Prediction of metals distribution in mill processes, Part 2: Fiber line metals profiles

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ABSTRACT: In a mill system, metals content in process streams depends on metals intake, process configuration, and equipment operating conditions. While fiber flows in all processes are straightforward, filtrate configuration is becoming increasingly complicated because of mill closure. Determining the impact of alternative process and filtrate configurations on mill metals profiles is a challenge because there are many combinations and permutations. Estimating the effects of new technologies on full mill metals management before mill implementation is another important challenge. This paper—part 2 of 3—addresses these challenges by showing that the metals profile in any mill system can be predicted by process simulation, coupled with the multiphase, multi-component metals equilibrium calculations described in Part 1 of this series of papers.

A general free-energy minimization engine has been integrated into a commercial process simulator, WinGEMS. The result is a WinGEMS block, named MetEQs, that is able to allocate metals among pulp binding sites, precipitates, and solutes in any stream according to specified equilibrium models. By inserting MetEQs into any existing WinGEMS simulation, we can predict metals profiles in mill processes. In this paper, we have validated simulation results in three mills: a totally chlorine free (TCF) fiber line, an elemental chlorine free (ECF) fiber line and a thermomechanical pulp (TMP) plant.

Application: Mills can use this information for identifying and preempting scaling problems in kraft mills are closed more and more tightly.

Because of mill closure, pulp and paper mill operators have to deal with issues (e.g. metals management related to scale formation [1] and bleaching efficiency [2]) that often can be ignored in an open mill. Making things more difficult is the fact that these issues are more mill and process specific than issues related to pulp or paper products. For example, **Table I** lists metals measurements from three North American kraft pulp mills. Calcium (Ca) in Mill B is more than twice as high as that in Mill A, and manganese (Mn) in Mill C is more than four times as high as that in Mill A. In a mill system, metals content depends on metals intake, process configuration, and equipment operating conditions. Metals measurements from one mill must be interpreted very carefully before they are applied to another mill.

A relatively small process change from the point view of filtrate arrangement may cause significant changes in metals distribution [5,6]. Mill measurements shown in **Table II** were taken during a mill Q-stage trial by partially re-circulating Q-filtrate to the pre-Q-stage washer (#2 POW, see **Figure 2** for mill process) [6]. For the base case, Eop filtrate was applied to #2 POW. During the trial, #2 POW had 55% Eop filtrate and 45% Q filtrate applied to the shower. Shower flow rates were constant. Table II shows that it only took 3 h to nearly double metals contents in #2 POW mat. Manganese in the Q mat almost tripled. Clearly, filtrate configuration has significant impacts on metals distribution in bleach plants. Mill metals measurements have to be clearly understood before a closed process is evolved.

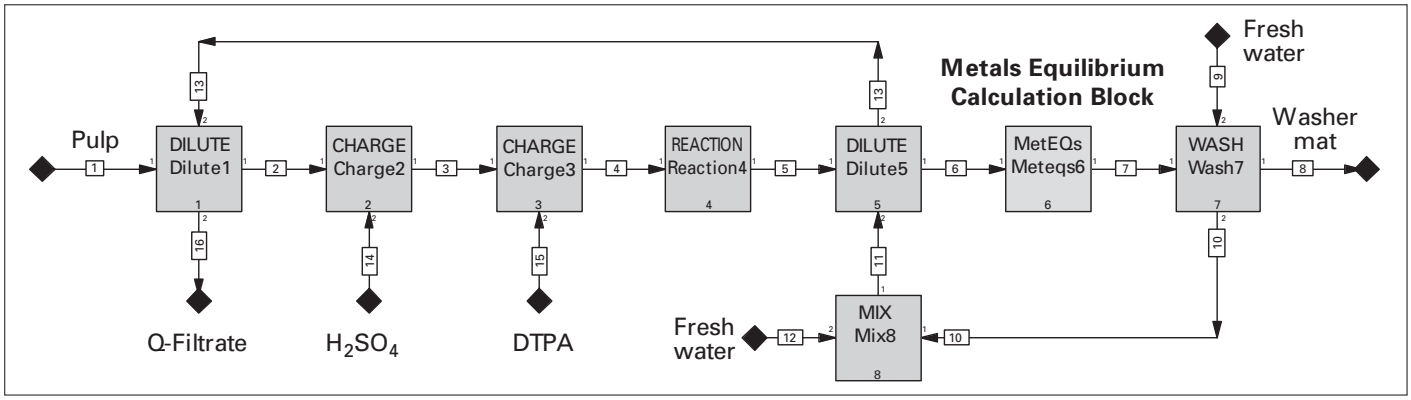
Because of the dependence on process details, mill measurements alone are not a cost-effective tool to understand general metals behavior. A more effective tool is needed to predict process effects on metals distribution from limited mill and laboratory measurements. Process simulation is an effective tool to address the process effects on volatile organic compound (VOC) air emissions [7] and bleaching [8]. This paper demonstrates that process simulation, coupled with metals equilibrium calculations, can predict metals profiles in mill processes. Using metals equilibrium models derived from laboratory and limited mill measurements [9], the affect of process modifications on metals distribution in mill processes can be predicted totally from calculations, as shown in the following sections of this paper.

