

Dynamic modeling of potassium and chloride in the recovery area

BARRY MALMBERG, LOU EDWARDS, TORBJÖRN JÖNSSON, HANS THELIANDER, AND JOHAN SALTIN

ABSTRACT: As kraft pulp mills recycle more of their water, non-process elements (NPEs) will accumulate, causing potential operating problems. “Kidneys” used for controlled removal of NPEs can help maintain efficient operation of a highly closed kraft mill. It is critical to determine the dynamic effect of process changes on NPE levels in order to optimize closure strategies and evaluate different “kidney” options.

We built a dynamic full-mill model that can represent general dynamic kraft mill behavior regarding NPE build up. It is used to test different mill recycle schemes and “kidney” strategies for NPE removal. The overall mill dynamics are assumed to be controlled by the liquor and pulp storage tanks. The model uses an equilibrium module based upon SOLGASWATER to predict the partitioning of NPEs between the aqueous and fiber phases. We based the equilibrium model upon a combination of literature thermodynamic data and mill-tuned results, and it is fully integrated into a commercial process simulation program (WinGEMS).

In this first paper, we demonstrate the dynamic impact of chloride (Cl^-) and potassium (K^+) levels on the sticky dust temperature in the recovery boiler due to the shutdown of a NPE chip kidney. Simulation results show that with “normal” chloride and potassium inputs, an open bleach plant, and no electrostatic precipitator (ESP) dust purge, the sticky dust temperature drops from 800°C to 580°C in 250 days. In a case with bleach plant filtrate recycling and an ESP dust purge of 16 kg/ton_{90} , the sticky dust temperature drops from 760°C to 700°C , reaching steady state in 80 days. In a case with high input chloride levels, a NPE chip kidney can alleviate sticky dust problems in the recovery boiler. The slow process dynamics indicate the NPE chip kidney can be safely shutdown on a periodic basis.

We based the mill model on specifications defined in the “Ecocyclic Pulp Mill (KAM)” program [1]. The aim of the program is to develop a completely ecocyclic system for high-quality paper products that efficiently use the energy potential of biomass.

Application: This study supports efforts to control non-process elements in closed cycle mills.

The buildup of non-process elements (NPEs) can cause a wide variety of operational problems in a closed cycle mill [2], including:

- Formation of scales and deposits
- Corrosion of process equipment
- Increased levels of inert chemical species in the recovery area leading to energy losses and capacity decreases.
- Catalytic decomposition of peroxide by transition metals.

NPE removal should proceed in a manageable and controlled fashion. Full mill dynamic simulation of NPE behavior provides a systems approach to quantify the effects of recycle strategies on various NPE concentrations and to evaluate different purging options or “kidneys.”

NPEs that form water-soluble complexes in alkaline solutions will accumulate over time in the recovery cycle. Since

sodium chloride (NaCl) and potassium chloride (KCl) are highly water soluble, the chloride anion (Cl^-) will build up over time in a tightly closed mill. Potassium (K^+) also builds up in a tightly closed cycle mill because potassium salts are even more water-soluble than their sodium analogs [3]. The buildup of potassium and chloride in the recovery area will lower the eutectic temperature of recovery boiler dust, and can lead to plugging problems in the upper boiler.

MAJOR INPUT VECTORS

The major sources of NPEs are typically the wood chips and make-up chemicals, with minor input from the process water. Bleaching chemicals will be a major input vector to the recovery area in mills that recycle bleach plant effluent to the brownstock washing. Several studies have been performed to determine chloride and potassium balances in the recovery area [4-8].

The major sources of chloride entering the mill are the wood, bleaching chemicals for elemental chlorine free (ECF) mills, caustic makeup, and saltcake makeup. Typical values for chloride in as-fired black liquor are about 0.2 to 0.5 Cl wt % dry solids for inland mills with an open bleach plant. For ECF mills that recycle bleach plant effluent or for coastal mills that use sea-borne logs, the chloride content can reach 3 to 5 wt % dry solids in the as-fired black liquor [9].

Wood chips are the major input vector for potassium. Softwoods typically contain 0.8 to 1.5 wt % K dry solids. For mills that pulp hardwood or use whole tree wood chips, the potassium concentrations are typically 2 to 5 wt % K dry solids [3]. The defined chloride and potassium levels in the chips for the ecocyclic pulp mill are 200 and 700 g/ton_{90} bleached pulp respectively. These are typical values for wood chips from central Sweden.

