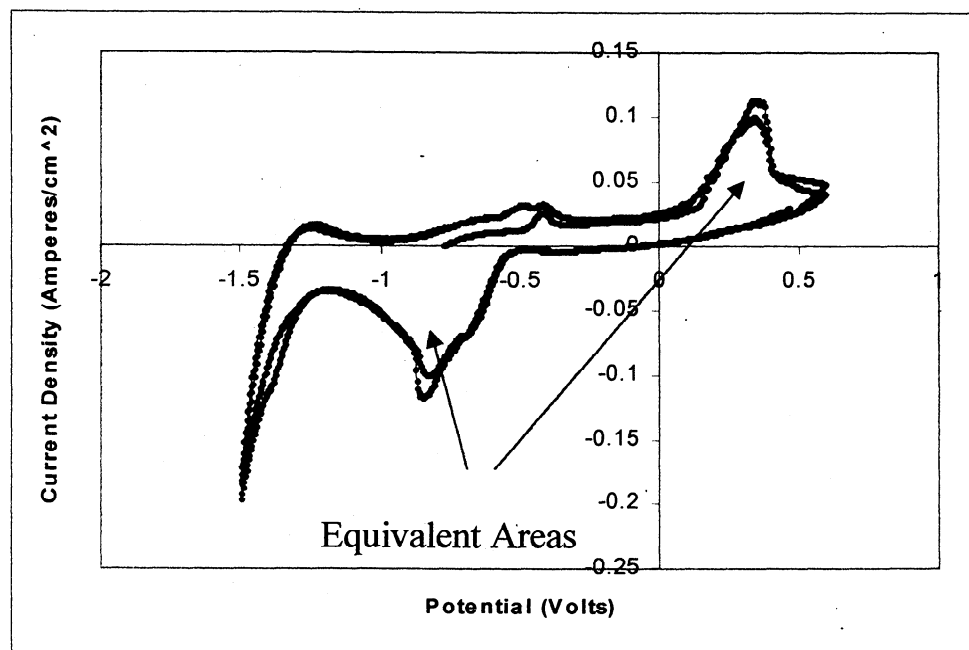


Figure 4: Sodium carbonate and sodium sulfate on nickel/nickel oxide at 865°C in an argon atmosphere.

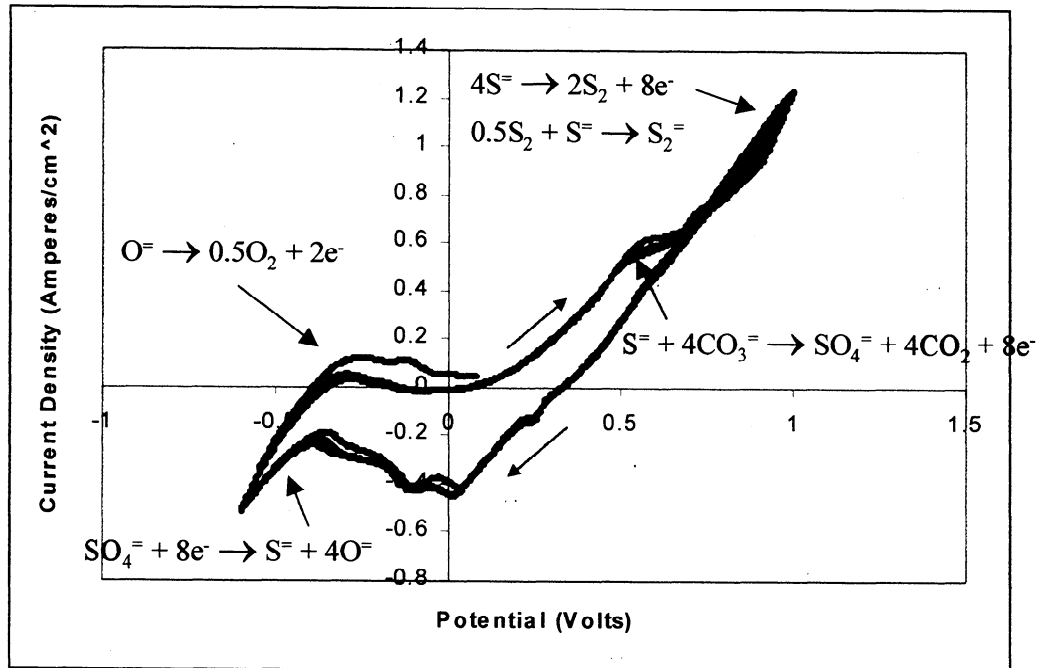


Figure 5: Sodium carbonate, sodium sulfide and sodium sulfate on platinum at 864°C in an argon atmosphere, oxidation first.

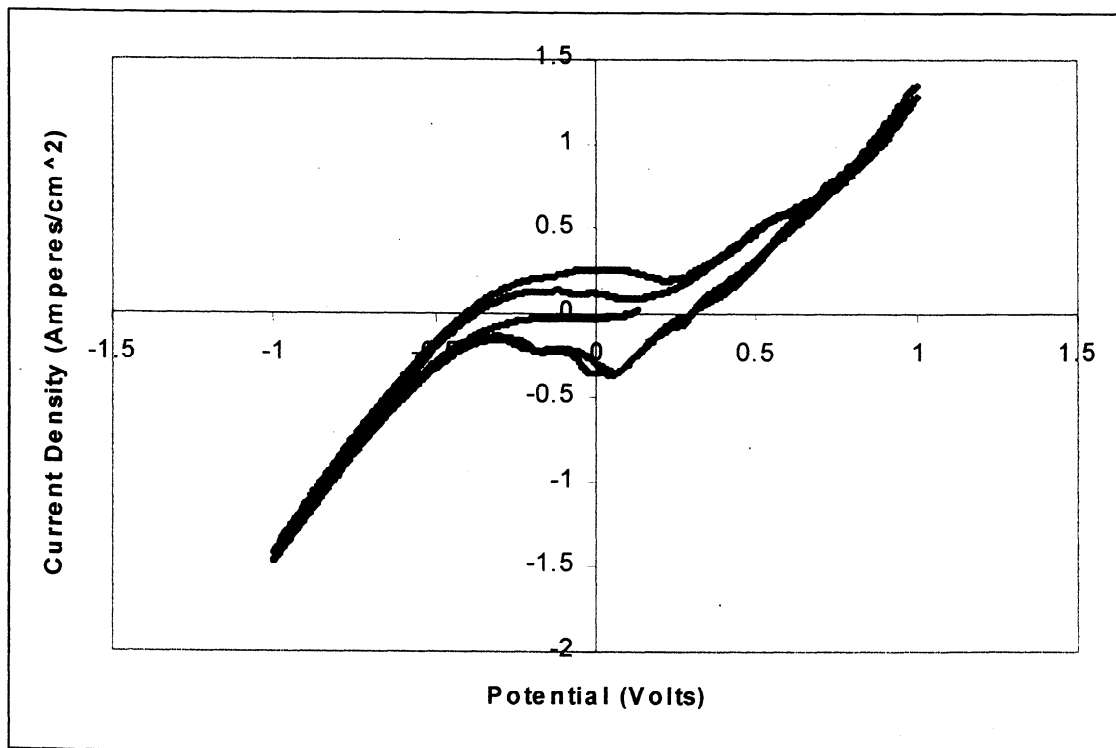


Figure 6: Sodium carbonate, sodium sulfide and sodium sulfate on platinum at 864°C in an argon atmosphere, reduction first.

APPENDIX 1

Operating Cost Comparison of Conventional, Electrolytical, and Borate-Based Causticizing

ESTIMATED OPERATING COSTS AND ENERGY DEMAND

Conventional vs. electrochemical and sodium borate causticizing

Operating Cost and Energy Demand Comparison to Existing Causticizing

short tons used, 1 ton = 2000 pounds

Based on: 1000 tons of pulp produced per day

General assumptions:

Electrical energy: 0.035 \$/kWh
 Fuel oil, kiln: 2.30 \$/million BTU

Sodium carbonate: 4609 mol of Na₂CO₃ per ton per day

	Operating Cost	Energy Demand	
Conventional causticizing (85% Conversion)			
Fuel oil, kiln:	7.00E+06 Btu/ton CaO	1.70 MM Btu/ton of pulp	496.89 kWh/ton of pulp
Fuel oil cost:	4.24 \$/ton of pulp		
Electrical power (pumping etc.)	1.50 megawatt	0.12 MM Btu/ton of pulp	36.00 kWh/ton of pulp
Electrical energy cost:	1.26 \$/ton of pulp		
Makeup lime:	13.00 tons/day		
Makeup lime cost:	1.95 \$/ton of pulp		
Steam:	0.50 \$/ton of pulp		
Maintenance	1.90 \$/ton of pulp		
Labor	1.50 \$/ton of pulp		
TOTAL, CONVENTIONAL:	11.35 \$/ton of pulp	1.82 MM Btu/ton of pulp	532.89 kWh/ton of pulp
Sodium Borate causticizing (80% Conversion)			
Additional Digester Steam		0.29 MM Btu/ton of pulp	84.97 kWh/ton of pulp
Additional Evaporator steam		0.44 MM Btu/ton of pulp	128.92 kWh/ton of pulp
Loss of steam generation at recovery boiler		1.86 MM Btu/ton of pulp	544.98 kWh/ton of pulp
Additional Energy due to Extra Inorganic		2.59 MM Btu/ton of pulp	758.87 kWh/ton of pulp
Additional Inorganic Energy Cost	6.48 \$/ton of pulp		
Electrical power (pumping etc.)	0.38 megawatts	0.03 MM Btu/ton of pulp	9.00 kWh/ton of pulp
Electrical energy cost:	0.32 \$/ton of pulp	assume 1/4 of conventional	
Make up sodium borate	23.25 lb/ton of pulp		
Make up sodium borate cost	6.95 \$/ton of pulp		
Maintenance	0.95 \$/ton of pulp	assume 1/2 of conventional	
Labor	0.75 \$/ton of pulp	assume 1/2 of conventional	
TOTAL, SODIUM BORATE:	15.44 \$/ton of pulp	2.62 MM Btu/ton of pulp	767.87 kWh/ton of pulp
Electrochemical causticizing:			
Electrical energy from amount of carbonate to causticize: 1 volt cell voltage,	8.75E+06 Amps needed per day		
Electrical power (80% current efficiency):	262.54 kWh/ton of pulp	0.90 MM Btu/ton of pulp	262.54 kWh/ton of pulp
Electrochemical Electrical energy cost:	9.19 \$/ton of pulp		
Electrical power (pumping etc.)	0.38 megawatts	0.03 MM Btu/ton of pulp	9.00 kWh/ton of pulp
Drive Electrical costs	0.32 \$/ton of pulp	assume 1/4 of conventional	
Maintenance	0.95 \$/ton of pulp	assume 1/2 of conventional	
Labor	0.75 \$/ton of pulp	assume 1/2 of conventional	
TOTAL, ELECTROLYTIC:	11.6 \$/ton of pulp	0.9 MM Btu/ton of pulp	271.5 kWh/ton of pulp
	operating cost	energy	
Electrolyt. Caust vs. Conventional:	2 %	-49 %	
Sodium Borate Caust. vs. Conventional (conventional =100%)	36 %	44 %	

DUES-FUNDED PROJECT SUMMARY

Project Title:	ATR Sensor for on-line Kraft Liquor Analysis
Project Code:	
Project Number:	F035
PAC:	Chemical Recovery PAC
Project Staff	
Principal Investigator:	J.Y. Zhu
Co-Investigators:	X.S. Chai, J.Li
Research Support Staff:	None
PAC Subcommittee	None
FY 99-00 Budget:	\$47,910
Allocated as Matching Funds:	0
Time Allocation:	
Principal Investigator:	5%
Co-Investigators:	33%
Research Support Staff:	
Supporting Research:	
Special Students:	
External (Where Matching Is Used):	

RESEARCH LINE/ROADMAP: Line – 12. Sensor and Process Control: Reduce Reduce pulp and paper product costs by 25% through increased productivity and improved pulp, paper, and product uniformity achieved with new developments in sensors and process controls.

- Develop on-line or off-line sensors to measure properties of interest (see Industry Needs Survey and Agenda 2020 pathways:)

PROJECT OBJECTIVE:

The objective of this project is to develop on-line/in-line sensors for simultaneously monitoring concentrations of NaOH, Na₂CO₃, and Na₂S in the white and green liquors, and the viscosity, solids content, and organic to inorganic ratio in black liquor in kraft chemical recovery process. The specific objectives include:

- 1) Design and fabricate the UV-ATR device suitable for kraft liquor analysis in very harsh environments.
- 2) Resolve the complex spectrum for simultaneous measurements of multi-component concentrations.
- 3) Finally, conduct field testing of these sensors at kraft mill sites.
- 4) Demonstrate feasibility for chloride, sulfate, and potassium analysis. (future work)
- 5) Demonstrate feasibility for pulping liquor analysis. (future work)

PROJECT BACKGROUND: A modern chemical recovery process can recover about 95% of sodium hydroxide for pulp production. Because kraft delignification rate and selectivity are strongly affected by the white liquor quality, *i.e.* NaOH and Na₂S concentrations, the goal of kraft recovery is to produce white liquor with high concentration of NaOH and Na₂S, and low concentration of Na₂CO₃ and Na₂SO₄. Reliable, rapid, and accurate on-line complete analysis of white and green liquor compositions, mainly, the concentrations of hydroxide (or alkali), carbonate, and sulfide, can provide in-situ data to allow operators to better control the recausticizing process to produce high quality white liquor to control pulp quality and reduce pulp mill upset. Unfortunately, most pulp mills all over the world rely on a classical offline titration method, *i.e.*, ABC titration [1], to determine the concentration of hydroxide (or alkali), carbonate, and sulfide in white and green liquors. Because the ABC titration method can only be performed offline and takes about 30 minutes to obtain results. Pulp mills only can monitor the green and white liquor composition every 2 to 4 hours and unable to control the recausticizing operation, resulting in the loss of productivity and operation upset. Attenuated total reflection UV spectroscopy has the potential for on-line kraft liquor analysis. This research is to demonstrate this potential.

MILESTONES:

- Calibration database development (established)
- Laboratory demonstration (achieved)
- Mill liquor demonstration (achieved)
- Mill site demonstration

DELIVERABLES:

- Sensor principle description (Report I issued, attached)
- An ATR sensor for on-line monitoring
- Sensor principle for pulping liquor analysis (future work)
- Sensor principle for chloride, sulfate, and potassium analysis (future work)

STATUS OF GOALS FOR FY 99-00:

Ready for mill site demonstration. Need to select mill site with PAC

SCHEDULE:

Task Descriptions (example)	1999 Apr - Jun	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
System development					
Lab demonstration					
Kraft liquor analysis					
Mill site selection					
Mill site demonstration					

SUMMARY OF RESULTS:

See Member Company Reports I attached:

Laboratory system developed.

Principle demonstrated using pure hydroxide, carbonate, and sulfide.

System demonstrated using kraft mill white and green liquors

SUMMARY OF KEY CONCLUSIONS:

See Member Company Reports I Issued

Proved feasibility of ATR on-line liquor analysis sensor

DISCUSSION:

See Member Company Reports I Issued

1. Topic 1

A. Significance

B. Approach

C. Results

D. Conclusions

- *Scientific Conclusions*
- *Economics*
- *Deliverables*

E. References

F. Tables

G. Figures

2. Topic 2

A. Significance

B. Approach

C. Results

D. Conclusions

- *Scientific Conclusions*
- *Economics*
- *Deliverables*

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F. Tables

G. Figures

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
Atlanta, Georgia

ATR-UV Sensor for Kraft Liquor Monitoring -

**Part I: Simultaneous and Rapid Analysis of
Hydroxide, Sulfide, and Carbonate in Kraft Liquors
by Attenuated Total Reflection UV Spectroscopy**

Project F035

**Report 1
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to the**

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By

J.Y. Zhu, X.S. Chai, and J. Li

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1. Zhu, J.Y., Chai, X.S., Li, J. (2000), "ATR-UV Sensor for Kraft Liquor Monitoring: **Part I: Simultaneous and Rapid Analysis of Hydroxide, Sulfide, and Carbonate in Kraft Liquors by Attenuated Total Reflection UV Spectroscopy**" (This Report)

Upcoming Reports of This Project (In Preparation)

Zhu, J.Y., Chai, X.S., Li, J. (2000), "ATR-UV Sensor for Kraft Liquor Monitoring: **Part II: Mill Site Demonstration of ATR-UV Sensor for Simultaneous and Rapid Analysis of Hydroxide, Sulfide, and Carbonate in Kraft Liquors**"

ATR-UV Sensor for Kraft Liquor Monitoring –

Part I: Simultaneous and Rapid Analysis of Hydroxide, Sulfide, and Carbonate in Kraft Liquors by Attenuated Total Reflection UV Spectroscopy

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EXECUTIVE SUMMARY

Kraft delignification rate and selectivity are strongly affected by the white liquor quality, *i.e.*, NaOH and Na₂S concentrations. The goal of kraft recovery is to produce white liquor with high concentrations of NaOH and Na₂S, and low concentrations of Na₂CO₃ and Na₂SO₄. Reliable, rapid, and accurate on-line analysis of white and green liquor compositions, mainly, the concentrations of hydroxide (or alkali), carbonate, and sulfide, can provide in-situ data to allow operators to better control the recausticizing process to produce high quality white liquor to control pulp quality and reduce pulp mill upset. Unfortunately, most pulp mills all over the world rely on a classical offline titration method, *i.e.*, ABC titration, to determine the concentration of hydroxide (or alkali), carbonate, and sulfide in white and green liquors. Because the ABC titration method can only be performed offline and takes about 30 minutes to obtain results, pulp mills only can monitor the green and white liquor composition every 2 to 4 hours and are unable to control the recausticizing operation, resulting in loss of productivity and operation upset.

The overall objective of this research is to develop a reliable and rugged on-line sensor for kraft liquor monitoring in mill recausticizing operations for process control. The capability can significantly improve mill operation, and pulp property uniformity, and reduce the possibility of evaporator fouling through better process control.

This study experimentally demonstrated Attenuated Total Reflection (ATR) UV Spectroscopy for rapid and simultaneous determination of hydroxide, sulfide, and carbonate in kraft liquors. On-line measurements were achieved using an ATR flow cell integrated with a commercial UV spectrophotometer. A multi-variant partial least-square fitting procedure was employed to develop a species concentration predictive model. The model is calibrated using a set of eighteen modified kraft liquor samples made from a mixture of a kraft mill green and white liquor (base liquor) through dilutions and additions of sodium hydroxide, sulfide, and carbonate. The concentrations of hydroxide, sulfide, and carbonate in these liquors were obtained by standard ABC titration. The ATR-UV measurements were then directly applied to one green and three white liquor samples collected from the same kraft mill. Very good agreements between ATR-UV measured and titrated concentrations of hydroxide, sulfide, and carbonate were obtained. The ATR-UV measurement is rapid and accurate and does not require sample pretreatment or dilution; therefore, it can be implemented on-line for process control in mill environments. Because of the low cost and ease in maintenance, the ATR-UV technique may provide a better alternative to ATR-NIR or -FTIR methods.