Integration of equilibrium calculation into modular process simulators

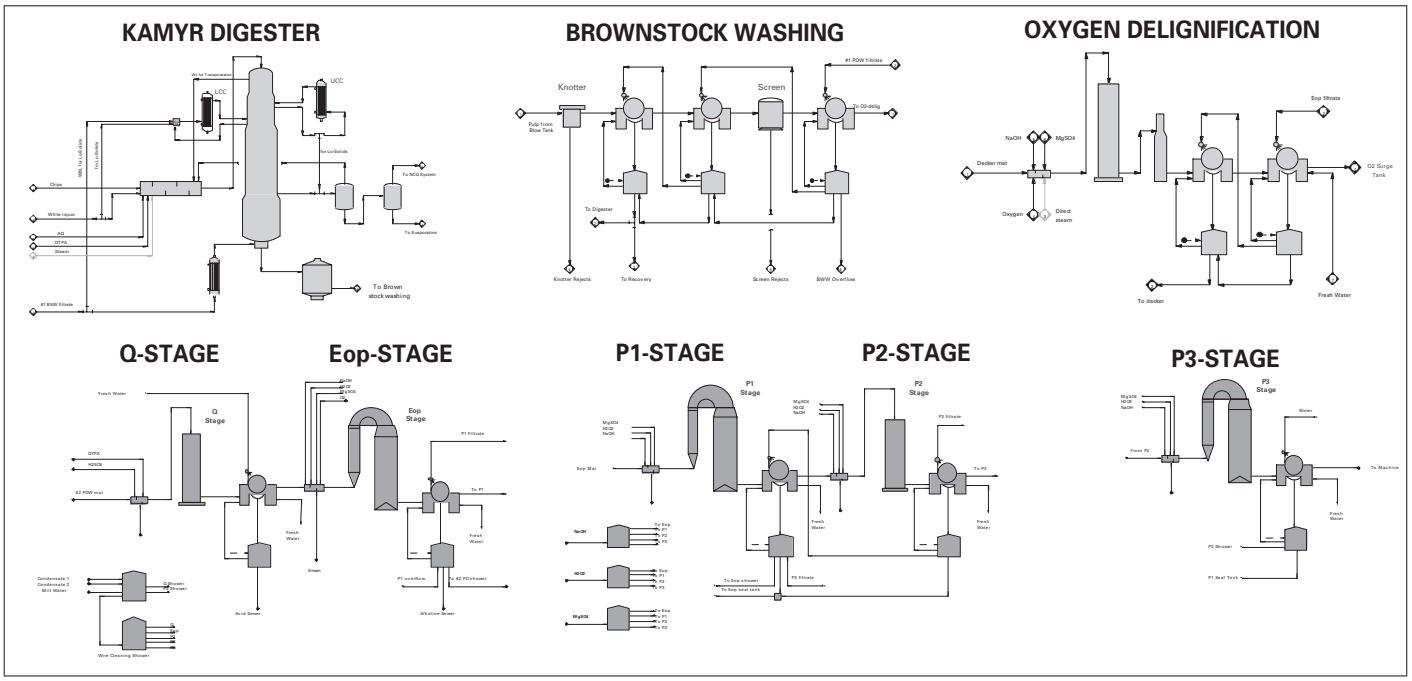
To effectively use simulation to understand metals distribution in mill processes, equilibrium calculation has to be integrated into process simulators. We have adapted a general multicomponent, multiphase equilibrium calculation program, SOLGASWATER [10], for metals equilibrium calculations in pulp slurries [9]. Free-energy minimization, needs the following inputs:

- All species involved, and their component stoichiometric coefficients
- Formation constants for all species
- Component total concentrations
- For non-ideal systems, species activity coefficients.