KRAFT RECOVERY

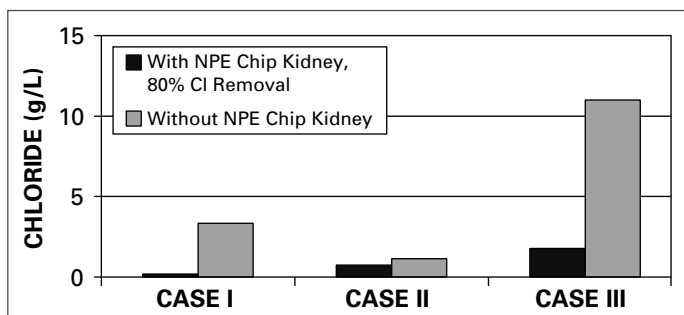
FIBER LINE	2000 TON ₉₀ /DAY VOLUME (m ³)	WinGEMS MODEL
Digester	10,000	Plug flow
Blow tank	4500	Plug flow
Displacement liquor tank	2500	CSTR
Unbleached storage tank	11,000	Plug flow
Filtrate tanks	1200	CSTR
Bleached storage tank	11,000	Plug flow
Brownstock spill tank	300	CSTR
Bleach spill tank	300	CSTR
O ₂ delignification towers	1330	Plug flow
Q ₁ tower	670	Plug flow
(OP) and (PO) towers	1340	Plug flow
ClO ₂ tower	2340	Plug flow
O ₂ tower	330	Plug flow
CHEMICAL RECOVERY		
Weak black liquor	12,000	Combination
Intermediate black liquor	1200	CSTR
Strong black liquor	2500	CSTR
Spill tank	2500	CSTR
Dirty condensate	800	CSTR
Soap	700	CSTR
Green liquor settling tank	2500	CSTR
Green liquor storage	6000	CSTR
Lime mud storage	1600	Plug flow
Weak wash	3500	CSTR
White liquor storage	8000	Combination
Spill tank, causticizing	1200	CSTR

1. Tank and tower volumes.

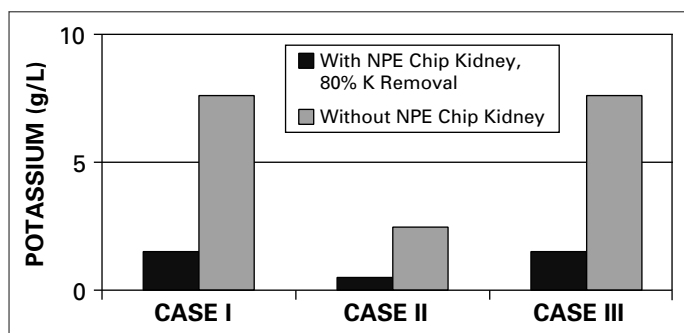
DYNAMIC MODELING

A combination of steady state process blocks interspersed with tank, tower, and equipment delays are used to simulate full-mill dynamic behavior. Two blocks, a plug flow block to represent pure delays and a perfectly mixed tank (CSTR) are used to simulate the dynamic mill behavior. Large tanks such as the white liquor storage tanks and the weak black liquor storage tank are not expected to exhibit either perfectly mixed flow behavior or perfect plug flow behavior. In these cases, hybrid storage tanks combining the elements of perfectly mixed flow and plug flow behavior were constructed. The strategy of using a combination of steady state and dynamic blocks to represent mill wide dynamic behavior of NPE buildup is thought to be adequate because of the slow dynamics involved. **Table I** shows tank, tower and equipment volumes used in the simulation.

Calculations for the prediction of potassium and sodium partitioning between the liquor and fiber phase are performed with MetEQ, a general equilibrium engine for the calculation of multi-component, multi-phase systems. MetEQ is based upon the Gibbs free energy minimization program SOLGASWATER [10] and is fully integrated into WinGEMS. Process operating conditions and species concentrations are directly imported from WinGEMS. Pertinent thermodynamic data for all chemical reactions considered are imported from an external Excel worksheet. The ideal Gibbs free energy minimization approach is fully equivalent to competitive Langmuir isotherm models commonly used to represent pulp fiber sorption phenomena [11, 12].



