

Impact of deadload reduction in the kraft chemical recovery system

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ABSTRACT: We developed a steady state Excel®-based model to study the effect of white liquor deadload reduction on recovery process performance. The process equipment affected includes the evaporators, concentrator, recovery boiler, smelt dissolving tank, green liquor clarifier, dregs filter, slaker, causticizers, white liquor clarifier, lime mud washer, and lime kiln. The model was developed using fundamental engineering principles and a set of assumed process parameters that were in turn based upon literature references and operating experience. The interactive model allows for specific base case parameters and can calculate liquor cycle mass balances. A subsequent change in white liquor composition will result in a new set of balances that can be compared with the base case. A reduction in white liquor deadload will also reduce the inorganic solids content of green liquor and black liquor, along with the water that carries the deadload. The energy performance and production capacity of the process equipment will improve, most notably the evaporators, concentrator, and recovery boiler. Reducing outages due to scaling, corrosion, and plugging will increase recovery boiler productivity. Increased productivity in evaporator performance should also increase because of improved heat transfer due to less scaling and a lower rise in liquor boiling point.

Application: Mills that can quantify the energy and capacity penalties resulting from high white liquor deadload can identify and pursue process improvement opportunities with high payback potential.

Production at nearly 50% of North America's kraft mills has been restricted by the rate of fireside deposit formation in the recovery boiler [1]. A major cause is the deadload of inactive and inert inorganic chemicals in the kraft liquor cycle. The kraft chemical recovery process reclaims and recycles more than 98% of the inorganic chemicals used in pulp production, but nearly 20% of these chemicals are not converted to the active white liquor pulping chemicals, sodium sulfide (NaOH) and caustic soda (Na_2S) [2]. As a result, these inactive pulping chemicals needlessly consume energy, reduce equipment capacities, and cause numerous scaling problems that compromise continuous operation. These so-called deadload chemicals—primarily sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4)—are a result of fundamental thermodynamic and kinetic limitations with the present process, coupled with inattention to daily operation. The recovery boiler smelt reduction efficiency leaves 5%-10%

Na_2SO_4 unconverted to Na_2S , while approach to chemical equilibrium in causticizing leaves 15%-20% unconverted Na_2CO_3 [3]. The solubility of Na_2CO_3 and Na_2SO_4 in white liquor makes physical separation extremely difficult and costly.

Our aim was to build a fundamental process model of the kraft liquor cycle that would quantify the negative impact of deadload on the various operating units. With the many process steps that make up the kraft chemical recovery process, complex process control capability using a computerized system can be used to control deadload in the system. In general, a control system can address the following overall objectives [4]:

1. Steady and satisfactory white liquor quality.
2. Adequate production capacity.
3. Minimum energy consumption.
4. Minimum deadload chemicals in white liquor.
5. Satisfactory air emissions requirements.
6. Minimum downtime.
7. Minimum chemical losses.

By specifying small changes in selected operating parameters, the model can be used to assess the energy and capacity impacts on the liquor cycle and identify the most beneficial opportunities for improvement in productivity, energy efficiency, and process control.

Other deadload chemicals in kraft liquor include calcium hydroxide ($\text{Ca}[\text{OH}]_2$); inert compounds containing sodium (Na), magnesium (Mg), iron (Fe), and manganese (Mn); aluminum complexes; silica complexes; chlorides; phosphates; and sulfates [5]. The deadload species enter the process with the wood, process water, and makeup limestone. Except for sodium carbonate and sodium sulfate, the other compounds are present in much smaller amounts and are generally controlled by purging with the dregs.

Figure 1 shows the kraft chemical recovery process flow diagram [6]. A more detailed description of the negative effects of deadload follows.

Digester

Although there is little effect of dead-

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load on the pulping chemistry, several aspects are affected by the deadload in digester operation [7].