SOLGASWATER consists of inputs, outputs, and a free-energy minimization engine. When equilibrium calculation is integrated into a process simulator, only the free-energy minimization engine is needed. The process simulator handles the inputs and outputs. Among the four inputs listed above, only the *component total concentrations* changes in the process. The rest of the inputs are dependent on the chemistry and can be supplied as "fixed inputs" for a simulation



1. WinGEMS simulation block diagram for Q-stage with metals equilibrium calculation.



2 . TCF mill fiber line simulation.

Mat Samples	Ca mg/kg[(a)]	Mg mg/kg[(a)]	Mn mg/kg[(a)]
Mill A[(b)], #2 BSW Mat	912	316	18
Mill B[(c)], #2 BSW Mat	2520	620	77
Mill C[(d)], BSW Mat	1067	280	78

(a). mg metals per kg of oven dry pulp (free & pulp bound metals)
(b). Mill A: 3 BSWs + Decker + O_2 + 2 POWs
(c). Mill B: 2 BSWs + Decker + O_2 + 2 POWs
(d). Mill C: 2 Diffusers + BSW + Decker (internal data)

I. Metals measurements from different softwood kraft pulp mills [3, 4].

	Q Mat			#2 POW Mat		
	Mn mg/kg	Mg mg/kg	Ca mg/kg	Mn mg/kg	Mg mg/kg	Ca mg/kg
Base	8	593	850	45	867	2333
3-hour into trial	22	738	1400	82	1475	3700
Difference, %	175	24	65	82	70	59

II. Effects of Q-filtrate partial recirculation on metals content.

project. In other words, in a modular process simulator, only component total concentrations have to be carried as stream components. The rest of the inputs can be supplied as block inputs.

How we integrate equilibrium calculation into existing process simulators depends on the process simulator. For our simulations, we integrated the equilibrium calculation into WinGEMS [11]. The following integration issues apply specifically to WinGEMS.

Solids and liquor are handled separately in pulp mill simulations through various solids-liquor separation stages. Therefore, WinGEMS stream components are divided into suspended solids and dissolved solids. Pulp-bound metals behave the same as pulp in the process and dissolved metals behave the same as other dissolved solids. If the amount of pulp-bound metals and metals in the liquor are known, the existing computation blocks in WinGEMS can predict metals distribution in mill systems. Therefore, the following conditions must be fulfilled to include metal prediction into a WinGEMS simulation:

- Streams need to carry equilibrium components as suspended solids and dissolved solids in WinGEMS streams.
- Equilibrium calculations must correctly re-allocate metals between suspended solids and dissolved solids before any solids-liquor separation calculation (e.g. a press).

Including too many stream components in WinGEMS will significantly increase calculation time. Most metals simulations only need total metals concentration in liquor and on pulp. However, equilibrium calculation needs all species that exist in the system. An interface between WinGEMS and the free-energy minimization engine has been developed to convert WinGEMS stream component concentrations into the component total concentrations for equilibrium calculations. The interface also converts species equilibrium concentrations back into WinGEMS component concentrations after the equilibrium calculations. **Table III** shows WinGEMS stream components and the species list for equilibrium calculation in a totally chlorine free (TCF) fiber line metal simulation (Case A in the following section).

The equilibrium calculation is packaged as an individual block (MetEQs) in WinGEMS (see **Figure 1**). MetEQs has one input stream and one output stream. The other inputs needed for equilibrium calculations are provided as block inputs. MetEQs takes the component total concentrations from its input stream, performs equilibrium calculations according to the selected equilibrium models and block inputs, then reallocates metals into dissolved and suspended solids according to equilibrium concentrations.