1. Steady state concentrations of chloride in white liquor.



2. Steady state concentration of potassium in white liquor.

Reliable thermodynamic data for pulp-cation interactions are scarce, with only a few detailed studies for disassociation behavior of the H⁺ ion with carboxylic and phenolic hydroxyl groups present on lignin and hemi-cellulose available [13, 14]. The relative sorption/desorption equilibria of potassium and sodium have been determined [15]. We used these results combined with mill data to tune formation constants for sodium-potassium-fiber interactions to reproduce mill results. These mill tuned formation constants can be viewed as modified formation constants where temperature and ionic strength effects are lumped into the overall constant.

The NPE chip kidney currently under development in the Ecocyclic Pulp Mill program at STFI and Chalmers removes NPEs from the chips by using an acid or chelating pretreatment step. Current bench scale results have shown approximately 80% removal efficiency of potassium and chloride from the incoming chips. A simple split calculation simulates the chip kidney. The mill simulation contains the pulping, recovery area, brownstock washing, with O₂ delignification, and a bleach plant with a Q₁(OP)DQ₂(PO) bleaching sequence.

Potassium and chloride enrichment factors used in the recovery boiler model are 1.6 and 2.5 respectively. The model predicts hydrochloric acid emissions using the HCl-SO₂ relationship presented in [16]. The ESP dust purge for the open bleach plant calculations is set to zero. The ESP dust purge for the bleach plant filtrate recycle case is set to 16 kg/ton₉₀ in order to maintain the Na/S balance.

LIMITATIONS OF THE CURRENT APPROACH

Ionization equilibria are typically obtained very rapidly (within the order of a few seconds). The calculations used in the simulation assume equilibrium has been established, and when dealing with highly water-soluble components, this assumption is

justified. If there are significant mass transfer effects, or if dealing with components that form precipitates slowly, equilibrium calculations will be in error. Algorithms have been presented that combine reaction kinetics or mass transfer with multi-component, multi-phase Gibbs free energy minimization [17, 18], and these algorithms could be implemented if more detailed simulation of a unit operation or process area is required. While equilibrium calculations are a simplifying assumption, they provide insight into the process and establish system boundaries.

A general lack of time dependent mill data of NPEs for model validation purposes is also a limitation, but our engineering approach should generate reasonable results.

RESULTS

Studied cases:

Case I: Shutdown of NPE kidney with typical K and Cl chip inputs, an open bleach plant, and no ESP dust purge.

Case II: Shutdown of NPE kidney with typical K and Cl chip inputs, bleach plant filtrate recycle, and ESP dust purge (16 kg/t₉₀).

Case III: Shutdown of NPE kidney with a typical K chip input, a high Cl chip input, an open bleach plant, and no ESP dust purge.

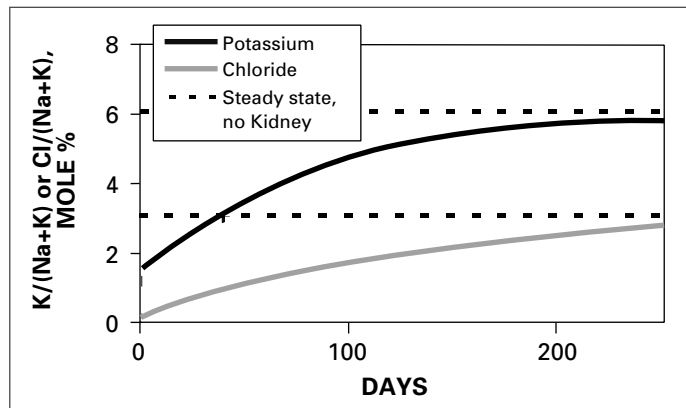
Figures 1 and 2 show the steady state values for chloride and potassium in the white liquor for each of the studied cases. The chloride and potassium levels should not exceed 5 g/L and 15 g/L respectively in order to avoid sticky dust problems in the recovery boiler. For this mill configuration, those concentrations correspond to a sticky dust temperature of approximately 550°C. In Case II, the steady state potassium levels are influenced to a greater extent than the chloride since the major input vector for potassium is the incoming chips versus the ClO₂ charge for chloride. In Case III, we would expect sticky dust problems to exist in the case without the NPE chip kidney.