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INTRODUCTION

Kraft pulping employs an aqueous solution, often called white liquor, of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to remove lignin from wood. Wood chips are subjected to digestion in the white liquor at an elevated pressure and temperature (about 170°C) in a pressure vessel (digester) to release cellulosic fibers. The spent pulping liquor containing dissolved wood lignin, often called black liquor due to its color, is concentrated and then burned in a furnace where sulfur compounds are reduced to sodium sulfide. The smelt of inorganic ash from the combustion processes is dissolved in water to form a green liquor, named from its color, containing mostly sodium sulfide and sodium carbonate (Na_2CO_3), and sodium sulfate (Na_2SO_4). The sodium carbonate reacts with calcium hydroxide (calcium dioxide in water), called recausticizing, to regenerate sodium hydroxide to remake the white liquor for pulping. The lime mud (mainly calcium carbonate) yielded from the recausticizing reaction is burned in a lime kiln to produce the calcium dioxide. A chemical recovery cycle consists of all the processes from the concentration of the pulping spent liquor to the regeneration of sodium hydroxide.

A modern chemical recovery process can recover about 95% of sodium hydroxide for pulp production. Because kraft delignification rate and selectivity are strongly affected by the white liquor quality, i.e., NaOH and Na_2S concentrations, the goal of kraft recovery is to produce white liquor with high concentrations of NaOH and Na_2S , and low concentrations of Na_2CO_3 and Na_2SO_4 . Reliable, rapid, and accurate on-line complete analysis of white and green liquor compositions, mainly, the concentrations of hydroxide (or alkali), carbonate, and sulfide, can provide in-situ data to allow operators to better control the recausticizing process to produce high quality white liquor to control pulp quality and reduce pulp mill upset. Unfortunately, most pulp mills all over the world rely on a classical offline titration method, i.e., ABC titration [1], to determine the concentration of hydroxide (or alkali), carbonate, and sulfide in white and green liquors. Because the ABC titration method can only be performed offline and takes about 30 minutes to obtain results, pulp mills can only monitor the green and white liquor composition every 2 to 4 hours and are unable to control the recausticizing operation, resulting in the loss of productivity and operation upset.

Although a few on-line sensors based on conductivity [2], Fourier transform infrared spectroscopy (FTIR) [3], near infrared spectroscopy (NIR) [4], and conventional ultra-violet (UV) spectroscopy [5], have been developed for kraft white and green liquor monitoring in kraft operations, most of these sensors can only provide single component measurements. For example, the conductivity sensor [2] and the FTIR sensor are only capable of monitoring hydroxide concentration, and conventional UV [5] can give sulfide concentration. Furthermore, sample dilution by a factor of 1000 is required when using conventional UV technique to measure sulfide in green and white liquors due to the saturation in absorption. A high dilution ratio not only compromises the measurement accuracy but also requires a high degree of dissolved oxygen removal. Otherwise, the sulfide in diluted solution can be easily oxidized by the dissolved oxygen (the equilibrium concentration of the dissolved oxygen at room temperature in water is at the same order of magnitude as the sulfide concentration). Recently, NIR spectroscopy [4, 6] has demonstrated the potential for simultaneous analysis of hydroxide (or alkali), sulfide, and carbonate in white and green liquors. However, the accuracy of any NIR spectroscopy is always compromised by the spectral interference from the absorption of water in the entire NIR range. Moreover, any IR instruments (including NIR and FTIR) are always more expensive to build and difficult to maintain, when compared to UV spectroscopy based instruments.

Attenuated total reflection (ATR) or internal reflection spectroscopy was developed in the 60s by Fahrenfort [7] and Harrick [8] based on Newton's discovery that an evanescent wave extends in the rarer medium beyond the interface between two media of different refractive indices. The interaction of the evanescent wave with the external medium provides the finger print of the properties of the external medium. Therefore, the absorption spectra of the external medium of the evanescent wave has many applications in nonintrusive diagnostics. Because the absorption pass length of the evanescent wave is greatly reduced to the order of micron meters, ATR is particularly applicable to analysis of very concentrated samples without dilution. ATR-UV technique [9] not only has the advantages of low cost and easy maintenance of the UV spectroscopy, but also eliminates the sample dilution requirements in analysis of kraft white and green liquors when conventional UV spectroscopy is employed. The present author Chai [10] demonstrated the feasibility of analyzing NaOH and Na₂S concentrations simultaneously in a synthetic white

liquor by ATR at the UV-Vis range in 1994. Later, Chai et al. [11] successfully performed in-line simultaneous monitoring of sulfide and polysulfide in a lab-scale electrochemical production of polysulfide from a synthetic kraft white liquor. It should be noted that the synthetic white liquors that Chai [10, 11] used did not contain carbonate. The objective of the present work is to demonstrate the feasibility of using the ATR-UV technique for simultaneous determination of hydroxide, sulfide, and carbonate in kraft white and green liquors.

PRINCIPLE AND METHODOLOGY

ATR Principle

Figure 1 shows the schematic of the measuring principle of an ATR-probe. A detailed description of the ATR principle can be found in the book by Harrick [8]. A transparent probe of high refractive index (n_p) is brought into contact with a sample that must have a lower refractive index (n_s). Light is introduced to the probe at an incident angle, θ , toward the interface between the probe boundary and the sample. If the angle of incidence, θ , is greater than the critical angle θ_c (given by Snell's law: $\sin\theta_c = n_s / n_p$), total reflection will occur when the light hits the probe boundary. At each reflection point, the light will extend into the medium (sample) in the form of an evanescent wave [7,8] and is absorbed by the sample. Therefore, the light reflected back to the probe carries the spectral information about the physical properties of the sample and can be recorded by a spectrometer.

The ATR absorption follows Beer's law

$$a = \varepsilon \cdot C \cdot b_{\text{eff}} \quad (1)$$

where ε is the absorption coefficient, C is the molar concentration of the substance to be analyzed, and b_{eff} is the effective absorption path length. Unlike the conventional absorption spectroscopy, the effective path length in ATR spectroscopy is a function of many parameters, such as wavelength, refractive indices of probe material and the sample medium, the angle of incidence, and the state of polarization of the incident light, according to Schlemmer and Katzer [9]. The refractive index of the sample medium is the dominant factor that contributes to the effective path. Because the refractive index of the sample

medium not only depends on the sample temperature and the concentration of the absorbing substances, but also on the concentration of the nonabsorbing substances, the ATR signal also contains information about the nonabsorbing substances that can be used to determine the concentration of nonabsorbing species, a unique characteristic of ATR spectroscopy.

The total transmittance for a probe with z reflections is:

$$T = (1-a)^Z \quad (2)$$

where a is the absorption parameter the light experiences in one reflection [8, 9]. The optical path length per reflection is about 1-2 μm . One can change the number of reflections and thus the sensitivity of an ATR system by varying the length of the ATR probe.

Calibration

If the total chemical strength of the liquors do not vary significantly, for example, in batch and many closed industrial processes, the effective path length of the ATR probe does not vary significantly because of small variations in the refractive index of the sample medium. Then, the linear calibration technique used in conventional absorption spectroscopy can be applied. However, when the variation of the refractive index of the sample medium is significant, and, when there is strong spectra interference in the region of a species of interest, a partial-least-squares (PLS) fitting method can be used to quantify multiple species concentrations in the sample medium from the ATR spectra. In this case, a calibration database needs to be built using a set of solutions from the same source of the sample solution, but varying in species concentrations. The database can then be used to obtain the parameters for the predictive model.

EXPERIMENTAL

Apparatus

All measurements were conducted in a laboratory ATR-UV system. The system consists of an ATR-UV flow cell with one path (reflection) (Axion, model TNL-120H23-3, CA, USA) for on-line analysis, a peristaltic pump (RP-1, Rainin, Emeryville, CA, USA), a 25-mL beaker, tubing and connectors, and a UV/Vis spectrophotometer (UV-8452, Hewlett-Packard, CA, USA.). The ATR cell consists of an ATR probe made of a quartz rod and a

housing unit. Figure 2 shows a schematic diagram of the ATR-UV system. Kraft white or green liquor is circulated through the ATR cell by the peristaltic pump. The ATR cell is placed at the flow cell position of the spectrophotometer for continuous absorption measurements over the entire UV/Vis range by the spectrophotometer equipped with an HP ChemStation for real-time spectral data collection.

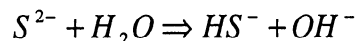
Chemicals and Materials

Analytical grade sodium hydroxide, sodium sulfide, and sodium carbonate from commercial sources were used to make aqueous solutions of NaOH, Na₂S, and Na₂CO₃. Actual kraft white and green liquors obtained from a kraft pulp mill were also used.

RESULTS AND DISCUSSIONS

ATR-UV Measurements in Aqueous Solutions of Hydroxide, Sulfide, and Carbonate

To demonstrate the ATR spectral response of hydroxide, sulfide, and carbonate in the UV range, we obtained absorption spectra of aqueous solutions of hydroxide, sulfide, and carbonate with concentrations of 2, 1, and 1 mole/L, respectively, using the present ATR flow cell. As shown in Fig. 3, the ATR spectra of these three species indicate that hydroxide and carbonate absorb in the range of 190 to 210 nm, while sulfide absorption showed a broad peak at 230 nm and high absorbance below 210 nm as well. This is because when sodium sulfide is dissolved in water, it forms both hydrogen sulfide and hydroxide ions [12], that is,



Therefore, the two species, hydrogen sulfide (HS⁻) and hydroxide (OH⁻) ions, contribute to the spectrum of sodium sulfide solution. The absorption at wavelength around 195 nm is from OH⁻ ions, and the absorption peak exhibited at 230 nm is due to HS⁻ ions. Figure 3 also shows that the absorption of hydroxide is much higher than that of carbonate.

Chai et al. [10, 11] were not able to obtain an ATR spectral response at a low UV wavelength range (below 210 nm) due to the technical limitation of their instrument. Therefore, very important spectra information about the absorption of hydroxide and carbonate was not obtained. Hydroxide was categorized as a nonabsorbing substance in

their studies. Therefore, hydroxide prediction must rely on sulfide absorption in the range of 210 to 260 nm, with spectral contribution from the changing of the solution refractive index, due to the presence of the nonabsorbing substances in the solution, i.e., hydroxide. As mentioned previously, the synthetic white liquors that Chai et al. [10, 11] used did not contain carbonate. The prediction of carbonate was not attempted in their studies [10, 11]. When the spectral contribution from the nonabsorbing substances presented in the aqueous solution of an absorbing analyte is not significant, the prediction of the concentrations of the nonabsorbing substances by PSL chemometric analysis will be inaccurate. In the present study, we extended the ATR-UV spectral range to 190 nm and found the absorption spectra of hydroxide and carbonate; therefore, these two substances will no longer be treated as nonabsorbing species. By using the spectral fingerprints of hydroxide and carbonate in ATR-UV spectroscopy, we can significantly improve the reliability in the analysis of kraft liquors.

ATR-UV Measurements in Kraft Mill White and Green Liquors

Figure 4 shows the spectra of white and green liquor samples from a kraft mill. These liquors consist of three major components, i.e., sulfide, hydroxide, and carbonate. Only HS⁻ ions contribute to the absorption at wavelengths around 230 nm, and the absorption of hydroxide and carbonate mainly contribute at the wavelengths below 210 nm. The concentrations of HS⁻ ions in these two liquors are quite close as shown in Fig. 4. In the green liquor, the concentration of carbonate is very high, while the hydroxide is the dominant species in the white liquor. Because the absorptivity of hydroxide is very high, the absorption of the white liquor is much higher than that of the green liquor below 210 nm.

Effect of Minor Species on the Measurements

There are several minor species in kraft white and green liquors, such as thiosulfate, sulfate, and chloride. The presence of these species alters the ATR-UV absorption spectrum through direct absorption (especially for thiosulfate in the lower UV wavelength) in the UV region and contribution to the refractive index of the liquor. Significant errors may result in the prediction of kraft mill samples if the calibration database is obtained using the synthetic solutions from pure aqueous solutions of hydroxide, sulfide, and carbonate. To obtain good

predictive accuracy, it is suggested that mill liquors from the same source (mill) should be used in calibration experiments to build the database.

Temperature Effect

The effect of temperature on ATR-UV spectrum was investigated by Chai et al. [11]. It was found that the absorption peak for sulfide was shifted about 5 nm toward the visible region at a temperature of 90°C compared to results obtained at room temperature of 25°C. Furthermore, the absorption peak intensity decreased about 17 % over a temperature range of 20 to 90°C. This temperature effect is not sample specific. Chai et al. [11] found that a change of temperature of about $\pm 5^{\circ}\text{C}$ only produces a 2% error in absorption. In this study, we confirmed that ATR absorption intensity decreases linearly with the increase of temperature. However, if relatively good temperature control of the testing liquor, e.g., $\pm 2^{\circ}\text{C}$, is obtained before the liquor enters the flow cell, it is not necessary to include temperature as a parameter in the calibration file to ensure the accuracy of the analysis. All measurements were conducted at room temperature in this study.

The Effect of Corrosion of the ATR Probe

Quartz is the only possible material to choose for UV spectroscopy applications. Theoretically, hydroxide can attack quartz, which could affect measurements. We conducted a corrosion test by submerging a similar quartz rod in a 10 mol/L NaOH solution for about one month. Visual inspection using SEM shows that the corrosion on the surface of the quartz is negligible. Furthermore, we did not find any spectra distortion after many hours (>1000 hours) of measurements using the present ATR probe, indicating that corrosion is negligible with proper water flush after each experiment.

Application

To demonstrate the capability of ATR-UV spectroscopy for kraft liquor analysis, we applied the present ATR-UV system to measure one green liquor and three white liquors collected from a kraft pulp mill. The green liquor was sampled after the clarification. The three white liquors were sampled in the first retention tank (WL-1), at the discharge of the 3rd retention tank (WL-2), and at the slaker discharge (WL-3), respectively. A set of eighteen solutions was made using various combinations of the green and the first white

liquor sample (WL-1) with dilution and the addition of various amounts of hydroxide, sulfide, and carbonate for calibration and validation. The final concentration range of the sixteen liquors was very broad to cover all the possible concentrations of green and white liquors in the mill that provided us with the samples. The concentrations of hydroxide, sulfide, and carbonate in these eighteen solutions were titrated by the ABC standard method [1]. The titrated values of the fourteen solutions were used for calibration to determine the parameters for the predictive model using a chemometric software. We reserved four solutions that were not used in calibration to conduct the first step validation of the predictive model. Figures 5 to 7 show the comparison between the titrated and model predicted concentrations of hydroxide, sulfide, and carbonate in the fourteen solutions for calibration (open symbols) and the four solutions for validation (solid symbols). The results shown in the figures also indicate that predicted concentrations in the four reserved solutions were validated by the titration results.

After the first-step validation using the four reserved solutions, we then measured the hydroxide, sulfide, and carbonate concentrations of the green and white liquors from the kraft mill using the same calibrated predictive model described in above. We also conducted ABC titration for these four kraft mill liquors. Table 1 shows the ATR-UV measurements along with ABC titrated values of the hydroxide, sulfide, and carbonate concentrations in these four liquor samples. Very good agreements were obtained between the ATR-UV measurements and the titration results, in particular, for hydroxide and sulfide. The maximum relative standard deviations in hydroxide and sulfide measurements in these four liquors are less than 5 and 2%, respectively. The relatively large errors (about 10%) in carbonate measurements are mainly due to the low absorptivities of carbonate in UV range. One can expect that a relatively large error may result in carbonate measurements in white liquors in which the carbonate concentration is relatively low.

CONCLUSIONS

This study demonstrated the principles and applicability of ATR-UV spectroscopy for simultaneous analysis of sodium hydroxide, sulfide, and carbonate concentrations in kraft white and green liquors. The ATR-UV spectra of kraft liquors can be analyzed and solved for the concentration of sulfide, hydroxide and carbonate using a calibration model

based on a multi-variant partial-least-squares fitting procedure. Very good agreement between ATR-UV measured and titrated concentrations of hydroxide, sulfide, and carbonate was obtained. The ATR-UV measurement is rapid and accurate, and does not require sample pretreatment or dilution; therefore, it can be used to develop on-line or in-line sensors for kraft process monitoring in mill environments.

ACKNOWLEDGEMENT

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List of Figures

Figure 1 A schematic diagram that demonstrates the ATR principle.

Figure 2 A schematic diagram of the UV-ATR system used in the present study.

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Figure 4 Typical UV-ATR spectra of kraft mill white and green liquors.

Figure 5 Comparisons between titrated and ATR predicted hydroxide concentrations in eighteen modified mixtures of kraft mill green and white liquors.

Figure 6 Comparisons between titrated and ATR predicted sulfide concentrations in eighteen modified mixtures of kraft mill green and white liquors.

Figure 7 Comparisons between titrated and ATR predicted carbonate concentrations in eighteen modified mixtures of kraft mill green and white liquors.

Table

Table I: Comparisons between ATR measurements and titrated concentrations of hydroxide, sulfide, and carbonate in four kraft mill liquors.