Figure 1 shows the WinGEMS block diagram for the TCF chelation stage (Q-stage) simulation. We can predict metals removals at the Q-stage from the calculation. The only difference from conventional process simulation is that an equilibrium calculation block, MetEQs, is included before the WASH block. Of course, metals have to be carried as stream components (see Table III). The input stream to MetEQs, Stream 6, only carries the correct component total concentrations. Stream 6 does not have the correct distribution metals between fiber and liquor. The calculation in

WinGEMS Stream Components

Stream Comp.	Description	Units	MetEQs Input (1)	MetEQs Output (2)
Flow	Liquor flow	mt/h	1375.65	1375.67
Ssol	Susp.solid	fraction	0.0152	0.0152
Temp	Temperature	°C	74.56	74.56
Pulp	Pulp	fraction	0.977313	0.978298
Na_Sorb	Na on pulp	fraction	0.000758	0.000146
Ca_Sorb	Ca on pulp	fraction	0.002145	0.001887
Mg_Sorb	Mg on pulp	fraction	0.000340	0.000244
Mn_Sorb	Mn on pulp	fraction	0.000024	0.000000
K_Sorb	K on pulp	fraction	0.000028	0.000014
DissSol	Diss.wood solids	kg/mt liquor	0.945	0.945
Na	Na in liquor	kg/mt liquor	1.173	1.182
Ca	Ca in liquor	kg/mt liquor	0.033	0.037
Mg	Mg in liquor	kg/mt liquor	0.010	0.011
Mn	Mn in liquor	kg/mt liquor	0.002	0.002
K	K in liquor	kg/mt liquor	0.002	0.002
DTPA	DTPA chelant	kg/mt liquor	0.336	0.336

SOLGASWATER Components and Component Total Concentrations (3)

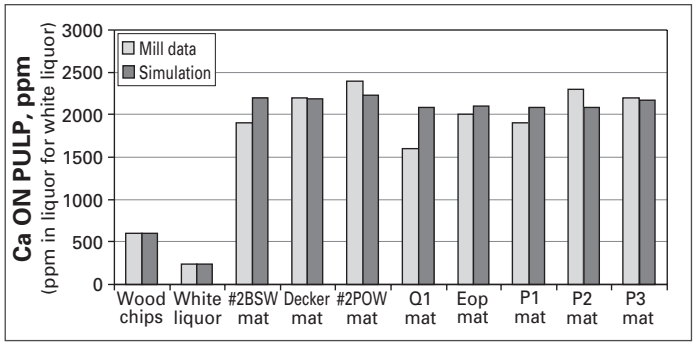
Component	Description	Comp. Total Conc. (mol/l)
H^+	Proton	Unlimited
Chp^-	Pulp binding site 1	1.305E-03
Pp^-	Pulp binding site 2	8.751E-04
Na^+	Sodium	5.150E-02
Ca^{++}	Calcium	1.633E-03
Mg^{++}	Magnesium	6.300E-04
Mn^{++}	Manganase	4.396E-05
Y^{5-}	DTPA chelant	8.656E-04
W^-	Diss. Woods	3.149E-03
Clp-	Pulp binding site 3	4.108E-04
K^+	Potassium	6.440E-05

SOLGASWATER Species and Species Equilibrium Concentrations (mol/l)(4)

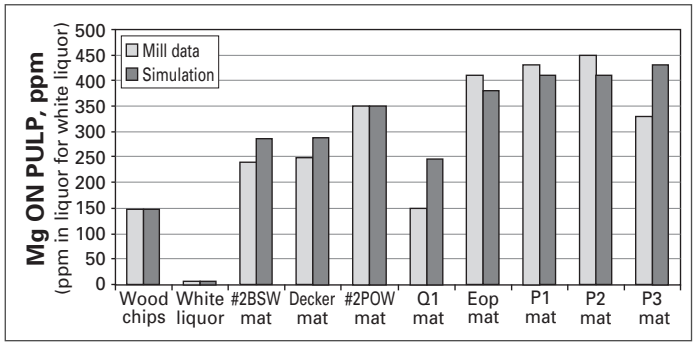
Species	EQ Conc.	Species	EQ Conc.	Species	EQ Conc.
H^+	3.162E-06	$CaClp^+$	7.357E-06	HW	2.390E-03
Chp^-	2.951E-04	$CaPp^+$	2.106E-09	CaW^+	7.241E-08
Pp^-	2.767E-08	CaY^{3-}	1.546E-04	MgW^+	4.508E-08
Na^+	5.140E-02	$MgClp^+$	1.448E-05	$Mn(OH)W_2^-$	3.908E-14
Ca^{++}	7.610E-04	$MgPp^+$	4.145E-08	KClp	5.694E-09
Mg^{++}	4.737E-04	MgY^{3-}	1.921E-06	KPp	1.630E-10
Mn^{++}	8.611E-09	$MnClp^+$	4.172E-11	HClp	3.849E-04
Y^{5-}	4.054E-12	$MnPp^+$	2.383E-14	NaChp	9.572E-05
W^-	7.559E-04	MnY^{3-}	4.395E-05	$CaChp^+$	7.102E-04
Clp^-	3.057E-06	H_5Y	1.143E-11	$MgChp^+$	1.398E-04
K^+	5.890E-05	H_4Y^-	5.860E-08	$MnChp^+$	4.028E-09
HChp	5.888E-05	H_3Y^{2-}	5.104E-05	KChp	5.497E-06
HPp	8.750E-04	H_2Y^{3-}	6.136E-04	$Mn(OH)Chp_2^-$	1.496E-09
NaClp	9.915E-07	HY^{4-}	3.372E-07	NaW	3.086E-06
NaPp	8.975E-09	$Mn(OH)Clp_2^-$	1.606E-13	KW	3.536E-09