1. Heat load for taking the inerts and their associated water up to the cooking temperature is increased.
2. Digester capacity is reduced because of the physical space that is taken by the inerts and their water.
3. White liquor or black liquor recirculation becomes limited. (Recirculation keeps the dissolved solids concentration in the black liquor in the chips below the point where soap precipitates. Soap precipitation is determined by the concentration of sodium counterion, which increases with inorganic deadload.)

Washer

The washer separates black liquor, diluted by wash water, from the pulp. Modern pulp washing normally recovers at least 98% of the chemicals applied in digesters [4]. Two deadload effects in the washer are

1. greater washing losses (the amount of inorganic chemical leaving the pulping and recovery system with the washed pulp); and
2. greater requirement for wash water to achieve a better washing efficiency, thus, increasing the evaporation loads and energy consumption in the evaporators.

Evaporators, concentrators

Multiple effect evaporators using low pressure steam carry out the evaporation or concentration of black liquor. A modern evaporator set normally consists of six effects with a steam economy of about 4.8 kg of water evaporated per kg of steam. Concentrators consist of two or three units with an additional steam demand. Deadload has a direct effect on several evaporation operations [4, 5].

1. Steam consumption must increase to evaporate water that carries deadload and the additional wash water from an inefficient washing operation.
2. The liquor boiling point rises,

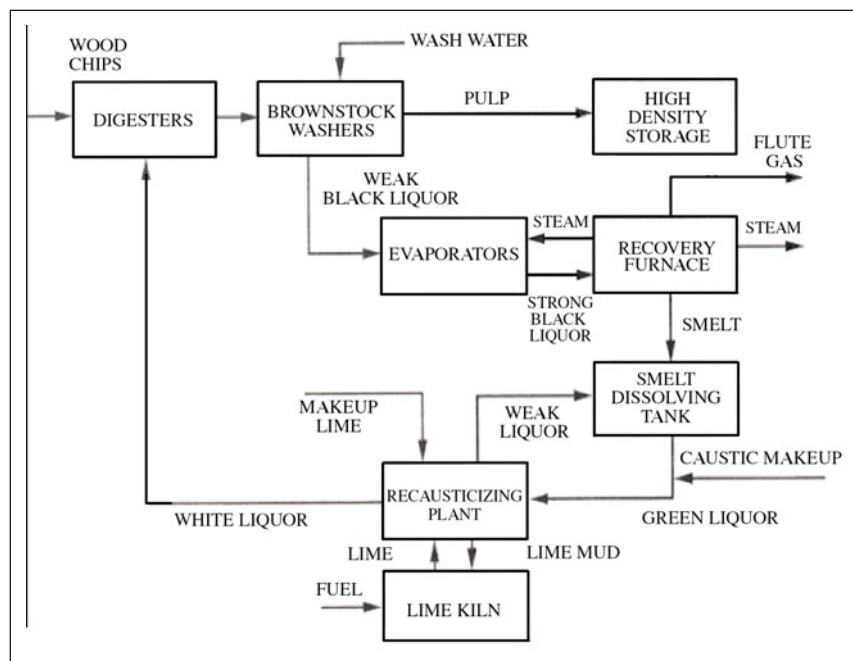
which lowers the ΔT for heat transfer. The boiling point rise is proportional to concentration of inorganics and thus increases directly with the amount of deadload.

3. Scaling problems increase. A double salt, $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$, can precipitate from black liquor at a solids concentration of ~50% [6]. Reduction of heat transfer and therefore reduced evaporator capacity will result.

Recovery boiler

Deadload affects the recovery boiler in several ways [5, 7, 8].

1. Black liquor heating value per kg of total solids decreases due to a lower ratio of organics to inorganics in the liquor.
2. Entrainment of particulates in the exit gas increases due to higher ash content of the liquor solids.
3. Unscheduled outages and higher cleaning costs result from plugged boiler tube passageways.
4. Total reduced sulfur (TRS) emissions increase.
5. Sulfate reduction efficiency decreases.