Figure 1

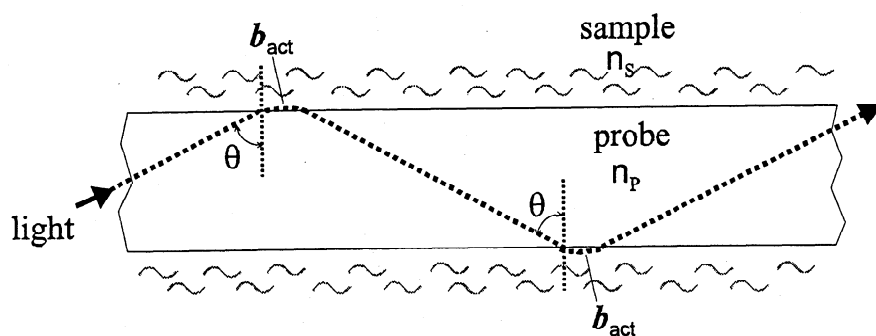


Figure 2

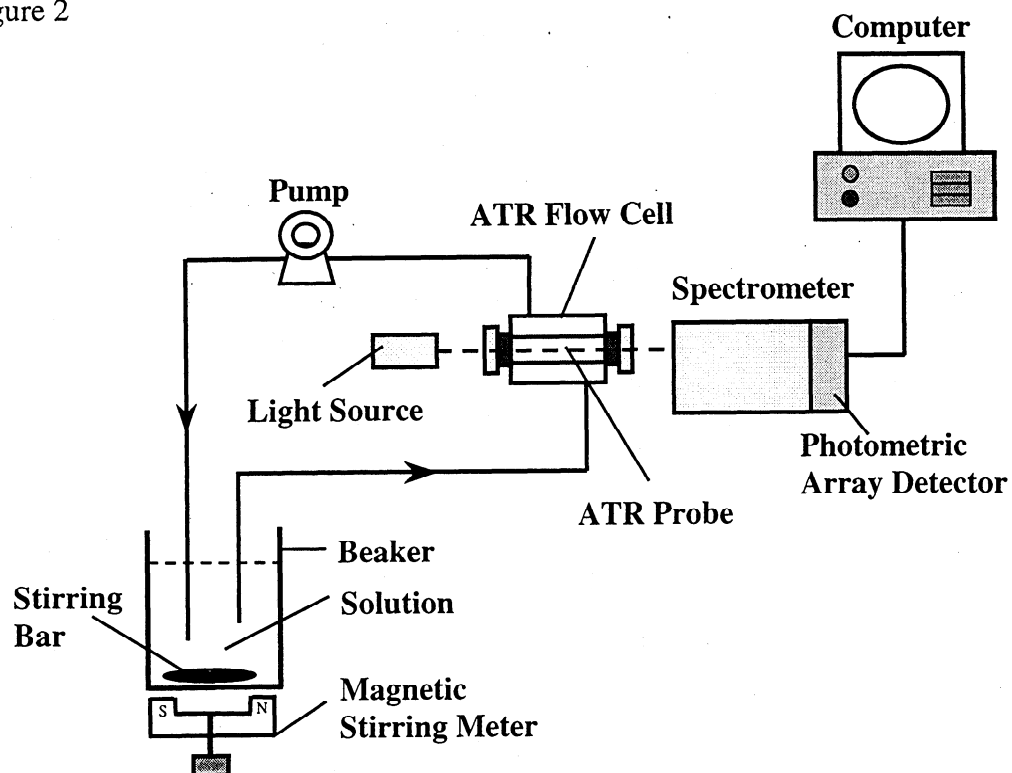


Figure 3

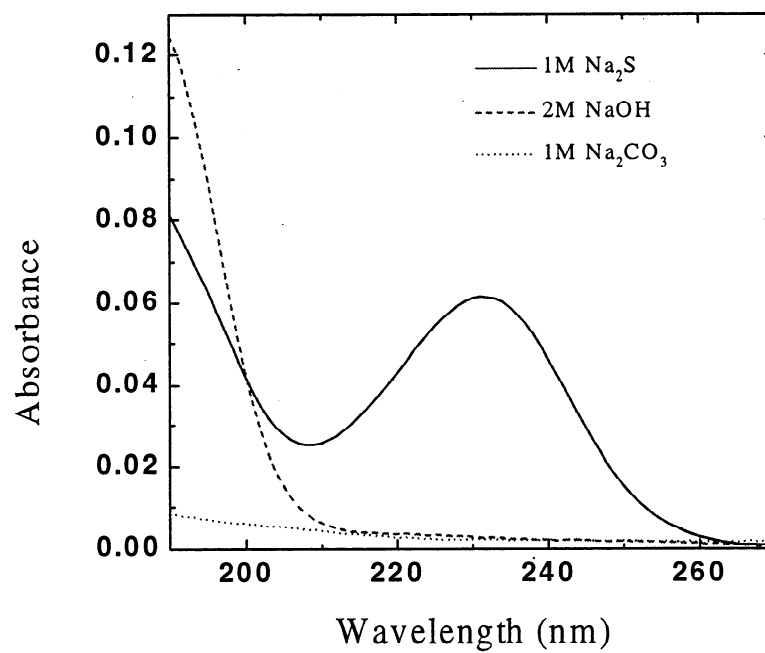


Figure 4

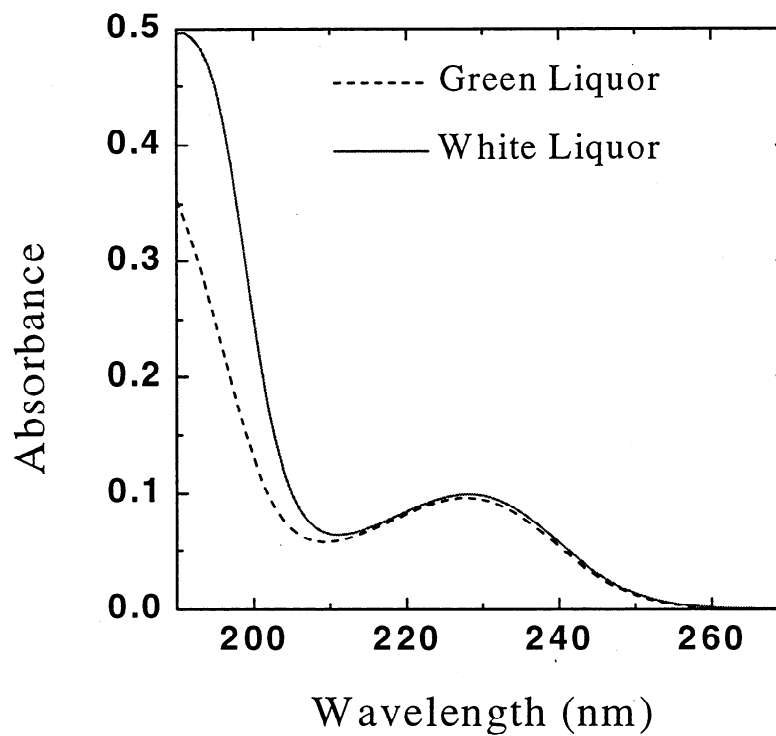


Figure 5

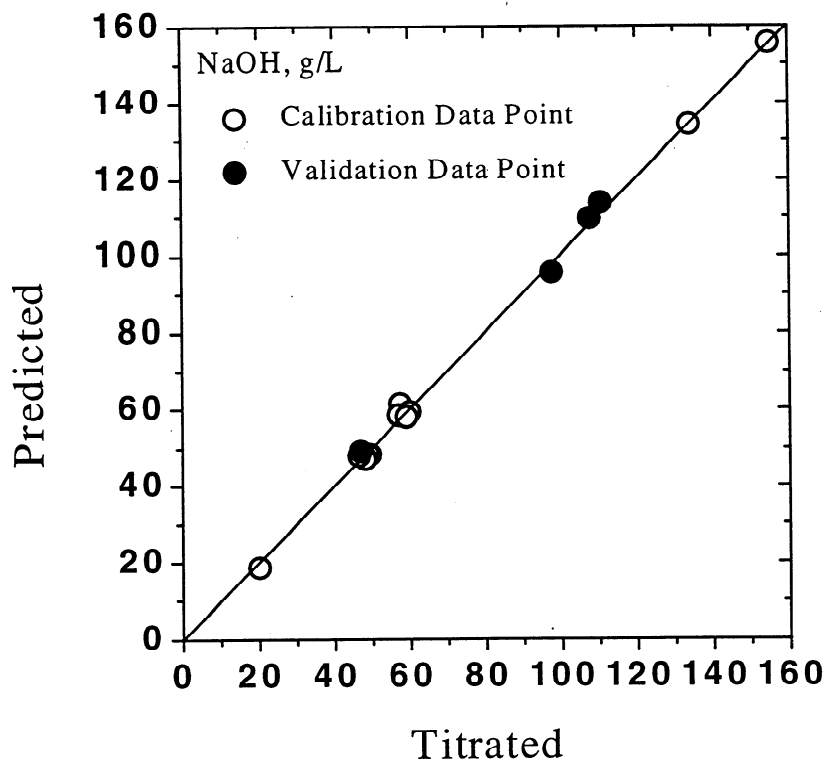


Figure 6

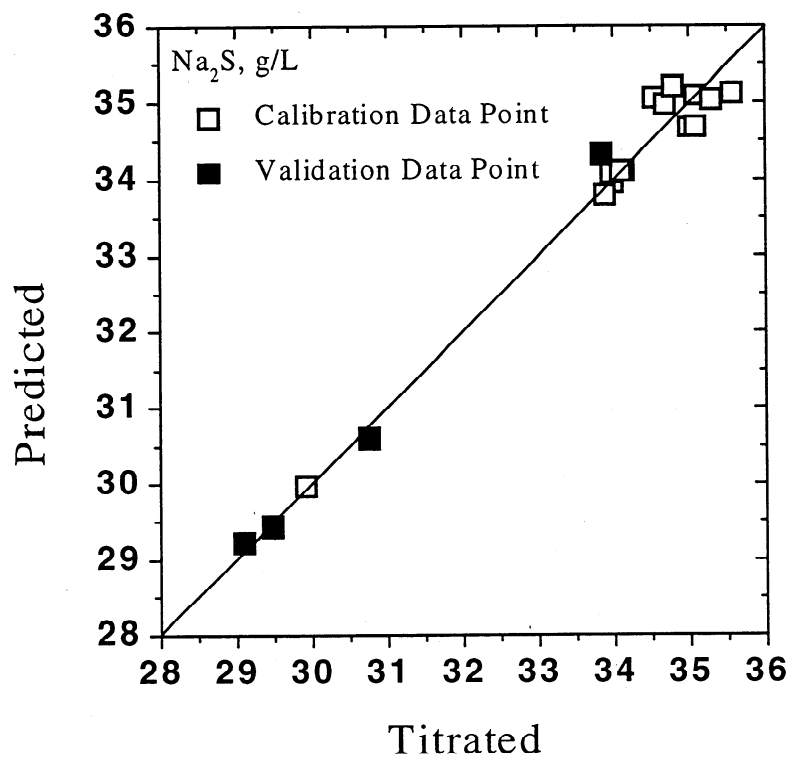


Figure 7

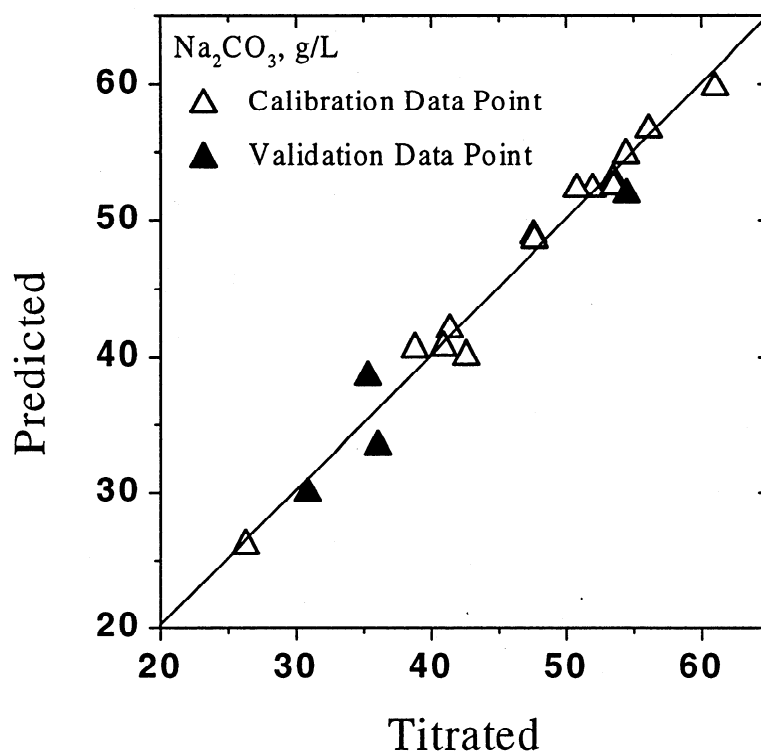


Table I. Comparisons between ATR measurements and titrated concentrations of hydroxide, sulfide, and carbonate in four kraft mill liquors

Sample*	NaOH, g/L			Na ₂ S, g/L			Na ₂ CO ₃		
	Titra.	ATR	RSD, %	Titra.	ATR	RSD, %	Titra.	ATR	RSD, %
GL	47.2	48.9	3.8	33.9	34.3	1.3	54.4	51.9	-4.7
WL-1	107.6	109.3	1.5	29.1	29.2	0.4	36.0	33.4	-7.2
WL-2	110.9	113.4	2.2	29.5	29.4	-0.1	30.8	29.9	-2.8
WL-3	97.9	95.6	-2.4	30.8	30.6	-0.6	35.3	38.6	9.3

* GL: green liquor. WL: white liquor.

DUES-FUNDED PROJECT SUMMARY

Project Title:	Fume Deposition and Hardening
Project Number:	F03801 F03802
PAC:	Chemical Recovery

Project Staff

Principal Investigator:	Steve Lien
Co-Investigators:	Jim Frederick
Research Support Staff:	Josefina Lindblom

PAC Subcommittee	Chemical Recovery
FY 99-00 Budget:	\$92,000
Allocated as Matching Funds:	30%

Time Allocation:

Principal Investigator:	40%
Co-Investigators:	15%
Research Support Staff:	25%

Supporting Research:

Special Students:	None
External (Where Matching Is Used):	DOE Project 4228 - Convection Pass Deposits in Recovery Boilers L. Baxter, Sandia National R. Wessel, McDermott H. Tran, U. of Toronto

RESEARCH LINE/ROADMAP: Improved Capital Effectiveness. 8. Develop technologies (compatible with present pulp-mill assets) to allow cost-effective expansion of kraft-pulp-equivalent fiber capacity (hardwood and softwood) by 30% without adding Tomlinson recovery boilers.

PROJECT OBJECTIVE: The overall objective of this project is to obtain additional data and a better understanding of the factors that influence the plugging and deposition in the upper furnace of recovery boilers. This work falls into two main categories. First measuring the rate of formation and understanding the mechanisms for the production of fine particles during black liquor combustion. And second to measure the sintering and deposition behavior of fine particles in the superheater, boiler bank, and economizer sections of the recovery boiler.

PROJECT BACKGROUND: A number of factors can limit the pulp capacity rate supported by a kraft recovery boiler, but the most important of these is normally plugging of gas passages in the superheater, boiler bank, and economizer. Research in this area has been performed at IPST, the University of Toronto, Sandia National Laboratory, and

Oregon State University, on topics including; the deposition of sub-micron fume particles, and investigation of how fume chemistry, gas composition, and temperature impact sintering and hardening of deposits in recovery boilers. As a result of this and earlier work, key questions were identified regarding the formation, properties, hardening, and removal of recovery boiler deposits.

A research project, funded by DOE/Agenda 2020, began in February of 1998 to address several of these questions. IPST's responsibilities in this project include obtaining data on:

- a) liquor-to-liquor differences in the amounts of fume and larger (10-100 micron) particles generated during burning of black liquor in-flight and on a char bed;
- b) the impacts of particle composition and gas composition on the rate of sintering and hardening of recovery boiler deposits, and
- c) radiation properties of entrained particles in kraft recovery boilers.

Current work on the project includes the measurement of the rate of sintering of electrostatic precipitator (ESP) fume dust. Early studies focused on the rate of sintering of fume dust formed into pellets with an initial density of 1.2 g/cm³. The next phase looked at the rate of sintering of loose agglomerations of ESP dust at densities of 0.4 g/cm³.

DELIVERABLES AND STATUS OF GOALS FOR FY 99-00:

1. Analysis of existing U of T data on the effect of fume composition and temperature on sintering rate of recovery boiler deposits – completed.
2. Obtain additional data on the effect of fume composition and temperature on sintering rate of recovery boiler deposits – completed.
3. Data on the impact of gas phase composition on the rate of sintering of recovery boiler dusts – testing started.

SCHEDULE:

Task Descriptions (example)	1999 Apr - Jun	1999 July – Sept	1999 Oct - Dec	2000 Jan – Mar	2000 Apr-Jun
Low Density Sintering Experiments	-----	-----X			
Data Analysis	----	-----	-----	-----X	
Modify Equipment			-----	---X	
Gas Composition Sintering Tests				-----	-----
Data Analysis					-----

SUMMARY OF RESULTS:

Fume particles may foul and plug the superheater, boiler, and economizer banks of kraft recovery boilers. Sintering, the process of densification of porous solids, is responsible for hardening of fume deposits of kraft recovery boiler. As deposits densify, their strength increases exponentially with pellet density, and they become more difficult to

remove by sootblowing. This project is focused on understanding factors that control the rate of sintering.

High Density Sintering

Sintering rates of recovery boiler deposits appear to be controlled by a combination of dust composition, particle packing density, and temperature. Data from three different sources was combined and analyzed to understand the sintering behavior. In these tests the ESP dust was formed into relatively dense pellets and then exposed to high temperatures. The rate of sintering was measured by recording the change in volume of the pellets. There is wide variation in the sintering behavior and composition of dusts from different recovery boilers.

The results reported in this phase were obtained from three separate studies, all using similar methods. In all three data sets, the dusts used were collected from the electrostatic precipitator (ESP) catch at the outlet of the recovery boiler. Each dust sample was from a different recovery boiler. These dusts were formed into pellets, weighed and measured, and then exposed to a high temperature environment at a fixed temperature for a given period of time. The sintering rate was determined by measuring the change in diameter of the pellets with time during sintering.

The data for all eight of these dusts were combined into a single data set and analyzed. Since there was no significant weight loss during sintering, the change in diameter of the pellets was used to characterize sintering. The data were normalized by dividing the change in diameter by the initial diameter L_0 .

Sintering in recovery boiler dusts proceeds initially by one or both of the two mechanisms. The first of these is sintering by solid-state diffusion, with ions diffusing across the contact area (neck) between two particles. Diffusion may occur along grain boundaries, along the surface of the particles, or by bulk diffusion. It is the most common method by which ceramic materials and metals sinter. It is well understood for pure substances, but not for mixtures.

The second mechanism is sintering by evaporation and condensation of volatile components within the particles. The volatile components evaporate from the low curvature surface of the particles, and condense in the high curvature neck region. The particles combine into a larger, single particle. This mechanism by itself results in far less shrinkage of particle compacts. NaCl particles have been shown to sinter by this mechanism.

During the initial sintering stage, dusts with moderate to high chloride content sinter by an evaporation-condensation mechanism. Those with no chloride sinter by a solid-state diffusion mechanism. Dusts with low to moderate chloride contents eventually switch to solid-state diffusion sintering.

The "Sintering Constant" is a unique property of a dust. It depends on dust composition (and the first melting temperature), but not sintering temperature. It can be used to estimate the sintering tendency of a dust, and to guide changes in recovery boiler operation to slow hardening of deposits.

Low Density Sintering

The objective in this phase was to characterize deposit growth and strength development mechanisms and rates, and to measure the development of critical deposit properties under commercial-scale conditions. Our strategy was to study sintering of ESP dusts at low densities, which more closely reflect actual recovery boiler conditions. The rate of sintering and strength development of fine particle assemblages was measured at temperatures below the onset of melting with precipitator catch particles from several kraft recovery boilers.

The basic approach was to start with a low-density non-compressed dust sample, and determine the rate of sintering. This is in contrast to the previous work where the initial dust sample was compressed to a higher density ($\sim 1.2 \text{ g/cm}^3$). This low-density ($0.3\text{-}0.4 \text{ g/cm}^3$) arrangement of fume particles is closer to what is seen in the upper regions of a recovery boiler and hopefully will provide more useful data. The dust samples were exposed to a range of temperatures and gas compositions for various time periods. The rate of sintering was determined by measuring the surface area of the dust (using a BET measurement of nitrogen adsorption) before and after sintering.

The experimental procedure was as follows. A weighed dust sample was inserted into the lower half of the quartz assembly. At the start of the test the lower half of the quartz reactor was attached to the upper male section of the quartz tube in the preheated furnace. After a fixed length of time the dust sample was removed from the furnace by disassembling the lower half of the quartz section. The quartz piece and dust sample were cooled and weighed. In these experiments the rate of sintering was determined primarily through the measurement of the surface area of the dust samples, before and after sintering. Surface area measurements were made with a BET nitrogen adsorption system at Chalmers University in Sweden. Additional analysis was performed using a scanning electron microscope (SEM) at IPST to obtain images of the microstructure of the dust particles before and after sintering.

A total of 28 different recovery boiler electro-static precipitator (ESP) catch dust samples were been collected from a wide variety of sources. Eighteen different fume samples were obtained from the electro-static precipitator (ESP) catch of sixteen recovery boilers at fourteen different mills. These fume samples were collected from different recovery boilers in a variety of geographic locations with a range of operating conditions. In addition 10 additional ESP samples were obtained from the University of Toronto. These samples have been analyzed to determine the chemical composition.

Significant progress was made in the effort to obtain data on the rate of sintering for ESP dusts, under conditions of low initial density. The apparatus was constructed, the dust samples were collected, and the first and second experimental test series were completed.

In the first phase, (Test Series I) the tests measured the sintering rate of a few dust samples over a wide range of time and temperatures. The initial data showed an increase in the surface area of the samples for short sintering rates, followed by the expected decrease in surface area for longer times. Test Series II has also been completed. In this test sequence a large number of different samples were tested, but only at temperatures of 400 and 500 °C. These temperatures reflect the conditions where the sintering rate is significant, but below the first melting temperature of the fume. The samples were selected in order to obtain a wide range of physical and chemical properties in the ESP dust samples.