Case I: NPE chip kidney shutdown

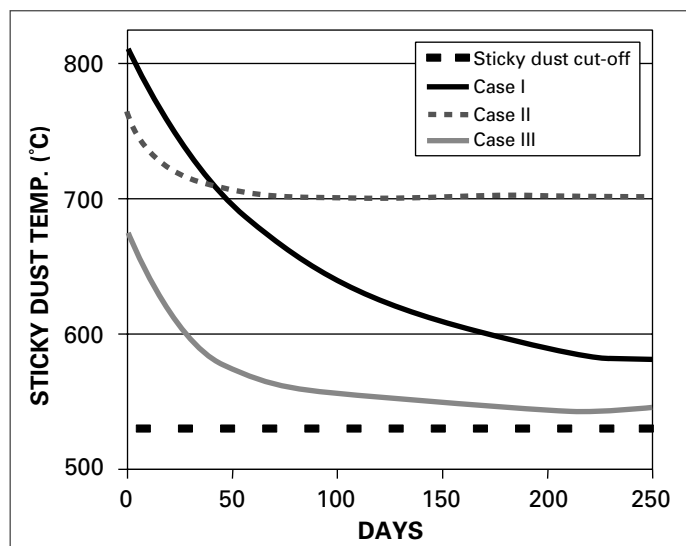
Figure 3 shows the dynamic effect of shutting down the NPE chip kidney on potassium and chloride concentrations in the as-fired black liquor. The chloride response is highly dependent upon the amount of chloride leaving the recovery boiler as HCl emissions. The HCl concentration in the flue gas is expected to be small because the recovery boiler is firing solids at 80%. The increased levels of potassium and chloride will lower the melting point of recovery boiler flue gas deposits and can cause potential plugging problems in the superheater and boiler bank [19]. Figure 4 shows the dynamic effect of shutting down the NPE chip kidney on the sticky dust temperature in the recovery boiler. The sticky dust temperature drops from 800°C to 580°C in 250 days.

Case II: Recycle of bleach plant effluent to the brownstock

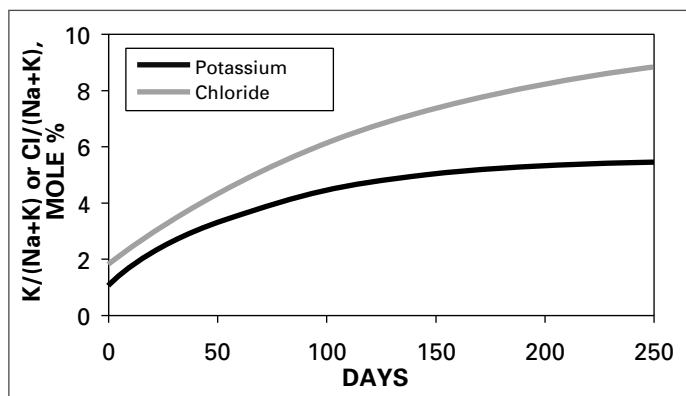
In this case, bleach plant filtrate from the (PO) stage of a Q₁(OP)DQ₂(PO) sequence was recycled to the brownstock washing area. We used an ESP dust purge of 16 kg/ton₉₀. Figure 4 shows the dynamic effect of shutting down the NPE kidney on the sticky dust temperature. The sticky dust temperature declines from 760°C to 700°C, reaching steady state in 80 days. The faster response in Case II is due to the ESP dust purge acting as an effective “kidney” for potassium and chloride.



3. Case I: Dynamic effect of NPE kidney shutdown on potassium and chloride concentration in as-fired black liquor.



4. Dynamic effect of cases I, II, and III on recovery boiler sticky dust temperature.



5. Case III: Dynamic effect of NPE kidney shutdown on potassium and chloride concentrations in as-fired black liquor.

KRAFT RECOVERY

Case III: High input chloride

In this case, we used a high level of chloride (600 g/ton₉₀) as an input with the chips. Figure 5 shows the effect of shutting down the NPE chip kidney on chloride and potassium levels in the as-fired black liquor. Figure 4 shows the dynamic effect of the NPE chip kidney shutdown on the sticky dust temperature in the recovery boiler. The sticky dust temperature decreases from 670°C to 545°C in 150 days. The chloride levels continue to increase after 150 days, but the effect on the sticky dust temperature is negligible after about 8 Cl/(Na + K) mole % in the dust.