1. Block flow diagram of kraft chemical recovery process [6].

Dissolving tank

Weak wash from the mud washer and the dregs filter is fed to the dissolving tank where the molten smelt (mainly Na_2CO_3 and Na_2S) flows from the smelt spouts to form green liquor. The presence of deadload in smelt increases the melting point and viscosity of smelt, making smelt handling more difficult [1].

Green liquor clarifier

The green liquor clarifier removes dregs by sedimentation before the green liquor is recausticized. The clarifier can also serve as a storage tank for green liquor, providing at least a 12 h supply of green liquor [4, 8]. If green liquor clarification is inadequate, then the inert materials will build up in the lime and decrease lime availability. While the effect of deadload in the green liquor clarifier is minimal, one of its most significant effects is to decrease the capacity of the clarifier. High deadload will require more time (i.e., lower feed rate) for adequate sedimentation at constant active alkali (AA) [7, 8].

Dregs filter

The dregs solids make up about 1% of the green liquor solids. The dregs consist

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of carbon (20% or more) and foreign materials (mainly insoluble metal carbonates, sulfates, sulfides, oxides, hydroxides, and silicates) and yield a black particulate material [6, 8]. Deadload reduction will reduce the amount of dregs that must be filtered out and transferred to a landfill.

Slaker

The slaker is a chemical reactor in which lime and green liquor are mixed to generate slaked lime, $\text{Ca}(\text{OH})_2$, which then starts the causticizing reaction. Grit, which is composed of nonreactive lime particles and insoluble impurities, accounts for 0.5%-2% of the lime feed and is removed from the classifier section and sent to a landfill [6]. The main effect of deadload in the slaker is to limit its capacity because the deadload and its associated water occupy volume [5].

Causticizers

Causticizers are two to four continuous-flow, stirred reactors in series that are used to drive the causticizing reaction to near-equilibrium. The extent of the causticizing reaction depends on the concentration of the Na_2CO_3 in the feed green liquor and on the amount of

lime used. With the concentration of actual chemical below 16%, the conversion to caustic is > 90%; at higher feed concentrations, the conversion drops quickly [9]. The effects of deadload on causticizers are [5, 7, 8]

1. lower causticizing efficiency,
2. probable increase in scaling problems, and
3. lost causticizing capacity because of the inert deadload and its associated water that occupy volume.

White liquor clarifier

The white liquor clarifiers are settling tanks (gravity sedimentation) used to remove the lime mud (CaCO_3) from the white liquor. The lime mud usually leaves with a solids content >35% to minimize entrained white liquor, most of which is subsequently removed by the lime mud washer. One result of deadload presence in the clarifier is reduced capacity because the deadload chemicals and their associated water occupy space in the clarifier [5, 9].