In general the results obtained are similar to what was seen in the previous study. In all cases the initial sintering rate is rapid and then shows a decreasing rate with time. At lower densities, slightly higher temperatures are needed to initiate the sintering. The study shows that the temperature needs to be 500 °C for all the dusts to sinter at the low densities used. The specific surface area decreases with increasing time and fits the German Munir model well. The reduction of the specific surface area was found to correlate with the first melting temperature of the dust, with increased sintering for dusts with low first melting temperatures. Moreover, the rate constant in the German Munir model was strongly related to the first melting temperature. No correlation between the sintering mechanism and the composition of the dust could be found.

Effect of Gas Composition on Sintering

The next stage of the sintering work is to measure sintering under conditions that are even closer to the upper furnace of the recovery boiler. The gas composition in the upper furnace of a recovery boiler is another variable, which may influence the sintering rate of ESP dust. The final stage of testing will be similar to the previous work at low densities - the same equipment and experimental procedure will be used - but with the addition of a variety of gases to the reactor.

The first step in this testing will be to determine which gases have a statistically significant impact on the sintering rate, using a small number of dust samples. The test conditions are listed in the table below. After determining which gases are important, additional experiments will be designed and performed to measure the effect on a range of ESP dusts.

Effect of Gas Composition on Sintering - (First Series Conditions – 48 tests)**Time and Temperature – 3 conditions**

400 C for 60 minutes

500 C for 10 minutes

500 C for 60 minutes

Gas Composition - 4 conditions – 10 slpm flowN₂ onlyN₂ (79%) + H₂O (18%) + O₂ (3%)N₂ (65%) + H₂O (18%) + O₂ (3%) + CO₂ (14%)N₂ (77%) + H₂O (18%) + O₂ (3%) + SO₂ (1%)**Dusts – 2 ESP Dusts**

Dust #5 – Low Sintering

Dust #8 – High Sintering

Duplicates – 2 of each**SUMMARY OF KEY CONCLUSIONS:**

- Sintering tests have been performed with a wide range of conditions:
 - With ESP dusts as both high density pellets and low density agglomerations
 - Using a number of different fume samples from a variety of mills, with a wide range of chemical compositions
 - At a range of times from 5 minutes to 5 hours
 - At temperatures from 300 to 700 C
- Qualitatively, the normalized sintering rates plotted against time were similar for both low and high densities:
 - Initial sintering rates are rapid and then shows a decreasing rate with time
 - Sintering rates increase with increasing temperature
- At lower densities, somewhat higher temperatures are needed to initiate the sintering
- The first melting temperature (FMT) of the dusts was found to be related to the rate of sintering, most dusts with a low FMT show higher sintering rates
- It is difficult to correlate dust composition to the sintering rates, but at least for high density pellets, the chloride level is important

DISCUSSION:

See the following papers for more details on the sintering work.

**SINTERING OF RECOVERY BOILER DUST –
THE INFLUENCE OF THE COMPOSITION OF THE DUST**

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Key words: Precipitator dust, Recovery boiler dust, Fume, Sintering, Specific surface area,

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Transport Processes in the Forest Products Industry

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ABSTRACT

Deposition of fume on heat transfer surfaces in the upper furnace of recovery boilers is often a problem. Production rates and boiler efficiency decrease with fouling and problems with corrosion increase. Soot-blowers are used to clean the surfaces but these may become ineffective if the fume has sintered and hardened.

It has been suggested that the composition of the dust may influence the sintering process and to study this, 13 industrial recovery boiler dusts were analyzed, and heat-treated in a quartz glass reactor. Run times were 5, 10, 30 and 60 minutes and the temperatures were 400 and 500 °C. Care was taken to obtain densities representative of those found in recovery boilers and the initial density was about 300 kg/m³.

Sintering was measured as the reduction of the specific surface area and it was found to increase with increasing time and temperature. Only a few dusts sintered measurably at 400 °C, while all dusts did, at 500 °C. At the higher temperature, sintering was found to correlate with the first melting temperature of the dust, with increased sintering for dusts with low first melting temperatures. The reduction of the specific surface area with increasing time was modeled with the German Munir equation. The rate constant was strongly related to the first melting temperature, while no relation could be found between composition and sintering mechanism.

INTRODUCTION

In the kraft pulping process, wood chips are treated in the digester with white liquor - an aqueous solution consisting of sodium hydroxide and sodium sulfide, and lignin and carbohydrates are dissolved to some extent. The liquid leaving the digester (black liquor) thus contains lignin and other organic, as well as inorganic components. The black liquor is valuable since its dissolved organic substances have a substantial heat value, and its inorganic compounds are reconverted to sodium hydroxide and sodium sulfide, to produce new white liquor, which is then recycled to the digester. The black liquor is combusted in the recovery boiler, which is the major producer of super-heated steam in the kraft pulp mill.

When black liquor is combusted in the recovery boiler, there are two types of fly ash particles in the flue gases, carryovers and fume. They can both form deposits on the tube surfaces further up in the boiler. Carryover is black liquor droplets or fragments of burning droplets, with a size ranging from about 20 µm to 3 mm. Most of the carryover deposits on tube surfaces in the superheater region while further up, in the boiler bank and economizer, the deposits are mainly

fume. Fume is formed since, during combustion, a fraction of the alkali compounds in black liquor vaporizes and forms particles of a size about 0.1-1 μm .

The flue gas temperature is about 600 °C on entering the generating bank and 400 °C on leaving it. The boiler bank tube surfaces temperature is typically about 320 °C. As the gases cool, particles nucleate and grow. They deposit where the temperature is low enough to allow condensation. The fume is mostly sodium sulfate with some sodium carbonate, but chloride and potassium can also be found. The pure salt mixture of sodium sulfate and sodium carbonate melts between 826 and 880 °C, depending on the composition. However, chloride and potassium compounds lower the first melting point significantly, in extreme cases to below 550 °C.

Fouling of heat transfer surfaces and plugging of the gas flow passages in the upper furnace has been an ongoing problem in recovery boilers, resulting in limits on production rates and boiler efficiency. Moreover, the deposits decrease thermal efficiency and contribute to corrosion. Fume deposits tend to sinter and harden over time so it is important to know how fast sintering occurs and what influences the rate of sintering. This knowledge would provide a tool for more efficient sootblowing and improved operation of recovery boilers. When sootblowing becomes ineffective, because of hard sintered deposits close to the tubes, the boiler must be shut down and an expensive water wash has to be done.

When dust condenses on tube surfaces, sintering will be slow because of the low temperature. As the deposit layer thickens, its outer surface temperature rises and sintering becomes more rapid, making the outer layer solid and hard while the inner layer remains porous and soft. Besides the outside of thick deposits, temperatures high enough for sintering can be reached if the deposit is located far from the tubes. Bridges between tubes caused by large pieces of “jammed” deposits, presumably removed from the upper part of the boiler by sootblowers, are example of deposits which are not cooled and rapidly become hard from sintering.

During sintering a grain boundary replaces the two original surfaces of two particles to reduce the total surface energy. As particles are packed together and heated, the difference in free energy between the joints and particle surfaces causes the transfer of material by the fastest means available. Material diffuses initially along the particle surfaces to points of contact, forming bridges between particles. This surface diffusion process only causes a modest increase in strength of the compacted particles. It does not cause shrinkage and densification. Subsequent bulk diffusion causes densification and an appreciable increase in strength.

Earlier studies (Lien et al. (1999), Duhamel and Tran (1998), Tran et al. (1988) Techakijkajorn et al. (1999), Hupa et al. (1989) and Skrifvars et al. (1991) have used dust formed into compact pellets. Sintering has then been determined by measuring either the volume shrinkage or the compression strength. In these studies, due to the formation of pellets, the initial density becomes

high, i.e. 900-1400 kg/m³. This is significantly higher than what can be found in a recovery boiler where low-density fume deposits grow from gradual accumulation of submicron fume particles on heat transfer surfaces. Accordingly, these studies have shown higher sintering rates than observed in commercial practice. The studies of Duhamel and Tran (1998), Hupa et al. (1989) and Skrifvars (1991) et al. showed that the combination of potassium and chloride enhanced sintering significantly.

In the study of Techakijakorn et al. (1999), sintering was determined experimentally by measuring the shrinkage of pellets. The dust used was low in chloride and high in potassium. It was found that sintering began at 350 °C and increased rapidly with temperature over the range investigated. At temperatures between 400 °C and the onset of melting, sintering was so rapid that deposit would densify to the point where they may not be removable by soot-blowing at normal frequencies. A model including two stages was presented and its constants are thought to depend on dust composition. It is concluded that the effect of heat transfer and other factors related to initial density clearly need to be accounted for in the model.

Lien et al. (1999) also investigated the shrinkage of pellets, but used eight different dusts all with different chemical composition. For all of the dust samples there is an initial period of rapid sintering followed by a period when the sintering rate decreases.

It was found that there is a wide variation in the sintering behaviour of the dusts and that those differences are due to different transport mechanisms causing the sintering. The transport mechanisms are in turn dependent on the composition of the dust where the concentration of chloride is important. The higher the concentration of chloride the more pronounced effect of evaporation condensation while for the dusts low in chloride, bulk and surface diffusion seem more important. A strong correlation between sintering and first melting temperature (FMT) was found for low FMT's (below about 535 °C).

Tran et al. (1988) sintered pellets as well and could see how the pellet density increased dramatically with temperature and compacting pressure (i.e. initial density). A strong correlation between the pellet compressive strength and density was observed, with markedly increased strength with increased density.

Duhamel and Tran (1998) measured the volume shrinkage of 61 dusts and ranked them according to an index, which showed a linear relation to the strength of the sintered dusts. Again, it was found that dusts with higher chloride content generally sinter more rapidly than dusts with low chloride content. Though, high chloride is not the only factor that causes rapid sintering, the potassium content (especially in combination with a high concentration of chloride) and the dust particle size also play an important role.

Hupa et al. (1989) and Skrifvars et al. (1991) investigated how different chemical compounds affect the sintering tendency of different fly ashes and their method was based on compression strength measurements of sintered pellets. Synthetic dusts were used to form pellets and the dust was screened to eliminate the impact of particle size on sintering. The mean particle size was 100 μm , which is the size of carryovers. Compression strength showed a strong dependence on chemical composition, in particular the content of potassium and chloride seemed to increase the sintering tendency. Besides the synthetic dusts, both studies used dusts collected from operating recovery boilers as well. Pellets were then made directly from the collected dusts. The potassium and chloride concentrations in the dust do not correlate very well with the sintering strength. These results show that the content of potassium and chloride in the dust are not the only important variables affecting the tendency to sinter. Particle size is known to be an important variable in sintering, and the particle sizes of the collected dusts were not controlled.

In the study of Sinquefield et al. (1998), black liquor was combusted in a pilot scale combustor. Temperature-controlled, cylindrical probes in cross flow were used to collect ash deposits. Both fume (submicron, 0.001-1 μm) and intermediate sized (1-100 μm) particles were produced. The fume was low in chloride while normal otherwise. Deposit microstructures that included long connected strings of particles in the direction of deposit growth was found. Bridges between these structures perpendicular to the direction of deposit growth were rare while particles within the strings were highly sintered. The slow sintering between the strings may be due to the fact that the concentration of chloride was low. However, it is suggested that the observed slow rates of bridging between such chain-like structures resolves the disagreement between the slower rates of sintering observed in commercial practice compared with laboratory experiments with pressed pellets of crushed deposit materials.

The objective of the current work was to study the influence of dust composition on the sintering process when the dust was not compacted into pellets but under conditions representative of those found in recovery boilers. To be able to do this, sintering takes place in a quartz glass reactor where the dust sample is placed on a fritted disc of quartz glass. This will allow the initial density of the fume to be much lower, approximately 300 kg/m³. Dusts with varying compositions were collected from different mills. In order to follow the changes in microstructure during sintering, SEM images were used. To quantify sintering, the reduction of the specific surface area was measured.

The decrease of the specific surface area with time can be modelled with the equation developed by German and Munir (1976):

$$\left(\frac{S_0 - S}{S_0} \right)^{\gamma} = k \cdot t$$

Eq. 1

S_0 is the initial specific surface area and S is that at time t . k is a rate coefficient depending on the temperature and composition of the system. The reduction exponent γ is a function of the transport mechanism during sintering and packing characteristics of the powder. The strong relationship between the γ -value and the sintering mechanism means that this value may be used to evaluate the mechanism. For this model, the particles are assumed to be monodisperse spheres when sintering begins. Deviations in either particle shape or size distribution may cause effects not accounted for by the model. The original calculations were made for isolated necks and, therefore the limit of the model is reached when neighbouring necks impinge on each other. This occurs approximately when the specific surface area has decreased to about 50 % of its original value.

EXPERIMENTAL

Equipment

The experimental apparatus has been designed in order to measure the rate of sintering of fume under conditions representative of those found in recovery boilers. In this system the initial bulk density of the fume will be very close to its green density, i.e. about 250 – 300 kg/m³. Sintering occurred in a quartz glass reactor, where the dust sample was contained inside a quartz tube, held between two fritted quartz discs. The quartz glass equipment consists of an upper male part with a fritted disc at the bottom and a lower female part, also with a fritted disc, which serves as the sample holder. The entire reactor system is contained within a high temperature furnace in order to achieve the desired test conditions.

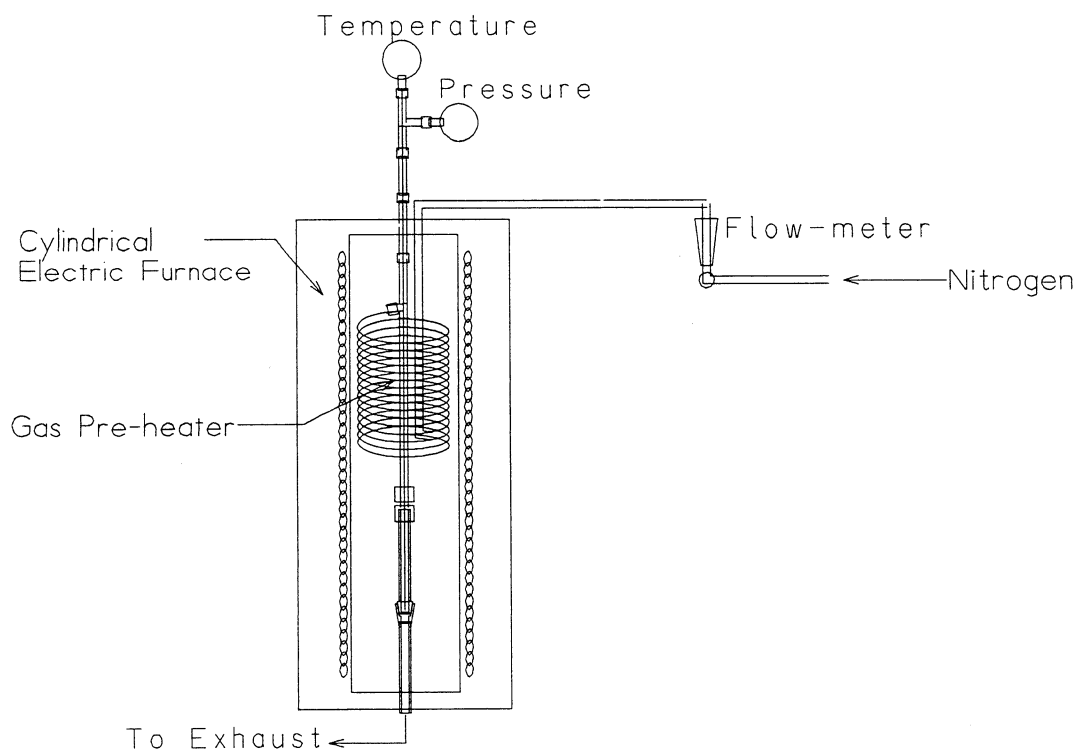


Figure 1. The experimental furnace.

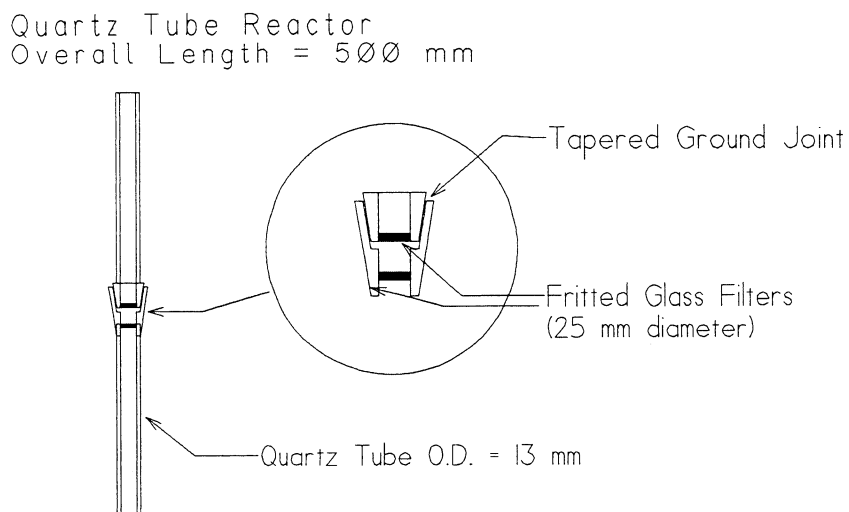


Figure 2. The quartz glass reactor.

The vertical high temperature furnace is 840 mm long. The gas enters the furnace at the top and first flows in a stainless steel tube (520 mm). A gas heating coil (360 mm long) surrounds the tube and, thus, the gas is heated. Next the gas goes through the quartz reactor; passes through a fritted disc, the dust sample, the second fritted disc and then finally out of the reactor. The upper part of the quartz glass equipment is attached to the stainless steel tube with a swagelok fitting. The furnace is open in the bottom and the lower part of the quartz glass is held in position by a support under the furnace. This part of the quartz glass can easily be removed by taking the support to the side. All in all, the length of the quartz glass parts is about 480 mm. The sample will be situated approximately 90 mm from the bottom of the furnace. The temperature is measured just above the upper fritted disc (about 20 mm above the top of the sample) and, also, in the middle of the sample.

Dusts

Different fume samples were collected from different recovery boilers in a variety of geographic locations in the US and Canada, with a range of operating conditions. The dust was obtained from the electrostatic precipitator catch from different boilers.

The dusts were characterized by analyzing their composition (sodium, potassium, chloride, sulphate and carbonate) and measuring their specific surface area. The specific surface area was determined using a five-point nitrogen B.E.T. technique. SEM images were also taken. Dusts with a homogeneous microstructure and with a wide range of chemical composition were selected for the sintering tests. The mean particle sizes were estimated by studying the SEM images but also by calculating them from the specific surface area and the density ($\sim 2650 \text{ kg/m}^3$) assuming uniform solid spheres. As can be seen, the results differ. The composition of the dusts can be seen in Table I and their original specific surface area and particle size is shown in Table II.

Table I. Composition of the 13 investigated dusts.

Dust #	5	7	8	9	10	12	14	15	17	18	21	43	52
Na ⁺ (mole-%)	59	56	56	57	61	59	63	62	58	52	61	54	54
K ⁺ (mole-%)	6	8	8	8	5	7	4	5	7	13	6	11	8
SO ₄ ²⁻ (mole-%)	30	23	23	22	15	33	22	30	24	24	25	23	18
CO ₃ ²⁻ (mole-%)	4	7	7	11	17	0.3	10	2	7	4	7	6	4
Cl ⁻ (mole-%)	1	6	6	2	2	0.3	1	2	3	7	1	6	16

Table II. Characteristics of the dusts.