1. Before equilibrium calculation, Stream No.6 in Figure 1
2. After equilibrium calculation, Stream No.7 in Figure 1
3. Converted from WinGEMS stream components into MetEQs input stream
4. Converted into WinGEMS stream components from MetEQs output stream

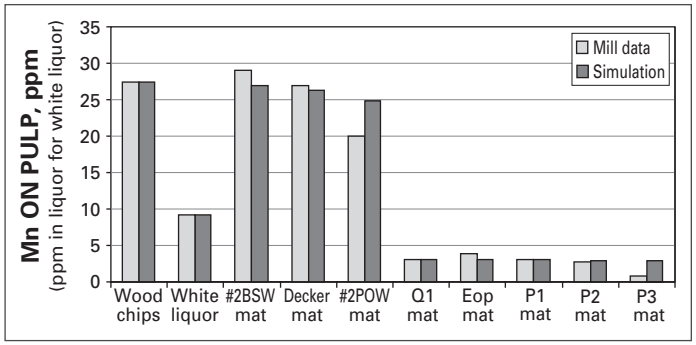
III. WinGEMS stream components and equilibrium species for a TCF fiber line simulation (Case A) and concentrations at Q vat.



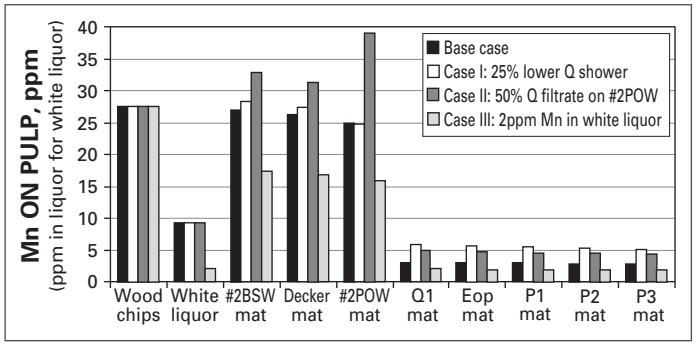
3. Comparison of metals simulation and mill measurements: calcium.



4. Comparison of metals simulation and mill measurements: magnesium.



5. Comparison of metals simulation and mill measurements: manganese.



6. Manganese profiles for simulated process modifications.

MetEQs re-allocates metals on fiber and in the liquor according to the selected equilibrium models. Because only metals in liquor can be removed in the following washing calculation, correctly allocating metals on pulp and in liquor is essential to correctly predict metals separation in the washer. For example, almost all manganese (Mn) is in the liquor when the Q-stage is operated correctly and about 70% of total Ca is still bound to pulp. Therefore, most Mn will be removed from Q mat with adequate washing, while about 80% of calcium (Ca) input to Q-stage still exists in the Q mat. This result is important in relation to bleach plant scale issues and hydrogen peroxide decomposition.

Figure 1 shows that it is not very difficult to include metal profile predictions into an existing process simulation when the equilibrium calculation tool and the related equilibrium model are available. The equilibrium calculation tool, MetEQs, is totally general. Further work should focus on developing the equilibrium models that are inputs for MetEQs.

Mill measurement: method and accuracy

Case A: TCF fiber line (analyzed by University of Idaho, Analytical Sciences Laboratory)

- Wood and pulp mat samples: Collected at mat consistency, ashed, dissolved, and analyzed using ICP-AES. Units are parts per million (ppm) metal (free and bound) by mass, based on oven dry pulp. Maximum 10% errors at minimum detection limit (MDL). The MDL for manganese is 0.4 ppm and 2.0 ppm for other metals reported. Above the MDL, the percent error drops substantially.
- White liquor: Acid digestion following by ICP-AES analysis. MDL is at least 10 times lower than for the pulp.