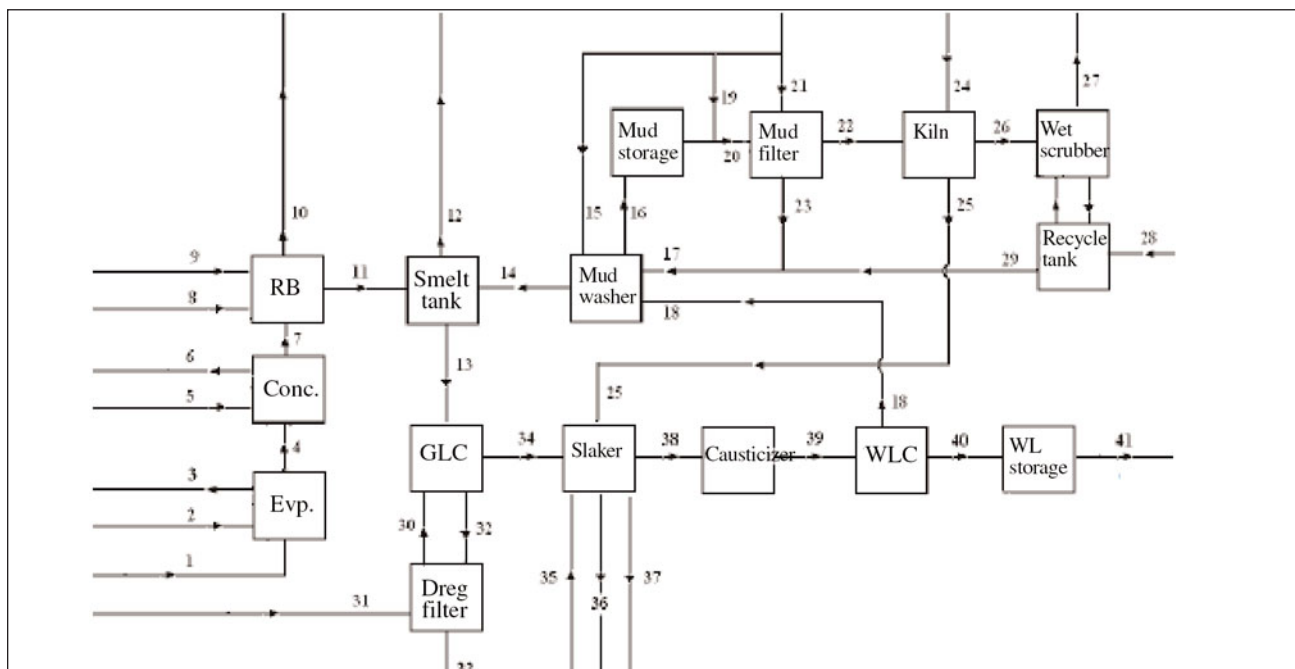
Lime kiln

The lime kiln is a chemical reactor in which lime mud (CaCO_3) is dried, heat-

ed, and calcined to calcium oxide (CaO). Fuel oil or natural gas (or occasionally biomass, coal, or petroleum coke) supplies the fuel to achieve the high temperature (1200°C) required [8, 10]. The lime's purity is characterized by lime availability, which is defined as the ratio of CaO to the total solids in the kiln product, namely CaO , CaCO_3 , and inerts composed largely of deadload. In the kiln, deadload carries water into the reactor, adding to sensible heating and evaporation requirements and resulting in an increase in fuel consumption and a decrease in kiln capacity.

DISCUSSION

To quantitatively assess the negative effects of deadload in the liquor cycle, we developed a steady state model of the kraft liquor cycle based on 1 o.d. ton of unbleached kraft pulp. The simulation is based on material balances in a Microsoft Excel® spreadsheet and is designed to predict the effects of reducing white liquor Na_2CO_3 and Na_2SO_4 on the different unit processes in the kraft recovery cycle. This model is based on technical fundamentals and operating experience [4, 7, 11, 12]. The simulation encompass-



2. Block diagram for recovery process simulation [13].

es the evaporators, concentrator, recovery boiler, caustic plant, and lime kiln. Inclusion of a heat balance calculation for the recovery boiler allows quantification of the effect on boiler steam generation rates. **Figure 2** shows the process block diagram that was used in constructing this model, configured according to the kraft recovery process shown in Fig. 1. Definition of the inputs and outputs in the block diagram and details of the model algorithm are found in [13].

Table I shows the assumed base case parameters for the model. A new case, also termed the deadload reduction case, was developed for comparison. **Table II** shows this new case as having a different composition of white liquor. Notably, the amount of Na_2CO_3 and Na_2SO_4 was taken to be approximately 50% of the base case values while the active alkali composition was held to the same value. Of course, different values can be assumed to assess the impact of specific improvements in the recovery process. From these new inputs, we calculated revised responses around the liquor cycle and made several observations regarding process improvement. White liquor requirement, green liquor composition, and black liquor composition were compared to understand more about the effects of deadload reduction. The results of the comparisons are summarized in **Tables II-VIII**.