Dust #	5	7	8	9	10	12	14	15	17	18	21	43	52
Specific surface area (m ² /g)	3.1	3.6	4.6	3.4	4.3	3.6	3.4	4.4	3.6	3.0	4.1	2.4	2.6
Particle size (μm), SEM	0.4	0.4	0.4	0.3	0.4	0.4	1.5	0.3	0.4	0.3	0.3	0.4	0.3
Particle size (μm), calculated	0.7	0.6	0.5	0.7	0.5	0.6	0.7	0.5	0.6	0.8	0.6	1.0	0.9

Procedure

Before using a dust in the furnace, it was dried at approximately 107 °C. Then either 2.00 or 2.50 grams (depending on the green density) of dry dust was placed in the sample holder of quartz glass. The sample holder containing the sample was shaken to get a homogeneous density of the dust. A light weight was placed on top of the sample bed to make sure that the density before sintering was the same for all the samples of the same dust (approximately 300 kg/m³). The sample was then ready to be placed in the furnace.

The sample holder was inserted through the opening in the bottom of the furnace. The female part (the sample holder) was connected to the male part, which was already in the furnace. The support under the furnace is put in place to hold the sample holder in its position. The gas flow of 5 l/min, STP, of pure nitrogen was turned on and the sintering time started. It took approximately 5 minutes for the sample to reach the predetermined temperature. The temperatures were recorded every minute.

After the predetermined sintering time the gas flow was turned off and the sample holder taken out and cooled by flowing air. The sample was then weighed and its volume estimated. The sample was stored in a dessicator until its specific surface area was measured and SEM images were taken.

The temperatures used were 400 and 500 °C. Run times ranged between 5 minutes and 1 hour. In the beginning, 3 or 4 tests were run for each set of conditions to check the repeatability. Since it was found that the average deviation from the average value was acceptably small (4 %), the rest of the experiments were run with duplicates. The average deviation from the average value of the measured surface area for the duplicates was 3.5 %.

RESULTS AND DISCUSSION

The results show that all 13 of the dusts investigated sintered considerably with time at 500 °C. At 400 °C, the results differ markedly. Four of the dusts sintered with a similar behaviour as at 500 °C, i.e. the specific surface area decreased with time, but to a lower extent. The other nine dusts hardly sintered at all at the lower temperature. Three of the four that did sinter are among the ones that sintered the most at 500 °C.

Earlier studies by Techakijajorn et al. (1999) and Tran et al. (1988) have showed that sintering of pressed dust pellets starts at temperatures as low as 300 to 350 °C. The fact that higher temperatures are needed in the present study may be because of the lower bulk density of the dust samples.

Figures 3 and 4 show all of the dusts investigated and how they sinter with time. Here, sintering is measured as the ratio between the actual specific surface area after sintering and the original specific surface area (S/S_0). As can be seen, the difference in sintering is substantial for the two temperatures.

The particle size is known to influence sintering so that, with everything else being equal, larger particles sinter more slowly (German, 1996). With the help of SEM images the mean particle size of the unsintered dust was estimated. According to that estimation, dust # 14 have a significantly larger mean particle size and is also one of the dusts that sinter the least. Dust # 43 was found to have the largest calculated mean particle size and this dust also sinters slowly.

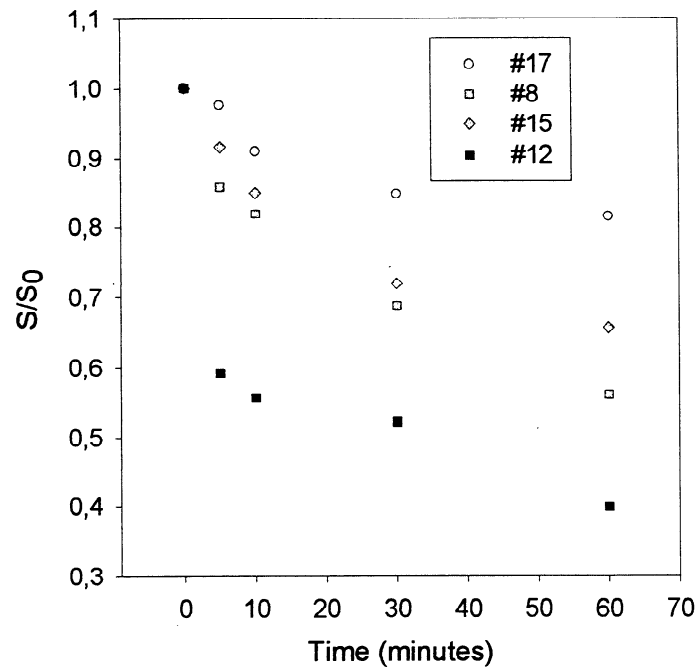


Figure 3. Sintering at 400 °C for the four dusts that sintered measurably. The numbers shown in the graph refer to the different dusts.

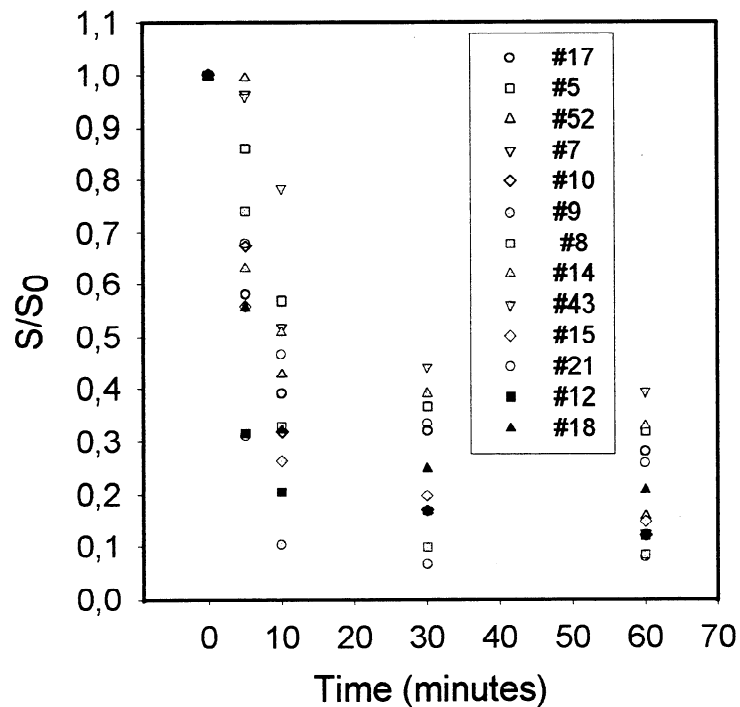


Figure 4. Sintering at 500 °C for all of the dusts.

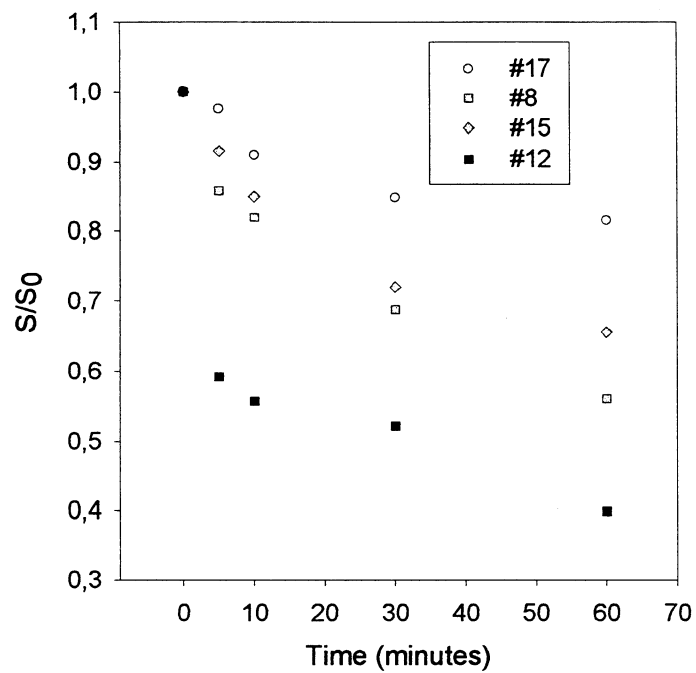


Figure 3. Sintering at 400 °C for the four dusts that sintered measurably. The numbers shown in the graph refer to the different dusts.

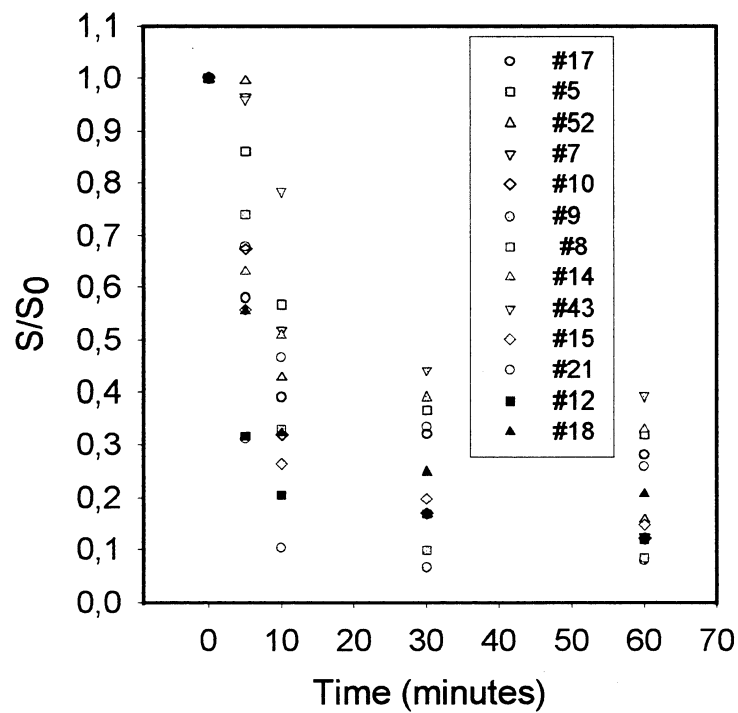


Figure 4. Sintering at 500 °C for all of the dusts.

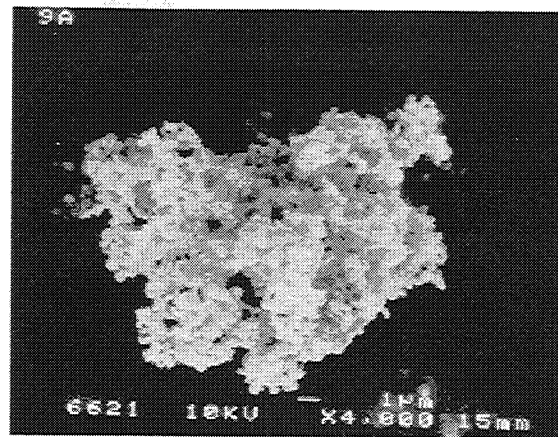


Figure 5a. Dust #9. Unsintered.

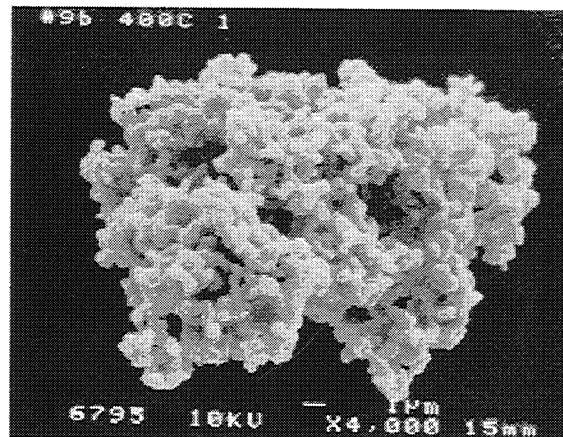


Figure 5b. Dust #9. Sintered for 1 hour at 400 °C.

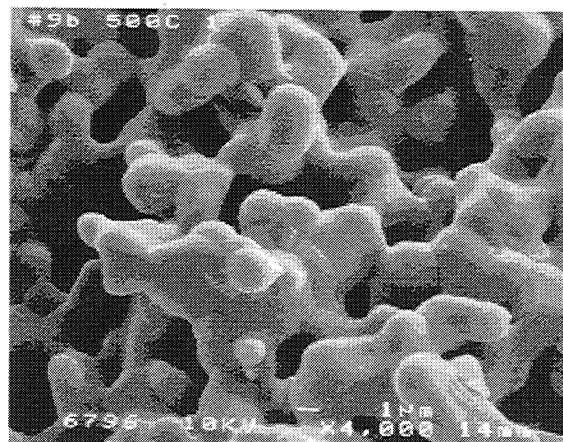


Figure 5c. Dust #9. Sintered for 1 hour at 500 °C.

The change in microstructure is evident when studying SEM images at different temperatures. Figure 5 shows dust # 9, unsintered as well as after 1 hour of heat treatment in both 400 and 500 °C. From a mean particle size of about 0.3 µm when the dust is unsintered, the particles grow and are about 0.6 µm when treated at 400 °C and over 2 µm when sintered in 500 °C. When studying the images, it is clear that several cycles of sintering have occurred, i.e. when particles of original size have sintered together and become larger and fewer, those large particles sinter in turn.

Sintering of precipitator dust has been related to the first melting temperature (FMT) of the dust (Lien et al., 1999). In the present study, based of the composition of the dusts, the software package ChemSage has been used to calculate FMT for each dust. Generally speaking, potassium, chloride and carbonate decrease FMT while sodium and sulphate increase it. Figure 6 shows how sintering is related to the FMT for the dusts investigated.

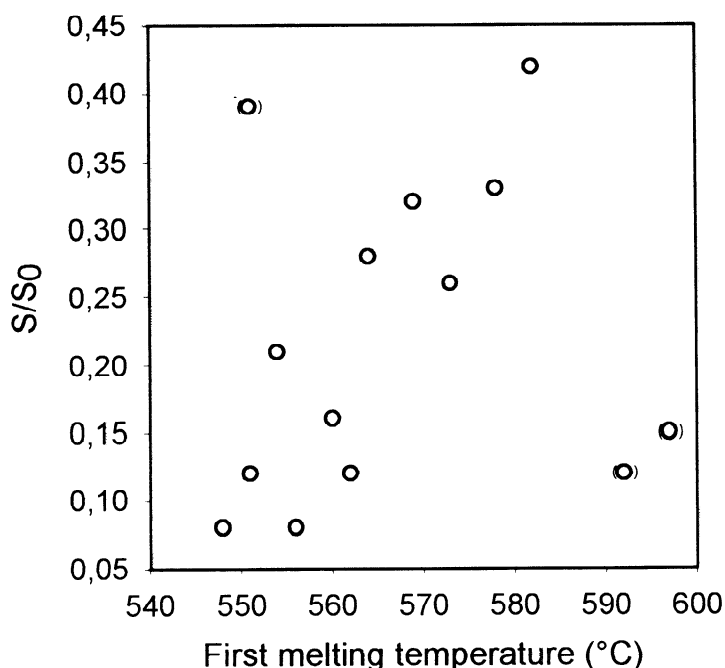


Figure. 6. Sintering versus the first melting temperature. The general trend shows increasing sintering (smaller S/S_0) with decreasing first melting temperature. The sintering temperature was 500 °C and the run time 1 hour.

The general trend seems to be that sintering increases with decreasing FMT but with a couple of severe outliers. This general trend seems reasonable, as mobility of ions in the solid increases as the FMT is approached. The outlier with a lower degree of sintering despite its low FMT is dust # 43. This dust has the second lowest original specific surface area. Figure 7 shows how the original specific surface area influences the degree of sintering and the trend seems clear. The

lower the original specific surface area, the lower the degree of sintering. This may explain the odd behaviour of # 43.

The two outliers on the other end, 12 and 15, are the two dusts with the highest concentrations of sulphate and lowest in carbonate, hence their high calculated FMTs. Earlier FMT calculations have been compared with experimental measurements made at the University of Toronto (Frederick, 1999). Those comparisons have shown that ChemSage consistently overestimates the FMT value and, also, that this overestimation is highest when the concentration of potassium is high and carbonate is low. Both # 12 and 15 fit this description well and, consequently, their calculated FMTs, are possibly too high compared to the other dusts. If their FMTs were reduced, the dusts would fit closer to the general trend.

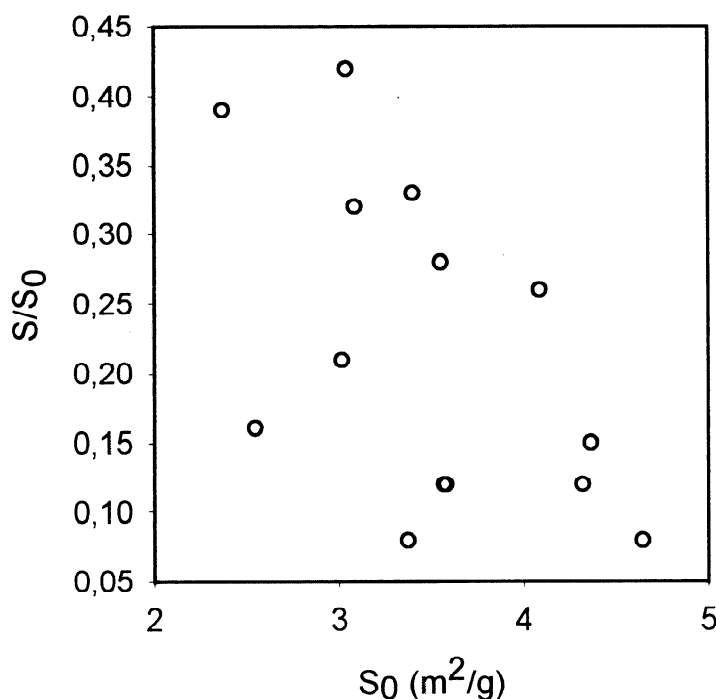


Figure 7. Sintering after one hour at 500 °C versus the original specific surface area

Attempts to fit the results to the German Munir model were made (German and Munir, 1976). This model is only valid up to about 50 % of sintering and, therefore, the sintering process was divided into two parts where the specific surface area after 50 % of sintering was used as S_0 for the latter part of the sintering process. Because of the rapid decrease of the specific surface area in the beginning, this $S_{50\%}$ used as S_0 for the latter part, was usually reached within five minutes. This makes it impossible to fit the first part of the sintering process to the German Munir equation since

this rapid decrease is represented by a straight line. Also, the heat-up period of the sample was about 5 minutes and this naturally affects the sintering behaviour as well. However, the latter part was fitted and k - and γ -values were obtained. The average standard deviation for k was 4 % and for γ , 3 %. The average deviation between calculated and measured specific surface areas was 13 %.

As mentioned before, the γ -value indicates the transport mechanism involved in the sintering process. Multicomponent materials such as recovery boiler dusts, which contain volatile alkali chlorides as well as far less volatile salts, may sinter by more than one mechanism. However, the γ -value may still be used to suggest what mechanisms may dominate. It should be noted that the dependency between k and γ is strong, hence, it has to be acknowledged that it is difficult to evaluate the transport mechanism using the γ -value in this case. However, most dusts had γ -values between 1 and 4, indicating more than one transport mechanisms such as evaporation condensation, volume diffusion, grain boundary diffusion and surface diffusion. It could not be shown that the γ -value was related to the composition of the dust.