Case B: Elemental chlorine free (ECF) fiber line (analyzed by Eka Chemicals R&D Laboratories in Sweden)

Case C: Thermomechanical pulp (TMP) plant (analyzed by University of Washington Pulp and Paper Laboratory, Seattle)

Mill simulation: case studies

Metals profiles in three mill systems were predicted from simulation:

- Case A: TCF fiber line, for peroxide bleaching metals control
- Case B: ECF fiber line, for scale control and potassium balance
- Case C: TMP plant, for calcium oxalate scale control.

We compared the simulation results with mill measurements. The equilibrium models used in these simulations are included into MetEQs as built-in equilibrium models. All calculations are conducted in WinGEMS.

Case A: TCF fiber line metals profile

The Samoa Pacific mill converted its bleach plant from CEDED into TCF bleaching ($QEopP_1P_2P_3$). Because transition metals, mainly Mn, cause peroxide decomposition, metals management became a new issue for the mill operation. Through better understanding metals behavior in the process, Mn in peroxide bleaching stages has been cut from about 10 ppm at the beginning of TCF conversion to 2-3 ppm now, while bleach plant effluent has been reduced to about 7 m^3/tp. The Mn decrease is mainly from:

- Better nonprocess elements (NPE) management in chemical recovery resulting in white liquor with lower NPE contents [12]
- Better metals purge at the digester through Lo-Solids™ cooking

Stream	Ca, %	Mg,%	Mn,%
Chips	43.2	53.3	53.7
White Liquor	43.0	5.6	46.3
Chemicals	0.0	41.0	0.0
Mill Water	13.9	0.0	0.0
Black Liquor	21.1	16.0	78.9
BP Sewers	11.1	16.8	18.5
Rejects	0.2	0.1	0.1
Bleached Pulp	67.6	67.1	2.4

IV. Metals sources and sinks for TCF fiber line.

- Better Q-tower pH control and better Q-stage washing.

The mill normally uses a mixture of 20% redwood and 80% Douglas fir for TCF production. The chips are cooked in a single vessel, hydraulic, Kamyr digester using Lo-Solid™ technology. Medium consistency oxygen delignification is followed by $QEopP_1P_2P_3$ bleaching to 87%-plus brightness.

Diaminetriethylenepentaacetic acid (DTPA) serves as chelant at the Q-stage and all Q-filtrate is purged. Fresh water or evaporator clean condensate is applied to the P_3 washer shower. P_3 filtrate is used for countercurrent washing to P_2, P_1, and Eop. All shower water at the No.2 post-oxygen washer is Eop filtrate. The rest of Eop filtrate overflows to the bleach plant alkaline sewer. The total bleach plant effluent is about 7 m^3/tp and 80% of the effluent is Q-filtrate. Figure 2 diagrams the flow.

Five metals—sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), and manganese (Mn)—are included in the simulation. Table III shows the 16 stream components related to metals equilibrium calculation. The metals equilibrium calculation includes 11 components and 45 species, as also shown in Table III. See Part 1 of this series for more details about the equilibrium model [9].

The metals content in wood chips and white liquor were specified according to mill measurements. Three MetEQs blocks are used in the digester (before the separation of UCC liquor, LCC liquor, and main extraction). One MetEQs block is used for each washer to allocate metals in the washer vat according to equilibrium calculation. pH was specified according to mill measurements. We used laboratory equilibrium data to develop the formation constants [9]. We made some adjustments for the digester calculation. The formation constants for species formed from metals and dissolved organics were determined from mill data plus trial and error simulation due to lack of laboratory equilibrium data.

Components

Serial No.	Component	Description	Serial No.	Component	Description
1	H^+	Proton	8	K^+	Potassium
2	Chp^-	Pulp binding site 1	9	Ba^{2+}	Barium
3	Clp-	Pulp binding site 2	10	Mn^{2+}	Manganese
4	Pp^-	Pulp binding site 3	11	W^-	Dissolved wood solids
5	Na^+	Sodium	12	OX^{2-}	Oxalate
6	Ca^{2+}	Calcium	13	SO_4^{2-}	Sulfate
7	Mg^{2+}	Magnesium	14	CO_3^{2-}	Carbonate