One of the most important aspects of the chemical recovery system is the white liquor composition that is charged to the digester. Tables II and III show the comparison. The amount of water that is carried to the digester will be reduced by 7.3% (from 2936 kg to 2721 kg) and the white liquor solids will be reduced by 11.7% (from 513.5 kg to 453.6 kg).

Another important aspect of this deadload reduction is higher white liquor activity, which is the ratio of active alkali to total alkali. The higher activity is due to the effect of lowering TTA (the sum of all the bases in the white liquor that can be titrated with strong acid) at constant AA. To accomplish this in actual operation, the causticizing efficiency

BASE PARAMETER	AMOUNT	UNITS	AMOUNT	UNITS
1 o.d. ton unbleached pulp	2000	lb	907.2	kg
Pulp yield	48.0	%	48.0	%
AA on o.d. wood	16.5	%	16.5	%
White liquor activity	85.0	%	85.0	%
Sulfidity	25.0	%	25.0	%
White liquor total alkali	75	lb/ft ³	120.2	kg/m ³
Excess lime	2.0	%	2.0	%
Lime availability	85.0	%	85.0	%
S.G. of white liquor	1.13		1.13	
$\text{Na}_2\text{SO}_4/\text{Na}_2\text{S}$ ratio	0.2		0.2	
Density of water	62.4	lb/ft ³	1000	kg/m ³
S.G. of green liquor	1.16		1.16	
Mud solids underflow	40	%	40	%
Fuel requirement in lime kiln	0.18	lb/lb CaO	0.18	kg/kg CaO
Fuel/air ratio in kiln	0.06	lb/lb air	0.06	kg/kg air
Grit solids in purge	60	%	60	%
Solids from concentrator	70	%	70	%
Concentrator steam economy	1.8	lb/lb H ₂ O	1.8	kg/kg H ₂ O
Evaporator steam economy	4.8	lb/lb H ₂ O	4.8	kg/kg H ₂ O

I. Base case assumed parameter values.

Chemicals	Base kg Na ₂ O kg chemical		New kg Na ₂ O kg chemical	
Na ₂ S	77.96	98.08	77.96	98.08
NaOH	233.89	301.78	233.89	301.78
Na ₂ CO ₃	55.03	94.08	25.85	44.20
Na ₂ SO ₄	8.56	19.62	4.28	9.81
Water	2935.65		2721.04	

II. Comparison of base case and deadload reduction case white liquors.

would have to be improved to 87.9% from 77.7%. The white liquor volume charged to the digester would be decreased by 7.9%, thereby opening up the possibility for increased capacity.

A result similar to the white liquor composition was determined for the preceding green liquor composition, as seen in Table IV. With the reduction of white liquor deadload, the deadload in the green liquor will have been reduced as well. The amount of water in green liquor itself would be reduced by 6.0% (from 3553 kg to 3342 kg) and the

green liquor solids would be reduced by 9.0% (from 708 kg to 645 kg).

The reduction efficiency will have to be increased also (presumably accomplished by recovery boiler operating changes) because of the deadload reduction that was assumed in the white liquor. Because reduction efficiency is the ratio of the amount of sodium sulfide to the total sodium sulfate and sodium sulfide in the smelt, the reduction of white liquor sodium sulfate would require an increase in reduction efficiency from 90.1% to 94.8%, as seen

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DESCRIPTION	BASE	NEW	UNITS
White liquor activity	85.00	92.34	%
Na ₂ SO ₄ /Na ₂ S ratio	0.20	0.10	-
AA	311.84	311.84	kg as Na ₂ O
White liquor TTA	366.87	337.70	kg as Na ₂ O
White liquor volume	3.05	2.81	m ³
Causticizing efficiency	77.67	87.90	%

III. Comparison of white liquor operation conditions.

DESCRIPTION	BASE	NEW	UNITS
SO ₄ ⁼ reduction eff.	90.10	94.79	%
GL TTA	433.41	404.24	kg as Na ₂ O
Volume GL	3.61	3.36	m ³

V. Comparison of green liquor (GL) operating conditions.

in Table V. Also, the resulting volume of green liquor would decrease by 6.9%.