The rate constant in the German Munir model can also be presented as $k^{1/\gamma}$, here called k' . Figure 8 shows k' for the latter part of the sintering process at 500 °C versus FMT. Except for the two outliers, # 12 and 15, the rate constant k' increases with decreasing FMT. Again, a better estimation of the FMT's of # 12 and 15 might make these dusts fit the trend better.

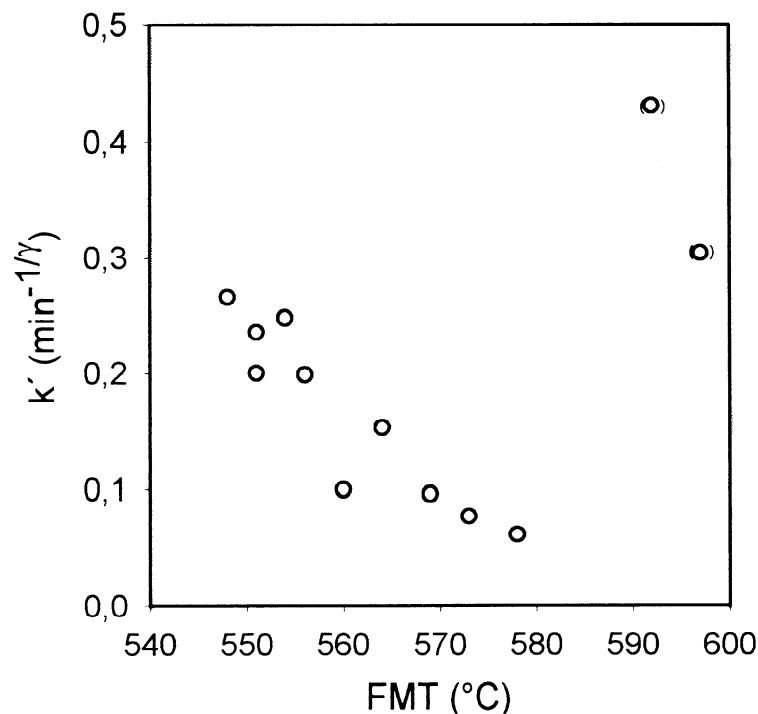


Figure 8. The rate constant k' for all dusts versus FMT.

CONCLUSIONS

The study shows that the temperature needs to be 500 °C for all the dusts to sinter at the low densities used. The specific surface area decreases with increasing time and fits the German Munir model well. The reduction of the specific surface area was found to correlate with the first melting temperature of the dust, with increased sintering for dusts with low first melting temperatures. Moreover, the rate constant in the German Munir model was strongly related to the first melting temperature. No correlation between the sintering mechanism and the composition of the dust could be found.

ACKNOWLEDGEMENTS

The authors want to thank Professor Honghi Tran for fruitful discussions. Mr. Aslan Akbas is gratefully appreciated for his work with analyzing the surface areas. The Swedish National Board for Industrial and Technical Development is acknowledged for the financial support of the project.

NOMENCLATURE

k	Rate coefficient of sintering (min^{-1})
k'	Modified rate coefficient of sintering ($\text{min}^{-1/\gamma}$)
S	Specific surface area (m^2/g)
S_0	Initial specific surface area (m^2/g)
t	Time (min)
γ	Exponent in the expression of German and Munir (-)

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PAPER NO. 20A

**Mechanisms of Hardening of Sodium Salt Deposits in the Boiler Banks of
Kraft Recovery Boilers**

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ABSTRACT

The sintering behavior of eight recovery boiler dusts was evaluated. The dusts were formed into pellets and exposed to a range of temperatures between 300 and 700°C. Sintering was measured by recording the change in volume of the pellets with time. The eight dusts sintered at widely different rates. The sintering rates did not correlate well with dust composition.

Each of the chloride-containing dusts sintered initially by evaporation and recondensation of NaCl and KCl, in parallel with solid-state diffusion. For dusts with more than 10 mol-% chloride, sintering proceeded by the evaporation-condensation mechanism throughout the initial sintering stage. Those with less chloride changed sooner to solid-state diffusion sintering.

There was a strong correlation between the first melting point of the dust and the rate constant for sintering by evaporation and condensation of NaCl and KCl. This correlation provides a method for estimating the sintering tendency of a dust, based on its composition and first melting point.

INTRODUCTION

The flue gas in kraft recovery boilers contains a high concentration of sub-micron condensation aerosol particles, typically 30–60 g/Nm³. These fine particles are often referred to as “fume” or “dust.” The particles can deposit in the superheater, boiler, and economizer banks of kraft recovery boilers, and can plug the gas passages. The result is reduced heat transfer efficiency and lower overall black liquor throughput rates. Sintering - the process of densification of porous solids - is responsible for hardening of fume deposits. As deposits densify, their strength increases exponentially with pellet density (1), and they become more difficult to remove by sootblowing. Fume particles begin to sinter at about 300°C, and the rate of sintering increases rapidly with temperature (2–4).

Sintering rates of recovery boiler deposits are apparently controlled by a combination of dust composition, particle packing density, and temperature. There is wide variation in the sintering behavior and composition of dusts from different recovery boilers. No clear trend of sintering rate with composition has as yet been reported for recovery boiler dusts.

A model for the rate of thermal sintering at recovery boiler conditions was developed and reported earlier (3). The model was based on rate equations for sintering by solid-state diffusion. Numerical constants for one dust were reported, but they do not predict sintering rates accurately for other dusts. The objectives of the work reported here was to determine the relationship between the composition and sintering characteristics of sub-micron aerosol particles from kraft recovery boilers.

EXPERIMENTAL PROCEDURE

The results reported in this paper were obtained from three separate studies, all using similar methods. In all three data sets, the dusts used were collected from the electrostatic precipitator (ESP) catch at the outlet of the recovery boiler. Each dust sample was from a different recovery boiler. These dusts were formed into pellets, weighed and measured, and then exposed to a high temperature environment at a fixed temperature for a given period of time (Figure 1). The sintering rate was determined by measuring the change in diameter of the pellets with time during sintering.

Table 1 summarizes the sintering conditions for the measurements made in all three studies. The first set of data was from the M.S. thesis of Techakijkajorn (3). In that study, sintering measurements were made for two different ESP dusts; one that contained low levels of chloride (#3) and one with relatively high levels of chloride (#4). Sintering tests were performed at temperatures of 300, 350, 400, 450, 500 and 550 C. The second set of data (dust L) was from Ling (4) and the third (current study) from subsequent measurements at the University of Toronto. Five different dusts were used in this study (B, C, D, E and G), and temperatures of 350, 400, 450, 475, 500, 550, 575, 600 and 700°C were employed.

The experimental method was very similar in these three studies. In all cases, pellets one inch (25.4 mm) in diameter with a thickness of 3.5 to 7.0 mm were formed by placing about 3 g of dust into a cylindrical pellet mold press. The pellets produced had an average initial density ranging from 0.88 to 1.43 g/cm³, but most of the dust pellets had an initial density of about 1.20 g/cm³. A few pellets were pressed at lower pressures to determine the effect of density on sintering rate. The pellets were weighed and measured, and then pre-heated to approximately 200°C in a conditioning furnace before testing. This temperature was low enough so that no sintering occurred. Testing was initiated by quickly transferring the pellets to the furnace at test condition. Thermocouple measurements indicated that the pellets reached the temperature of the sintering furnace in 2-3 minutes.

In the first study (with dusts #3 and #4) the pellets were removed from the furnace at the end of the test period, and then weighed and measured with a micrometer to determine the change in the thickness, diameter and weight of the sample. In the second and third studies, for the six dusts labeled B, C, D, E G, and L, the shrinkage was measured through the use of a video camera to monitor the diameter of the pellets over time as they sintered and contracted (Figure 1). This has the advantage of providing a continuous record of the pellet diameter vs. time throughout the test and produced significantly more data for each test run. At the end of the test, the pellet was removed from the furnace, cooled, and then weighed and measured.

SINTERING DATA

The data for all of seven of these dusts were combined into a single data set and analyzed. The combined data could be presented in several different formats, either as density or volume or one-dimensional lengths. Since there was no significant weight loss during sintering, the change in diameter of the pellets was used to characterize sintering. The data were normalized by dividing the change in diameter by the initial diameter as shown below (Equation 1) where $L(t)$ is the pellet diameter at time t and L_0 is the initial pellet diameter. The normalized dimension change will have an initial value of zero and will increase to a maximum value of less than one.

Equation 1:

$$\frac{\Delta L}{L_0} = \frac{L_0 - L(t)}{L_0}$$

The sintering behavior of the eight recovery boiler dusts was evaluated graphically using the format shown in Equation 1, above. The normalized change in diameter ($\Delta L/L_0$) was plotted as a function of time for each of the dusts and sintering temperatures. A typical set of data is shown below in Figure 2. This data is for seven of the dust samples sintered at 450°C, and one (Dust G) at 475°C. All of the dusts except dust G sinter rapidly at first, but the rate of sintering slows with time. Dust G sintered so slowly at 450°C that it was not possible to measure its sintering at that temperature.

SINTERING MECHANISMS

Sintering in recovery boiler dusts proceeds initially by one or both of the two mechanisms illustrated in Figure 3. The first of these is sintering by solid-state diffusion (Figure 3A), with ions diffusing across the contact area (neck) between two particles. Diffusion may occur along grain boundaries, along the surface of the particles, or by bulk diffusion. The particles combine into a larger particle that is shorter than the length of the two original particles. This mechanism leads to shrinkage of particle compacts such as boiler bank deposits or the pellets used in this study. It is the most common method by which ceramic materials and metals sinter. It is well understood for pure substances, but not for mixtures (5).

The second mechanism is sintering by evaporation and condensation of volatile components within the particles (Figure 3B). The volatile components evaporate from the low curvature surface of the particles, and condense in the high curvature neck region. The particles combine into a larger, single particle. This mechanism by itself results in far less shrinkage of particle compacts. NaCl particles sinter by this mechanism (5).

As the necks become larger, the void space between the particles shrinks and at some point, smaller particles will combine with larger particles, resulting in a measurable increase in average grain-size. This is where the intermediate stage of sintering starts. In this stage, the growth of the particle (or grain) size is the critical factor. The final stage occurs when all the pores are closed and only grain growth continues. Shrinkage or densification occurs mostly in the first two stages. In the final stage, the densification rate is extremely low and this stage is not expected to be an important factor in the sintering behavior of these dusts. In real particle assemblages, there is no clear transition point between each stage because the compact material contains particles with a distribution of sizes and packing densities.

Initial Sintering Stage

Kingery et al. (6) have developed closed-form equations to predict sintering as a function of time, temperature, and materials properties. Equation 2 is their equation for sintering by solid state diffusion processes. The constants γ , a , D^* , and k can be combined into a single, dust-specific constant, yielding Equation 3. It predicts that sintering by solid state diffusion processes will be proportional to the ratio of sintering time to absolute temperature to the 0.4 power.

Equation 2:

$$\frac{\Delta L}{L} = \left(\frac{20 \gamma a^3 D^*}{\sqrt{2} k T} \right)^{0.4} \frac{t^{0.4}}{r^{1.2}}$$

where:

$\Delta L/L_0$	= relative linear shrinkage
γ	= surface energy
a	= atomic radius
D^*	= diffusion coefficient for the specific diffusion process involved
r	= initial particle size
k	= Boltzmann's constant
T	= absolute temperature
t	= time

Equation 3:

$$\frac{\Delta L}{L} = \frac{K_D}{r^{1.2}} \left(\frac{t}{T} \right)^{0.4}$$

where: K_D = Dust specific sintering constant for solid-state diffusion mechanism

Equation 4 is the Kingery et al. equation for sintering by evaporation-condensation processes. The constants γ , M , R , and d can be combined into a single, dust-specific constant, yielding Equation 5. It predicts that sintering by evaporation-condensation processes will be proportional to the product of sintering time times the partial pressure of NaCl to the 1/3 power, divided by the square root of absolute temperature.

Equation 4:

$$\frac{\Delta L}{L} = \left(\frac{3\sqrt{\pi}\gamma M^{1.5} p_o}{\sqrt{2}R^{1.5} T^{1.5} d^2} \right)^{1/3} \frac{t^{1/3}}{r^{2/3}} = \frac{K_{E-C}}{r^{2/3}} \left(\frac{t^{1/3} p_o^{1/3}}{T^{0.5}} \right)$$

where:

M	= molecular weight of the evaporating compound
P_o	= vapor pressure of the pure evaporating compound
R	= ideal gas constant
d	= density of the void-free solid
P_{NaCl}	= $X_{NaCl} P_{o,NaCl}$

Equation 5:

$$\frac{\Delta L}{L} = \frac{K_{E-C}}{r^{2/3}} \left(\frac{t^{1/3} P_{NaCl}^{1/3}}{T^{0.5}} \right)$$

where: K_{E-C} = Dust specific sintering rate for evaporation-condensation mechanism

ANALYSIS OF SINTERING DATA

The sintering data for all eight dusts were evaluated by plotting them in the form of 3 and 5. The plots shown in Figures 4-6 are typical of the three groups into which the eight dusts fell.

Dust G, shown in Figure 4, contained neither chloride nor carbonate. Its potassium content was typical of all but one of the dusts. Because this dust contained no chloride, its sintering data plot is shown only for the solid-state diffusion model, Equation 3. The data plot as straight lines that fall into two sets of nearly coincident lines. This result indicates that the solid state diffusion model is appropriate for Dust G.

The data at the two lower temperatures fall together in a separate pair of lines from the three higher temperature sets. The decrease in slope at longer times indicates the transition from primary sintering to secondary sintering. This dust sintered very little at these temperatures - only 2-3% before stopping altogether. This may be because the temperature was too low for significant diffusion.

Dust C was one of the highest chloride content dusts. It follows the Evaporation-Condensation model rather well, to at least 10% shrinkage (Figure 5A). The Solid State Diffusion model does not fit well at all. We conclude that, for this dust, the sintering mechanism during the initial sintering stage is Evaporation-Condensation, most likely of NaCl and KCl. The two other high chloride content dusts (D, 13.6% Cl) and #4 (13.5% Cl) showed the same trends in each plot.

Dust E was a moderate Cl-content dust. It seems to follow the Evaporation-Condensation model at shorter sintering times, up to 2-8% linear shrinkage (Figure 6). The Solid State Diffusion model does not fit well at all. It is likely that the amount of chloride present in the dust was not enough to complete the initial stage of sintering. At some point, therefore, sintering by Evaporation-Condensation became slower than by Solid-State Diffusion, and the latter eventually becomes the dominant mechanism. We conclude that, for this dust, the sintering mechanism during the initial sintering stage was first Evaporation-Condensation, but that a transition to Solid-State Diffusion occurred before the initial stage sintering was complete. The two other low-to-intermediate Chloride content dusts (B, 0.5% Cl) and #3 (2.2% Cl) showed the same trends in each plot.

EFFECT OF FIRST MELTING TEMPERATURE ON SINTERING RATES

Efforts to correlate sintering rate with dust composition have not previously yielded useful results, and did not in this study. The melting temperature of pure compounds (first melting temperature of solid solutions and mixtures) has been shown to correlate better with sintering rate. To determine whether a useful correlation between sintering rate and first melting temperature (FMT) could be obtained, we took the slopes of the linear sintering versus $(P_{\text{NaCl}})^{1/3}/T^{1/2}$ from the Evaporation-Condensation sintering plots for Dusts C, D, E, L, #3, and #4. The slopes were fairly constant for each individual dust, independent of temperature. This indicated that (a) the slopes were a unique property of the individual dusts, and (b) the contribution of solid state sintering was either small (more likely) or increased with temperature in proportion to that of evaporation-condensation sintering (less likely). We refer to these slopes as the "Sintering Constant" for dusts that contain at least moderate amounts of chloride.

The slopes obtained are included in Table 3. All slopes for which accurate measurements could be obtained from the evaporation-condensation sintering plots were included. The FMT and the chloride content are also included for each dust.

The data from Table 3 are plotted as Sintering Constant versus FMT in Figure 7. The results show a surprisingly strong correlation for FMT's below about 535°C. Above this, there is apparently no strong relationship between FMT and sintering.

CONCLUSIONS

During the "Initial Sintering" stage, dusts with moderate to high chloride content sinter by an evaporation-condensation mechanism. Those with no chloride sinter by a solid-state diffusion mechanism. Dusts with low to moderate chloride contents eventually switch to solid-state diffusion sintering.

The "Sintering Constant" is a unique property of a dust. It depends on dust composition (and the first melting temperature), but not sintering temperature. It can be used to estimate the sintering tendency of a dust, and to guide changes in recovery boiler operation to slow hardening of deposits.

ACKNOWLEDGEMENTS

Funding for this research was provided by the Recovery Boiler Research Consortium at the University of Toronto and the Office of Industrial Technologies of the U.S. Department of Energy.

Kimberly Chao assisted in the analysis of the sintering data and prepared the figures.

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Table 1. Elemental composition (wt %) and first melting temperatures for the dusts used in this study.

Dust	K	Cl	CO ₃	FMT, °C
B	3.7	0.5	6.5	552
C	4.0	12.4	0.6	560
D	4.4	13.6	5.5	544
E	4.7	2.4	13.5	529
G	5.2	0.0	0.0	810
L	6.5	2.0	2.5	530
#3	9.9	2.2	3.1	526
#4	5.9	13.5	4.9	534

Table 2. The sintering temperature and times and the initial density of the sintered pellets.

Dust	Source	Temperature, °C	Initial density, g/cm ³
#3	Ref. 3	300-550	1.43
#4	Ref. 3	350-500	1.18
B	This study	350-500	1.20
C	This study	350-550	1.20
D	This study	400-550	1.20
E	This study	350-500	1.20
G	This study	475-700	1.45
L	Ref. 4	350-550	1.36

Table 3. Sintering Constants, first melting temperatures, and chloride contents for the six dusts that contained more than 0.6% chloride.

Dust	Cl, wt-%	FMT, °C	K _{E-C} Sintering Constant ^a , fractional shrinkage/(min atm) ^{1/3} K ^{1/2}					
			350°C	400°C	450°C	500°C	550°C	Average
#3	2.2	526	1365	2195	1303	1407		1568
#4	13.5	534		762	675			719
C	12.4	560		386	455	384	478	426
D	13.6	544		283	270	198	272	256
E	2.4	529			1083	1539		1311
L	2.0	530	906	1045	968	1407	1297	1125

^aInitial slope of linear shrinkage versus $(P_{\text{NaCl}} t)^{1/3}/T^{1/2}$

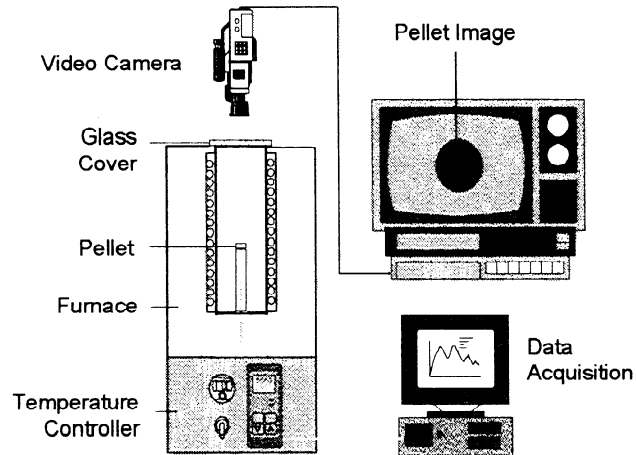


Figure 1. Sintering measurement apparatus at the University of Toronto.