Formed Species

Serial No.	Species	Formation Reaction	Constant (1)	Serial No.	Species	Formation Reaction	Constant (1)
1	HChp	$H^+ + Chp^- === HChp$	3.4	21	$Mn(OH)Clp_2^-$	$Mn^{2+}+OH^-+2Clp^- ===Mn(OH)Clp_2^-$	2.0
2	HClp	$H^+ + ClpF^- === HClp$	5.5	22	MnW^+	$Mn^{2+} + OH^- + 2W^- === Mn(OH)W_2^-$	-4.60
3	HPp	$H^+ + Pp^- === HPp$	10.0	23	$BaChp^+$	$Ba^{2+} + Chp^- === BaChp^+$	3.50
4	HW	$H^+ + W^- === HW$	6.0	24	$BaClp^+$	$Ba^{2+} + Clp^- === BaClp^+$	5.00
5	NaChp	$Na^+ + Chp^- === NaChp$	2.2	25	$BaPp^+$	$Ba^{2+} + Pp^- === BaPp^+$	5.00
6	NaClp	$Na^+ + Clp^- === NaClp$	3.0	26	BaW^+	$Ba^{2+} + W^- === BaW^+$	-1.00
7	NaPp	$Na^+ + Pp^- === NaPp$	2.5	27	$BaSO_4(a)$	$Ba^{2+} + SO_4^{2-} === BaSO_4(a)$	1.67
8	NaW	$Na^+ + W^- === NaW$	-1.1	28	$CaChp^+$	$Ca^{2+} + Chp^- === CaChp^+$	4.00
9	KChp	$K^+ + Chp^- === KChp$	2.5	29	$CaClp^+$	$Ca^{2+} + Clp^- === CaClp^+$	3.50
10	KClp	$K^+ + Clp^- === KClp$	1.5	30	$CaPp^+$	$Ca^{2+} + Pp^- === CaPp^+$	2.00
11	KPp	$K^+ + Pp^- === KPp$	2.0	31	CaW^+	$Ca^{2+} + W^- === CaW^+$	-0.90
12	KW	$K^+ + W^- === KW$	-1.1	32	CaOX(a)	$Ca^{2+} + OX^{2-} === CaOX(a)$	1.66
13	$MgChp^+$	$Mg^{2+} + Chp^- === MgChp^+$	3.5	33	$CaCO_3(a)$	$Ca^{2+} + CO_3^{2-} === CaCO_3(a)$	5.10
14	$MgClp^+$	$Mg^{2+} + Clp^- === MgClp^+$	4.5	34	HOX^-	$H^+ + OX^{2-} === HOX^-$	3.55
15	$MgPp^+$	$Mg^{2+} + Pp^- === MgPp^+$	4.0	35	H_2OX	$2H^+ + OX^{2-} === H_2OX$	4.59
16	MgW^+	$Mg^{2+} + W^- === MgW^+$	-0.9	36	HCO_3^-	$H^+ + CO_3^{2-} === HCO_3^-$	10.34
17	$MnChp^+$	$Mn^{2+} + Chp^- === MnChp^+$	3.2	37	H_2CO_3	$2H^+ + CO_3^{2-} === H_2CO_3$	16.64
18	$MnClp^+$	$Mn^{2+} + Clp^- === MnClp^+$	3.2	38	CaOX(s)	$Ca^{2+} + OX^{2-} === CaOX(s)$	6.90
19	$MnPp^+$	$Mn^{2+} + Pp^- === MnPp^+$	2.0	39	$CaCO_3(s)$	$Ca^{2+} + CO_3^{2-} === CaCO_3(s)$	8.06
20	$Mn(OH)Chp_2^-$	$Mn^{2+}+OH^-+2Chp^- ===Mn(OH)Chp_2^-$	2.0	40	$BaSO_4(s)$	$Ba^{2+} + SO_4^{2-} === BaSO_4(s)$	5.00

Note: 1. Formation constants, pKf

V. Equilibrium model for ECF fiber line simulation.

In addition to metals input from wood chips and white liquor, $MgSO_4$ was added for oxygen delignification, Eop, and P stages. **Figures 3-5** show the comparison of mill data with simulation results. The simulation reasonably matches mill data.

When metals distribution can be predicted from simulation, many process alternatives related to metals can be conducted by simulation. Better process configurations can be developed quickly and economically using simulation, followed by confirmation from mill trials.