A similar result was achieved with the black liquor composition as a response to deadload reduction (see Table VI). The 4.7% decrease in black liquor solids, from 1212 kg to 1155 kg, occurs due to the reduction of deadload chemicals in the white liquor that would be charged to the digester. The amount of water in the black liquor would be decreased as well by 4.7%, from 5920 kg to 5639 kg.

An important consequence of deadload reduction would be to increase black liquor higher heating value due to lower inorganic content. This would increase recovery boiler steam generation by 1.1% from 1.297E10 to 1.311E10 kJ. Naturally, this is important because it would reduce power boiler purchased fuel cost to achieve a constant total steam flow. At a purchased fuel cost of US\$ 7.58/kJ, this would give a benefit of US\$ 1.23/metric ton (US\$ 1.12/ton).

Because less black liquor solids (BLS) would be produced, there would be less water that carries them. Consequently, this would decrease evaporation requirements in converting weak black liquor to 70% solids. For the multiple effect evaporator, steam usage would drop from 1233 kg to 1175 kg with the accompanying energy usage falling from 3.37E9 kJ to 3.21E9 kJ, a difference of 4.7%. For the concentrator, steam usage would drop from 674 kg to 642 kg with energy usage falling from 1.88E9 kJ to 1.78E9 kJ, a difference of 5.1%. Together, there would be a net increase in export of steam from the recovery cycle of 5.2% (see Table VIII) and a benefit of US\$ 3.30/metric ton (US\$ 3/ton).

With a reduced inorganic load, another likely benefit to multiple effect evaporation would be reduced scale formation and hence longer times between water washes. The combined salt solubility limit would be reached further along the evaporator train, possibly not

CHEMICALS	BASE	NEW
Dregs	3.27	3.27
Na ₂ S	115.87	117.40
NaOH	54.73	59.46
Na ₂ CO ₃	511.02	452.78
Na ₂ SO ₄	23.17	11.74
Water	3553.1	3342.1

IV. Green liquor comparison (kg as chemical).

CHEMICALS	BASE	NEW
Na	266.75	242.37
C	446.68	424.88
H	42.44	42.52
S	36.39	34.24
O	416.98	407.66
Inerts	3.27	3.27
Water	5919.9	5638.8

VI. Black liquor composition comparison (kg).

ELEMENT	BASE	NEW
Na	22.00	20.99
C	36.84	36.79
H	3.50	3.68
S	3.00	2.96
O	34.39	35.30
Inerts	0.27	0.28

VII. Black liquor solids elemental analysis comparison (%).

until the liquor reaches the concentrator. Also, there would be a reduction in black liquor boiling point rise and hence a higher ΔT for heat transfer, signifying an increase in evaporator capacity.

The lime mud cycle operation,

DESCRIPTION	BASE	NEW	UNITS	BASE	NEW	UNITS
HHV	6300	6614	BTU/lb	14,623	15,352	kJ/kg
Rec. boiler heat-to-steam	1.229E7	1.243E7	BTU	1.30E10	1.31E10	kJ
Evaporator steam usage	2719.0	2589.9	lb	1233.3	1174.8	kg
Evaporator energy usage	3.19E6	3.04E6	BTU	3.37E9	3.21E9	kJ
Concentrator steam usage	1485.1	1414.6	lb	673.6	641.7	kg
Concentrator energy usage	1.78E6	1.69E6	BTU	1.88E9	1.78E9	kJ
Net steam for export	7.32E6	7.70E6	BTU	7.72E9	8.12E9	kJ

VIII. Energy generation comparison.

which was also analyzed in this study, didn't show any changes with deadload reduction. Several studies have shown that there is either little or no effect on the lime mud cycle in the chemical recovery system [3]. However, there would be energy benefits from heating and evaporating less water in the lime kiln.