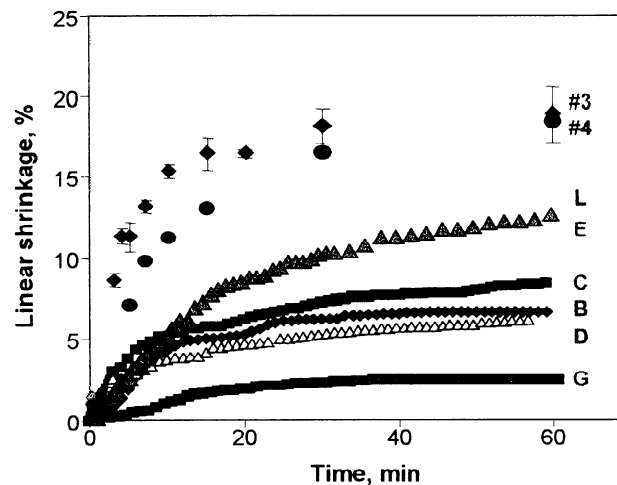


Figure 2. Linear shrinkage versus time for eight precipitator dusts. Dust G was sintered at 475°C, the others at 450°C.

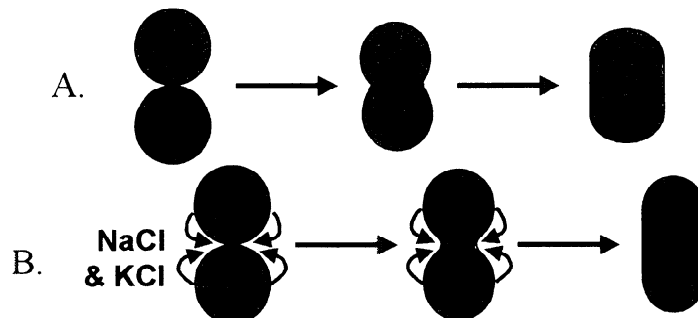


Figure 3. Sintering mechanisms for recovery boiler dusts: A. sintering by Solid-State Diffusion; B. sintering by Evaporation-Condensation.

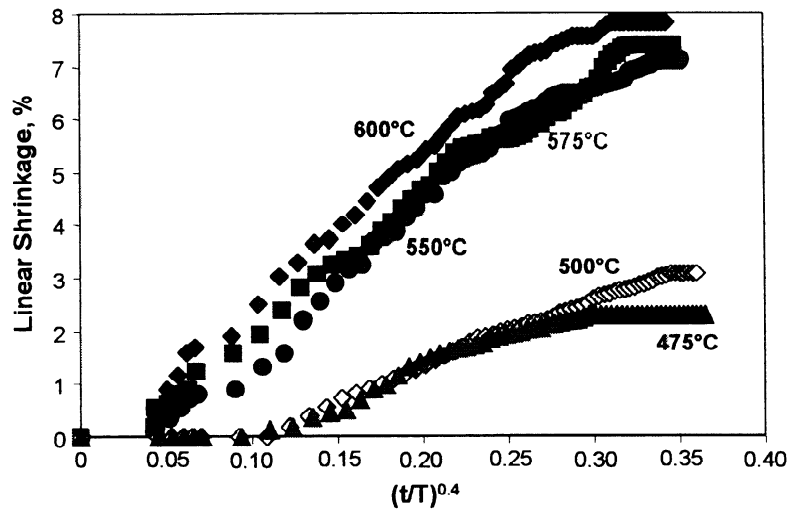


Figure 4. Test of solid state diffusion sintering for Dust G (0% Cl, 0% CO₃, 5.2% K).

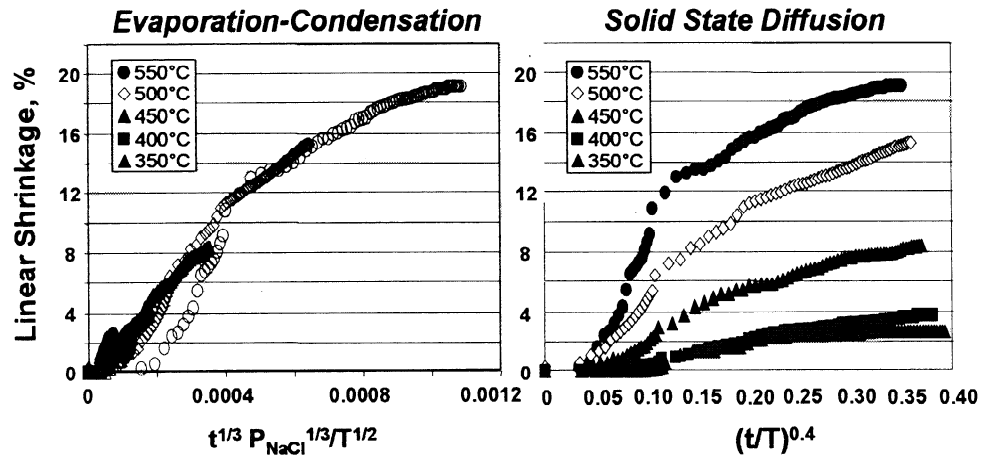


Figure 5. Test of both sintering mechanisms for Dust C (12.4% Cl, 0.6% CO₃, 4.0% K).

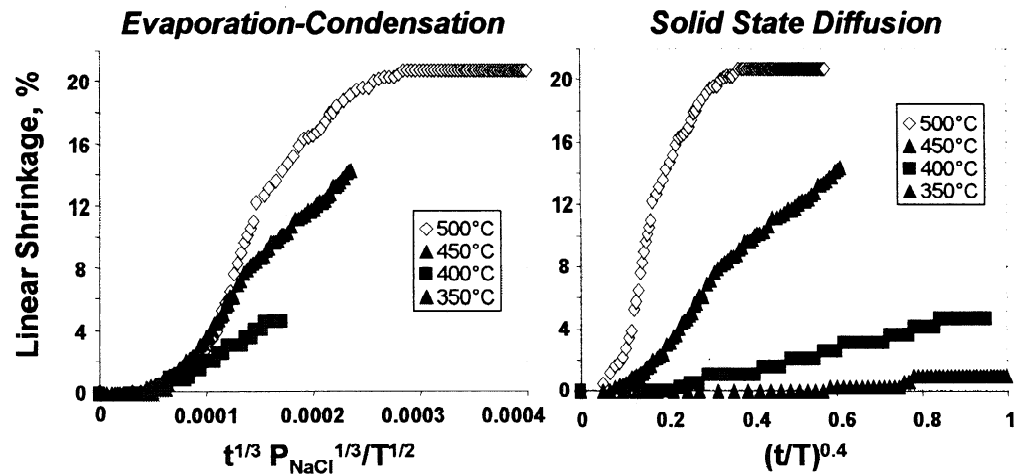


Figure 6. Test of Both Sintering Mechanisms for Dust E (2.4% Cl, 13.5% CO_3 , 4.7% K).

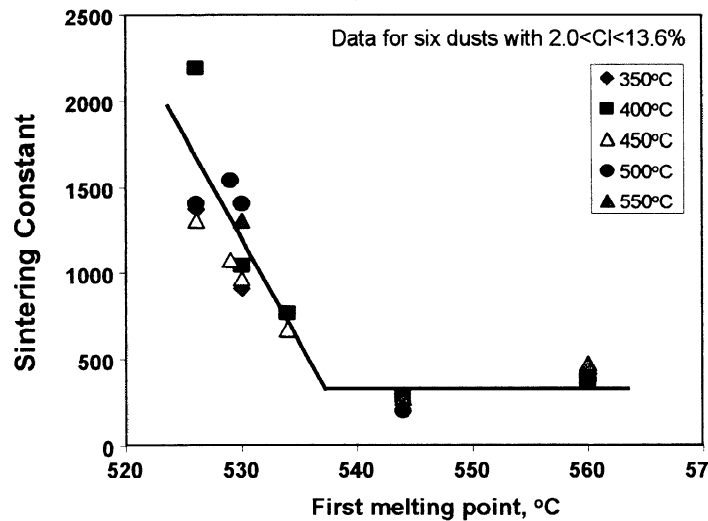


Figure 7. Plot of Sintering Constants versus temperature for the six dusts containing more than 2% chloride.

DUES-FUNDED PROJECT SUMMARY

Project Title: BLACK LIQUOR
DEVOLATILIZATION KINETICS
Project Code:
Project Number: F038-03
PAC: CHEMICAL RECOVERY

Project Staff

Principal Investigator: Kristiina lisa
Co-Investigators: Scott Sinquefield
Research Support Staff: Qun Jing

PAC Subcommittee N/A

FY 99-00 Budget: \$57,540
Allocated as Matching Funds: 0%

Time Allocation:

Principal Investigator: 9%
Co-Investigators: 8%
Research Support Staff: 25%

Supporting Research:

Special Students: None
External (Where Matching Is Used): None

RESEARCH LINE/ROADMAP: Line #8 - Develop technologies (compatible with present pulp-mill assets) to allow cost-effective expansion of kraft-pulp-equivalent fiber capacity (hardwood and softwood) by 30% without adding Tomlinson recovery boilers.

PROJECT OBJECTIVE: Brief statement of the objective of the dues funded research project. The objective should be clear and to the point, such that the PAC will be able to judge when the project has been successfully completed.

PROJECT BACKGROUND:

The energy performance and capacity of kraft recovery boilers are highly sensitive to black liquor drying and devolatilization (pyrolysis) processes. Rates of drying and volatiles release strongly affect the temperature profile and combustion stability in recovery boilers. Devolatilization conditions affect the reactivity and yield of char which, consequently, affect carbon removal and sulfate reduction reactions in the char bed.

The intrinsic kinetics of black liquor devolatilization have not been measured and the effect of black liquor drop size on fundamental burning processes has not been experimentally verified. This information is needed to improve the design and operation of kraft recovery boilers, to improve energy efficiency, and to maximize throughput and availability of recovery boilers.

MILESTONES:

Completion of project – June 2000.

DELIVERABLES:

Rate data for black liquor devolatilization at high temperatures, including the evolution of carbon, sulfur, nitrogen alkali metal and chlorine.

STATUS OF GOALS FOR FY 99-00:

Modifications to laminar entrained-flow reactor – under progress

Devolatilization experiments – to be done February – March 2000

SCHEDULE:

Task Descriptions (example)	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
1. Modification to LEFR			---X	
2. Devolatilization experiments			-----X	
3. Data analysis				-----X
4. Final report				---X

SUMMARY OF RESULTS:

The devolatilization experiments have been scheduled for February-March 2000. The first results of these experiments will be reported at the spring PAC reports.

DUES-FUNDED PROJECT SUMMARY

Project Title: SULFATION OF FUME PARTICLES IN RECOVERY BOILERS
Project Code: -
Project Number: F038-04
PAC: CHEMICAL RECOVERY

Project Staff

Principal Investigator: Kristiina lisa
Co-Investigators: Scott Sinquefield
Research Support Staff: Qun Jing

PAC Subcommittee None

FY 99-00 Budget: \$48,139
Allocated as Matching Funds: 0%

Time Allocation:

Principal Investigator: 9%
Co-Investigators: 8%
Research Support Staff: 25%

Supporting Research:

Students: None
External (Where Matching Is Used): None

RESEARCH LINE/ROADMAP: Line #8 - Develop technologies (compatible with present pulp-mill assets) to allow cost-effective expansion of kraft-pulp-equivalent fiber capacity (hardwood and softwood) by 30% without adding Tomlinson recovery boilers.

PROJECT OBJECTIVE: Develop a kinetic model for the sulfation of alkali metal salts (Na_2CO_3 , NaOH , NaCl) in recovery boilers.

PROJECT BACKGROUND: The chemical composition of fume particles affects both the formation and hardening of deposits on heat exchanger surfaces. A crucial factor affecting both stickiness and strength is the chloride content of the deposits. Deposits with even high K but low Cl content do not harden as much as deposits with a high chlorine content. Therefore the key to controlling recovery boiler plugging and fouling is to obtain fume with a low Cl content. The fume Cl content can be kept low by keeping Cl volatilization low or by enhancing NaCl/KCl conversion to Na_2SO_4 . The objectives of the proposed research are to define optimum conditions for producing fume particles with low Cl content and at the same time keeping SO_2 emissions acceptable

MILESTONES:

1. A comparative assessment of the rate of each sulfation reaction, due date May, 2000.
2. Kinetic expression for each salt deemed to be of interest, due date May 2001.

3. Assessment of the importance of each reaction in recovery boilers, and recommendation for optimum conditions, June 2001.

DELIVERABLES:

1. Kinetic data and expressions for the sulfation of sodium salts (Na_2CO_3 , NaCl , NaOH) in the vapor and condensed phase.
2. Provide basis for assessing if it is possible to obtain low (near-zero) SO_2 emissions at the same time as providing desirable fume properties.

STATUS OF GOALS FOR FY 99-00:

Goal by the spring PAC meeting (March 2000):

- Finish equilibrium analysis, completed.

Goals by the end of the current fiscal year (July 31, 2000):

- Finish screening experiments to determine relative sulfation rates.
- Kinetic data for one sodium compound.

SCHEDULE:

Task Descriptions	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
1. Equilibrium Analysis		-----	-----X	
2. Screening Experiments			----	---X
3. Sulfation of one salt.				-----X

SUMMARY OF RESULTS: Due to equipment availability, the experimental part of this project has been scheduled for the last third of the fiscal year and has not begun yet. So far, only equilibrium analysis has been performed. The aim of the equilibrium analysis was to assess if there are any thermodynamic limitations for the sulfation reactions, and if the partial pressures of the compounds are high enough for studying the reactions in the laminar entrained-flow reactor.

SUMMARY OF KEY CONCLUSIONS:

The conclusions of the thermodynamic analysis are as follow:

- NaOH and Na_2CO_3 may thermodynamically be sulfated to above 99% both at the planned experimental conditions and at gas concentrations typical of recovery boilers.
- The sulfation of NaCl is thermodynamically limited. At the planned experimental conditions, over 99% conversion can be obtained at 900°C but only 70% at 1100°C .
- The vapor pressures of NaOH and NaCl are sufficient for the study of the reactions both in the vapor and condensed phase in the laminar entrained-flow reactor
- NaOH vapor could alternately be formed by feeding Na_2CO_3 in water vapor.

DISCUSSION:

The aim of thermodynamic analysis was twofold: to determine if quantities sufficient for the detection of the products will vaporize in the laminar entrained-flow reactor, and if there are thermodynamic limitations to the sulfation reactions either in the experimental conditions or in recovery boilers. The calculations were made using HSC Chemistry Version 2.03.

1) Partial pressures of the sodium salts.

In the laminar entrained-flow reactor, typical solid feed rates are 0.2-1.0 g/min and gas feed rates 10-20 l/min. The conversion in the vapor phase is measured from submicron particles that condense upon cooling. For reliable analysis, at least 0.01 g/min of the submicron particles need to be collected. Therefore, a minimum of 1-5 % of the feed solids needs to become vaporized. If a compound has a vapor pressure higher than 0.001 atm, it will be completely vaporized at equilibrium under the experimental conditions. The rate of vaporization, however, is limited by heat and mass transfer and the limit for successful experiments may be higher than the equilibrium analysis predicts.

The vapor pressures of NaCl and NaOH are shown in Figure 1 and Figure 2. The vapor pressure of NaCl is above 0.02 atm at all conditions. This means that thermodynamically, all of the NaCl in a typical experiment (10 l/min gas flow, 0.3 g/mol solid flow) vaporizes. Besides NaCl, considerable amounts of gaseous Na_2Cl_2 are present at equilibrium: 39-45% of the Na will be Na_2Cl_2 .

Na_2CO_3 does not exist in the vapor phase. In N_2 , some Na_2CO_3 may decompose to Na_2O or vaporize as Na(g) but the amounts are not significant in the planned experimental conditions. In a typical experiment less than 3.5% of the Na_2CO_3 would decompose to Na_2O and less than 1.5% would be vaporized as Na at equilibrium. The decomposition could be prevented by adding as little as 1% CO_2 in the feed gas, and the fractional vaporization to elemental Na could be reduced by increasing the solids flow rate.

The vapor pressure of NaOH is lower than that of NaCl. At 900°C, with 10 l/min, only 0.02g/min of NaOH will become vaporized at equilibrium, 0.09 g/min at 1000°C, and 0.30 g/min at 1100°C. These are, however, expected to be sufficient for accurate measurements.

Another possible problem with NaOH is that it is extremely hygroscopic and hence difficult to feed. One option would be to feed Na_2CO_3 and have it react with water vapor to form NaOH. The equilibrium partial pressures of NaOH at varying fractions of H_2O in the feed gas are shown in Figure 3. These are approximately half of the vapor pressures of NaOH and may thus be sufficient.

2) Sulfation of the sodium salts

NaOH and Na_2CO_3 and NaOH will be completely sulfated at the planned experimental conditions (900-1100°C, 2-5% SO_2). The sulfation of NaCl, on the other hand, is thermodynamically limited in particular at the higher temperatures. Over 99% sulfation can be obtained at 900°C but only 70% at 1100°C as can be seen in Figure 4. This

thermodynamic limitation needs to be taken into account when interpreting the experimental data.

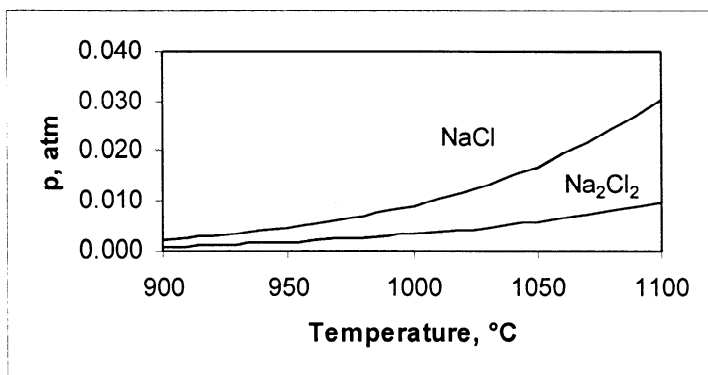


Figure 1. Partial pressures of NaCl and Na₂Cl₂ over pure NaCl.

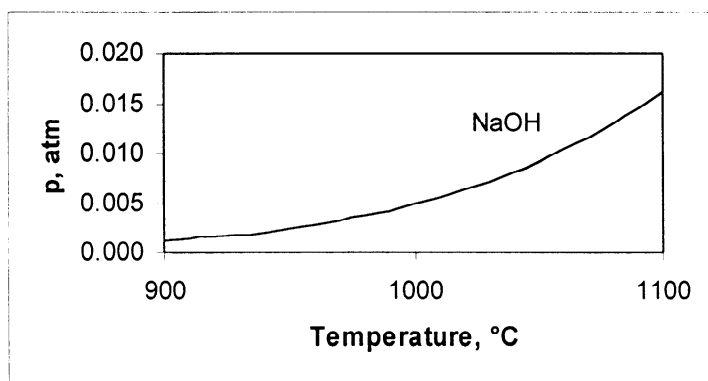


Figure 2. Vapor pressure of NaOH.

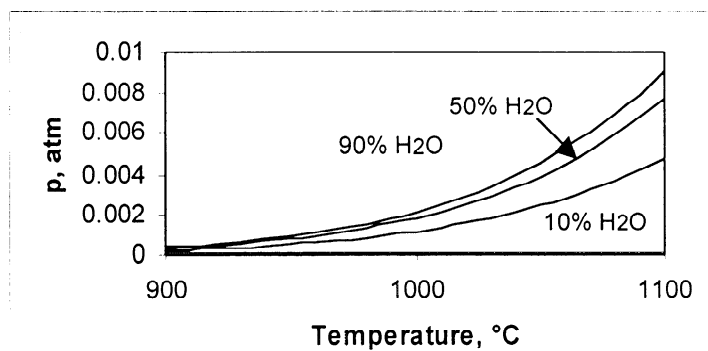


Figure 3. Partial pressure of NaOH over Na₂CO₃.