CONCLUSIONS

Simulation results show that sticky dust temperature in the recovery boiler will decrease from about 800°C to 580°C in 250 days with the shutdown of an NPE chip kidney in a mill with no bleach plant recycle and no ESP dust purge. The effect of shutting down an NPE chip kidney on the sticky dust temperature in a mill with bleach plant recycle and an ESP dust purge (16 kg/ton₉₀) is 60°C over 80 days. The dynamic effect of recycle and “kidney” strategies on the sticky dust temperature in the recovery boiler is significant as shown in figure 4.

The time response of potassium and chloride buildup provides insight into operational strategies of an NPE chip kidney. Since the overall dynamics are slow, it is safe to periodically shut down the NPE chip kidney, in regards to potassium and chloride.

FUTURE WORK

We are currently integrating other NPEs (silicon, aluminum, magnesium and phosphorous) into the full mill dynamic model and will report on their dynamic behavior in the recovery area in a subsequent paper. Mill dynamics of NPEs should be tested and verified with mill data. **TJ**

ACKNOWLEDGMENTS

This work is a part of the “Ecocyclic Pulp Mill” research program financed by MIS-TRA, the Swedish Foundation for Strategic Environmental Research.

LITERATURE CITED

1. KAM Report A32, Swedish Foundation for Strategic Environmental Research, Stockholm (2000).
2. Ulmgren, P., *Nord. Pulp and Pap. J.* 12: 32(1997).
3. Gilbert, A.F., Rapson, H., *Pulp Paper Can.* 81(2):T43(1980).
4. Tran, H.N., Barham, D., Reeve, D.W., *Pulp Paper Can.* 91(5): T185(1990).
5. Magnusson, H., Mörk, K., Warnqvist, B., “Non-process chemical elements in the kraft recovery system,” TAPPI/ATCP Pulping Conference Proceedings, TAPPI PRESS, Atlanta, Georgia, USA, 1979, pp. 77-83, September 1979.
6. Ahlers, P., Norrstrom, H., Warnqvist, B., *Pulp Paper Can.* 79(5): T169(1978).
7. Keitaanniemi, O., Virkola, N., *Paperi ja Puu – Papper och Trä*, 60(9): 507(1978).
8. Blackwell, B., Lincoln, D., *Pulp Paper Can.*, 99(1): T34(1998).
9. Karjalainen, P.O., Lofkrantz, J.E., Christie, R.D., *Pulp Paper Mag. Can.* 73(12): 95(1972).
10. Eriksson, G., *Analytica Chimica Act.*, 112: 375(1979).
11. Hartler, N. and Rydin, S., *Svensk Papperstid.*, 10, 367(1975).
12. Malmberg, B., Gu, Y., Edwards, L., Sukamto, J.H., et al., “Electrically switched ion exchange (ESIX), for the removal of potassium to enhance water recycle opportunities,” *TAPPI J.*, 83(6): 53(2000); full text at <www.tappi.org>.
13. Laine, J., Lövgren, L., Stenius, P., Sjöberg, S., *Colloids and Surfaces*, 88: 277(1994).
14. Norgren, M., Lindström, B., *Hotzforschung*, 54: 519(2000).
15. Andersson, S., Aveberg, V., *Massan – en Utställningsväg för Processframmande Ämnen*, STFI report 558. (1980). (In Swedish)
16. Someshwar, A.V., Jain, A.K., *Tappi J.*, 78(12): 77(1995).
17. Alberty, R., *J. Phys. Chem.* 95: 413(1991).
18. Koukkari, P., Laukkanen, I., Liukkenen, S., “Combination of Overall Reaction Rate with Gibbs Energy Minimization,” *Fluid Phase Equilibria*, 136, 345-362, (1997).
19. Adams, T. ed., in *Kraft Recovery Boilers*, TAPPI Press, Atlanta, 1997.

Received: July 5, 2001

Revised: October 25, 2001

Accepted: November 10, 2001

This paper is also published on TAPPI's web site (www.tappi.org) and summarized in the June Solutions! for People, Processes and Paper magazine (Vol. 85 No. 6).



Malmberg



Edwards



Jönsson



Theliander

Malmberg and Edwards, are with the University of Idaho, Moscow, Idaho, USA; Jönsson is with STFI in Stockholm Sweden; Theliander is with CTH in Göteborg, Sweden, and Saltin is with Solvina AB, in Göteborg. Contact Malmberg by email at malmb921@uidaho.edu.