SUMMARY AND CONCLUSIONS

Reduced deadload in white liquor would reduce the inorganic solids content of green liquor and black liquor as well as decrease the amount of water that carries the deadload. The energy performance and production capacity of the equipment would increase. Steam requirements for the concentrator and evaporators can be cut, because less inorganic chemical and water would be cycled around the chemical recovery system. Evaporator performance productivity should also increase due to improved heat transfer, less scaling, and reduced liquor boiling point rise.

The two most important process parameters for reducing deadload are causticizing efficiency (sets the amount of Na_2CO_3 in the liquors) and reduction efficiency (sets the amount of Na_2SO_4 in the liquors). If the white liquor content of these chemicals is cut in half, then the net export of steam from the

recovery cycle can be increased by 5.2%. Other energy benefits not quantified in the model include less purchased fuel for the lime kiln and a lower digester heating requirement.

Several assumptions used in this model were based on fundamental engineering principles. Because the assumption of constant density or specific gravity isn't rigorous, a detailed study of liquor density would be beneficial. An expanded model featuring an overall heat balance would also give a more accurate and less conservative model for predicting the energy benefits of deadload reduction. Finally, another important outgrowth of this work would be to test the model results against mill data. **TJ**

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LITERATURE CITED

1. Blackwell, B.R. and MacCallum, C., *Pulp Paper Can.* 88(7): 51(1987).
2. Kietaanniemi, O. and Virkola, N-E, *Paperi Puu* 60(9): 507(1978).
3. Misra, M.N. and Sowul, L., *Pulp Paper Can.* 91(8): 99(1990).
4. Kocurek, M.J., *Pulp and Paper Manufacture Vol. 5: Alkaline Pulping*, 3rd edn., Joint Textbook Committee of the Paper Industry, TAPPI, Atlanta, Georgia, USA, and CPPA, Montreal, Quebec, Canada, 1989.
5. Blackwell, B.R., Randall, R.S. and Betts, J.L., *Pulp Paper Can.* 87(10): 57(1986).
6. Green, R.P. and Hough, G., *Chemical Recovery in the Alkaline Pulping Processes*, TAPPI Press, Atlanta, Georgia, USA, 1992.
7. Grace, T.M., *Tappi J.* 61(11): 75(1978).
8. Biermann, C.J., *Handbook of Pulping and Papermaking*, 2nd edn., Academic Press/Elsevier, Amsterdam, The Netherlands, 1996.
9. Smook, G.A., *Handbook for Pulp and Paper Technologists*, 2nd edn., Joint Textbook Committee of the Paper Industry, TAPPI, Atlanta, Georgia, USA, and CPPA, Montreal, Quebec, Canada, 1992.
10. Empie, H.J., personal communication, 2003.
11. Adams, T.N., *Kraft Recovery Boilers*, TAPPI Press, Atlanta, Georgia, USA, 1997.
12. TAPPI TIP 0418-02 "Recausticizing material balance equations relating to digester requirement."
13. Chandra, Y., "Alkaline pulping: deadload reduction studies in chemical recovery system," M.S. thesis, Georgia Institute of Technology, Atlanta, Georgia, USA, 2004.

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INSIGHTS FROM THE AUTHORS

This was an interesting topic because of the potential to have promising payback for low capital cost improvements in the kraft recovery cycle. Our research quantifies the benefits claimed for alternative causticizing technology based on laboratory experiments with barium salts as published in the Journal of Pulp and Paper Science in 2006.

The most difficult aspect of this research was determining how and where to start; we began with a thorough literature review. The most interesting finding was the potential for increasing recovery boiler steam production by as much as 5% as a result of deadload reduction.

Mills may benefit from this work by realizing the incentive they have for reducing deadload through better control of their daily operations and optimizing recovery

process conditions. The next step will be to refine the model to include rigorous energy balances for the several unit processes in the recovery cycle.



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