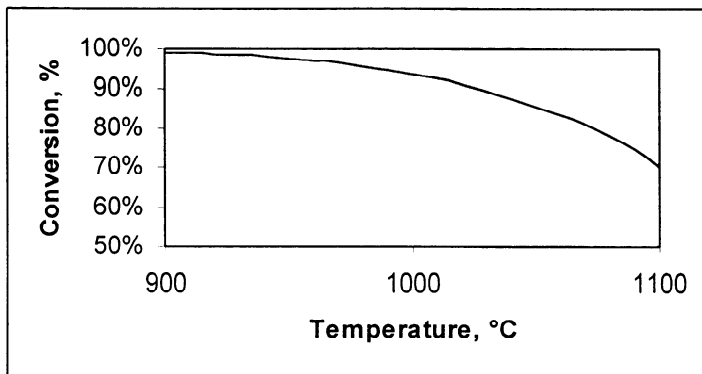


Figure 4. Equilibrium conversion of NaCl with 0.25 g NaCl and 10l/min (at 25°C) gas.

DUES-FUNDED PROJECT SUMMARY

Project Title: HEAVY METALS EMISSIONS
FROM RECOVERY BOILERS

Project Code:

Project Number: F038-05

PAC: CHEMICAL RECOVERY

Project Staff

Principal Investigator: Kristiina Iisa

Co-Investigators: -

Research Support Staff: Qun Jing

PAC Subcommittee

-

FY 99-00 Budget: \$48,000

Allocated as Matching Funds: 0%

Time Allocation:

Principal Investigator: 8%

Co-Investigators:

Research Support Staff: 34%

Supporting Research:

Special Students: -

External (Where Matching Is Used): -

RESEARCH LINE/ROADMAP: 5. Reduce emissions of the entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule criteria while maintaining global competitiveness.

PROJECT OBJECTIVE:

The objectives are to assess the impact of recovery boiler operating conditions on the heavy metals emissions, and the relationship between metal inputs and purges to/from the liquor cycle on metals emissions.

PROJECT BACKGROUND:

Heavy metals are included in hazardous air pollutants (HAP), whose emissions are limited as part of the new MACT regulations for the pulp and paper industry. Any new or remodeled recovery boiler will have limits either for HAPs combined or separately for each compound, including the metals. Some mills may not be able to comply with the new heavy metals regulations. The heavy metals that are emitted from boilers are in the form of submicron fume particles that are formed by the vaporization of the metals in the furnace and subsequent condensation in the cooler parts of the boiler. The vaporization of heavy metals in fossil fuel combustion is fairly well characterized but the results are not directly translatable for recovery boilers. In general, reducing atmospheres and the presence of species like chlorine increase the volatilization of metals. The large fraction

of inorganics in black liquor may considerably change the chemical reactions of the metals and thus affect their volatilization and ultimately the emissions of heavy metals.

DELIVERABLES:

- 1) Laboratory data on the effect of temperature and gas atmosphere (reducing vs. oxidizing conditions, chlorine concentration as well as sulfur concentration) on heavy metals volatilization during black liquor combustion
- 2) Phase distribution factors for heavy metals as functions of temperature and gas concentration.
- 3) Estimates for the impact of recovery boiler operating conditions on heavy metal emissions.

STATUS OF GOALS FOR FY 99-00:

Experiments at different O₂ levels and gasification conditions - completed

SCHEDULE:

Task Descriptions (example)	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
1. Experiments at different O ₂ levels	-----x			
2. Gasification and pyrolysis experiments		-----	----x	
3. Data analysis	----	-----	-----x	
3. Annual Report				----x

SUMMARY OF RESULTS:

The volatilization of seven heavy metals that are classified as hazardous air pollutants (As, Be, Cd, Cr, Pb, Mn, and Ni) was studied in a laminar entrained-flow reactor. Due to the low concentrations of the heavy metals in black liquor, the liquors were spiked with the metals to increase their concentration to 500 ppm. Experiments were performed at five different conditions: at 1100°C in 0, 8 and 21 % O₂ and at 1000°C at 8% O₂ and a mixture of 15% CO₂ and 15% H₂O.

SUMMARY OF KEY CONCLUSIONS:

- Chromium, manganese and nickel were the least volatile heavy metals, and in most cases less than 10% volatilized.
- Beryllium was of low to medium volatility, and up to 15% volatilized.
- Arsenic and cadmium were medium volatile, and up to 38% volatilized
- Lead was the most volatile element, and up to 94% volatilized.
- The volatilization of the heavy metals is lower during gasification than during combustion. Thus conversion to gasification will decrease the heavy metals emissions.

DISCUSSION:

The volatilization of heavy metals was studied in a laminar entrained-flow reactor at different gas atmospheres. Both the char or molten residues and the fume particles that are formed by condensation of vaporized compounds were collected and analyzed for the heavy metals by ion conductive plasma (ICP).

The heavy metals concentrations in the base liquor are given in Table 1. Of the heavy metals, only Mn and Ni were present above detection levels, 125 and 8 mg/kg respectively. To increase the concentrations above detection limits, the liquors were spiked with heavy metals. The concentrations of As, Cd, Cr, Pb, Mn and Ni were increased to 500 mg/kg and that of Be to 10 mg/kg. Some of the experiments were performed with both the spiked and unspiked liquor. In addition, experiments were also made with liquors spiked with NaCl to increase the Cl content in the liquor to 2%, and with Na₂S to increase the S content to 7%.

Table 1. The concentrations of hazardous air pollutant metals and Na, K, S, and Cl in the base black liquor.

Element	mg/kg (ppmw)
Sb	ND (<12)
As	ND (<23)
Be	ND (<0.1)
Cd	ND (<1.6)
Co	ND (<2.6)
Cr	ND (<1.8)
Pb	ND (<19)
Mn	125
Ni	7.6
Se	ND (<28)
Na	184000
S	46700
K	16400
Cl	4270

ND = not detected, detection limit given in parenthesis

Experiments were performed at five different conditions: at 1100°C in 0, 8 and 21 % O₂ and at 1000°C at 8% O₂ and a mixture of 15% CO₂ and 15% H₂O. The remainder of the gas was N₂. The residence time in all experiments was 1.2 s.

In general, good material balance closures (95-115%) were achieved for all other heavy metals except Cd. The Cd recovery was very poor, only 20-70% was recovered. The reason for this is not known. The closure for Cr under gasification condition was low as well.

Comparison between Oxidation and Gasification

A comparison of the volatilization of the heavy metals between combustion and gasification is shown in Table 2. The hazardous heavy metals with the possible exception of Cd were more volatile during combustion than during gasification. Cr, Mn and Ni were the least volatile in both ags atmospheres, As, Cd and Be were medium volatile, and Pb was the most volatile. Up to 94% of the Pb volatilized. One reason for the lower volatilization during gasification than during combustion may be the lower particle temperature. Even though the furnace temperature was the same, the particle temperatures were not. The exothermic combustion reactions are estimated to increase the particle surface temperature by as much as 200°C. The gasification reactions are endothermic, and the particle surface temperature during gasification may be lower than the furnace temperature. Similar differences between boiler temperature and particle temperature exist in boilers and therefore, the results do indicate that the volatilization of heavy metals will be less during black liquor gasification than in recovery boilers. During low temperature gasification, the metals volatilization is expected to be even lower.

Table 2. Volatilization of heavy metals during combustion and gasification.

Element	in 8% O ₂	in gasification
As	19-33%	11-18%
Be	9-14%	2.9-5.7%
Cd	17-25%*	23-38%*
Cr	1.0-2.5%	<0.5%*
Pb	80-94%	78-88%
Mn	1.5-2.5%	<0.5%
Ni	2.0-5.0%	<0.5%

*Recovery poor.

Interestingly, there were four elements that had higher volatility during gasification than during combustion. They were Al, Si, P, and Sr. The reason for their lower volatility during combustion is most likely the formation of refractory oxides during combustion, e.g. Al₂O₃ and SiO₂. A general comparison of volatility of different elements during gasification and combustion is given in Table 1.

Table 3. Comparison of the volatility of different elements during combustion and gasification

➤ Gasification > Oxidation	Al, Si, P, Sr
➤ Gasification ≡ Oxidation	Ba, Pb
➤ Oxidation > Gasification	Cr, Mn, Fe, Ni, Cu, Zn, Al, Si, P, S, As, Cd, Pb, Sr, Ba, Be, Na, Mg, K, Ca, V, Cl

Effect of Temperature

The fraction of the metals volatilization increased as temperature was increased for all other heavy metals except for lead.

Table 4. Volatilization of heavy metals at different temperatures in 8% O₂.

Element	1000°C	1100°C
As	19-33%	29-37%
Be	9-14%	12-16%
Cd	17-25%*	16-24%*
Cr	1.0-2.5%	5.7-11%
Pb	80-100%	48-79%
Mn	1.5-2.5%	3.9-4.8%
Ni	2.0-5.0%	6.1-11%

*Recovery poor.

Volatilization during Pyrolysis

At 1100°C, the vaporization of these trace elements were investigated at three conditions: pyrolysis with no oxygen, combustion with 8% oxygen, and 21% oxygen. For most heavy metals, the vaporization was low during pyrolysis. Exceptions were Pb and Cd. For Cd, the fraction of the heavy metal in the fume was actually higher during pyrolysis than during combustion.

Table 5. Volatilization of heavy metals during pyrolysis at 1100°C.

Element	100% N ₂	8% O ₂ , 96% N ₂
As	1.2-8.6%	29-37%
Be	0.2-0.3%	12-16%
Cd	25-60%*	16-24%*
Cr	0.1-0.4%	5.7-11%
Pb	36-71%	48-79%
Mn	0.2-0.3%	3.9-4.8%
Ni	0.2-0.4%	6.1-11%

The Fate of Nitrogen in the Chemical Recovery Process

Nikolai DeMartini
Process Chemistry Group, Åbo Akademi University
Turku, Finland

Project Background:

Considerable work has been done at Åbo Akademi University (ÅAU) to better understand the behavior of nitrogen compounds in the liquid streams of the chemical recovery process. Of particular interest is the formation of ammonia in green liquor and its subsequent release from various parts of the recovery cycle. Laboratory work is being done to understand the formation mechanism for this ammonia. Both mill samplings and laboratory experiments are being carried out to understand the effect of process variables, such as white and black liquor oxidation, on this ammonia.

This is the first of a two-year co-operative project. In June of 1998 I made arrangements to attend ÅAU to obtain an MS in Chemical Engineering. Research related to this recovery process nitrogen is being done as partial fulfillment of the requirements for the MS degree. This work is in an area that IPST has not been involved in and it was found mutually beneficial for IPST to partially fund my work at Åbo Akademi with exploratory funds in exchange for the transfer of information related to the work that I am involved in.

An important forum for the transfer of this information is the Spring Chemical Recovery PAC meeting.

Project Objective:

The objective of this project is to gain a clearer understanding of the behavior of nitrogen throughout the recovery cycle while promoting co-operative efforts between IPST and other internationally renowned research organizations such as the Process Chemistry Group at ÅAU.

A Brief Overview:

The research of Aho and Forssén at ÅAU suggests a reaction pathway for the black liquor nitrogen in the recovery boiler [1,2], Figure 1. Furthermore, Forssén has determined that approximately one-third of this black liquor nitrogen is bound in the char residue and may leave the recovery boiler with the smelt [2].

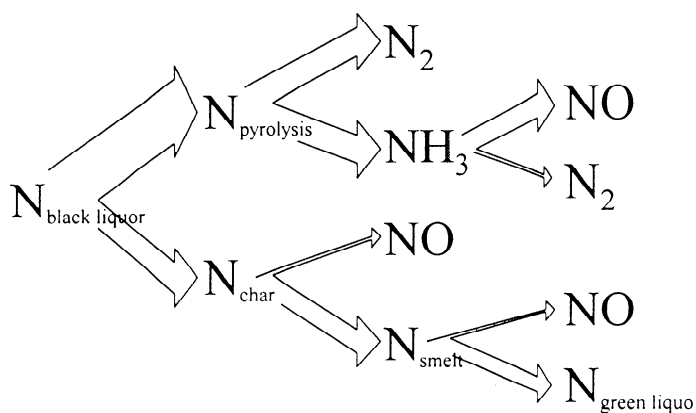


Figure 1. Suggested fuel nitrogen pathways in black liquor combustion [2]

The work of Maritta Kymäläinen has confirmed Forssén's findings regarding the retention of nitrogen in the smelt. She has conducted a sampling campaign at a Finnish pulp mill as an initial step in understanding the fate of this smelt nitrogen [3]. The sampling points for this campaign are given in Figure 2 and an overview of the nitrogen flows is given in Figure 3. In the overview, a value of 100 represents the input of black liquor nitrogen to the recovery boiler and the numbers of the other input and exit streams are relative to the black liquor nitrogen input.

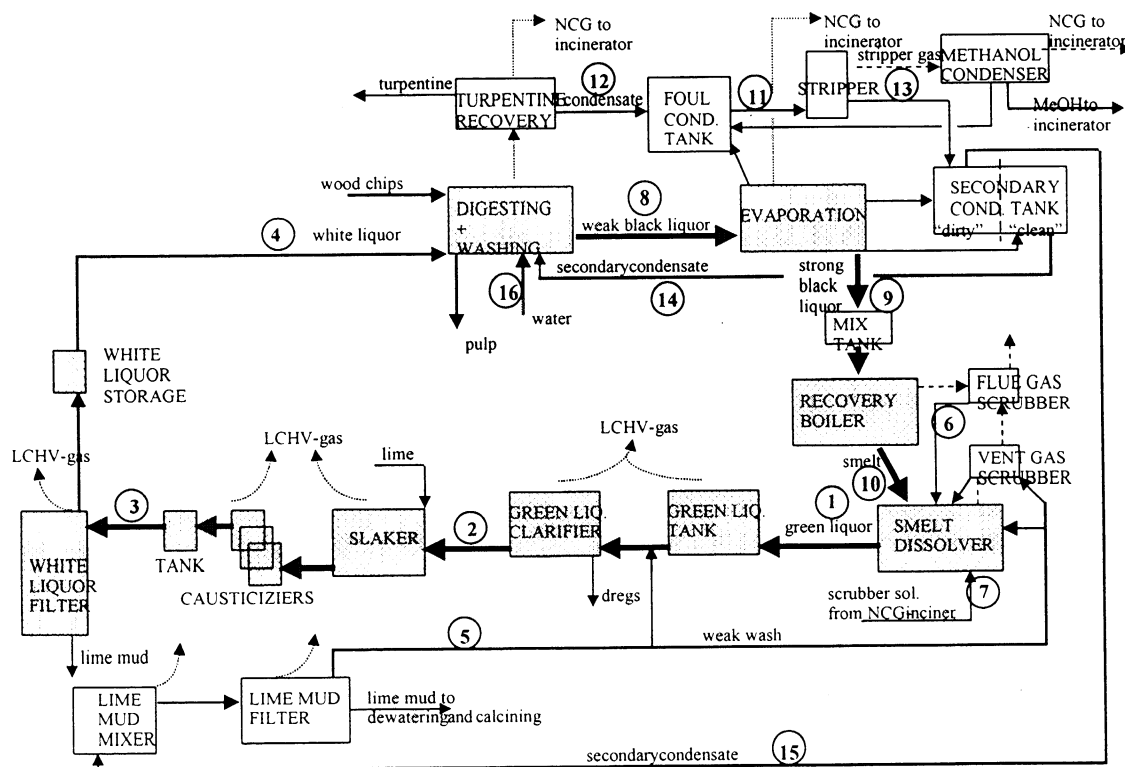


Figure 2. Flowsheet of the recovery process with main sampling points numbered [3].

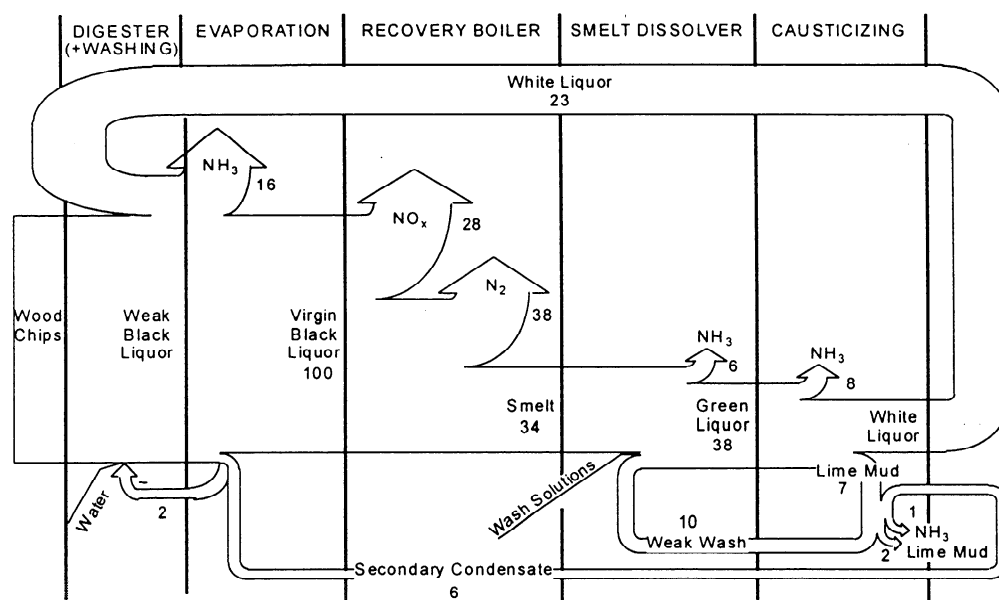


Figure 3. An overview of the nitrogen flows in the recovery cycle [3].

Future Plans

Analysis of Inorganic Nitrogen in the Recovery Process: Direct methods using wet chemistry have not proven wholly satisfactory for quantitative analysis of the relevant inorganic ions in the recovery process (CNO⁻, CN⁻, SCN⁻, NO₂⁻, NO₃⁻). Methods will be developed using IC for better quantitative analysis of these inorganic nitrogen anions.

Kinetic Information for the NH₃ forming Reaction: Kinetic experiments in both mill and synthetic green liquors will be carried out to better understand the role of hydroxide and carbonate concentrations on the ammonia forming reaction.

Effect of Oxidation on White and Black Liquor NH₃: The effect of oxidation on the NH₃ found in white and black liquor will be studied both through the pulling of mill samples around the oxidation tanks and the running of oxidation experiments in the lab.

Further Mill Campaigns: A sampling campaign at another Finnish pulp mill will be carried out, highlighting process variables found to be interesting.

References

1. AHO, K., "Nitrogen Oxides Formation in Recovery Boilers", Lic. Tech. Thesis, Åbo Akademi University, 1994.
2. FORSSÉN, M., HUPA, M., PETTERSON, R., MARTIN, D., "Nitrogen Oxide Formation During Black Liquor Char Combustion and Gasification", *J. Pulp Paper Sci*, 23 (9):J439-J446 (1997).
3. Kymäläinen, M., Forssén, M., Hupa, M., "The Fate of Nitrogen in the Chemical Recovery Process in a Kraft Pulp Mill Part 1: A general view", *J. Pulp Paper Sci*, 25 (12): (1999).