For the TCF process shown in Fig. 2, further effluent reduction can be achieved through eliminating the alkaline sewer and reducing Q-filtrate to the acid sewer. Actually, the alkaline sewer was totally eliminated for a short period of mill operation.

Both simulation and the mill trial show that eliminating the alkaline sewer did not cause any problems in metals management. Eliminating the alkaline sewer also allows the mill to recycle residual peroxide (about 2 g/L H_2O_2). However, the water balance for nine countercurrent vacuum washers is hard to manage. The reduction of acid sewer flow is much more difficult.

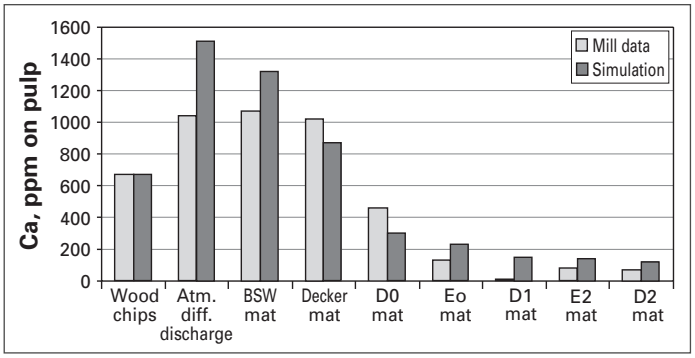
Figure 6 shows the affects on Mn from the following process changes:

- Case I: Cutting Q shower flow 25%
- Case II: Applying 50% Q-filtrate to #2 POW shower (mixing Q-filtrate with Eop filtrate)
- Case III: Using white liquor with 2 ppm Mn (9.2 ppm Mn for base case).

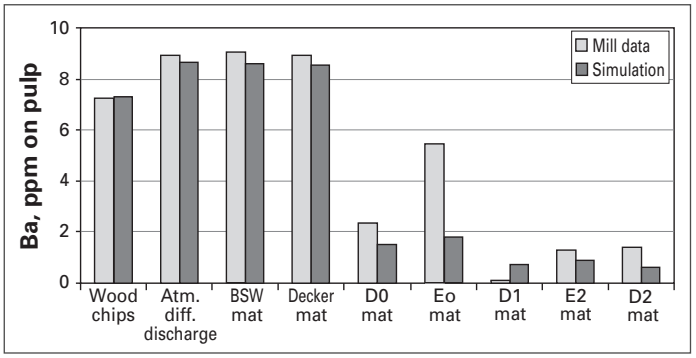
Figure 6 demonstrates that less washing results in more Mn carryover into peroxide stages. When Q-filtrate is applied on #2 POW showers, a circulation of metals is formed between #2 POW and the Q-stage, which makes Q-stage metals input higher. Lower Mn in white liquor reduces Mn carryover to Q-stage, which makes acid sewer flow reduction easier.

Table IV shows an overall mass balance for the full fiber line Ca, Mg, and Mn from simulation. $MgSO_4$ additions account for 50% of Mg intake. Good management of Mg addition in oxygen delignification is helpful to lower Mg entering the chemical recovery system. About two thirds of Ca and Mg are left on bleached pulp. How to purge Ca and Mg from the process has to be considered if the machine white water is closed and/or recirculated to the bleach plant.

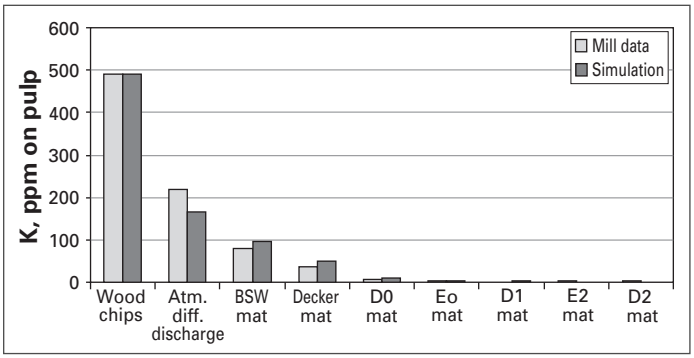
For TCF bleaching, Mn control is the most important issue for metals management. From the view of a full pulp mill (TCF), all Mn is from wood and is purged either from through the chemical recovery system or Q-filtrate. When Mn reaches the bleach plant, removing Mn represents a Q-stage cost (chelant, pH adjustment, and washing). Purging Mn from the recovery system is a more cost-effective



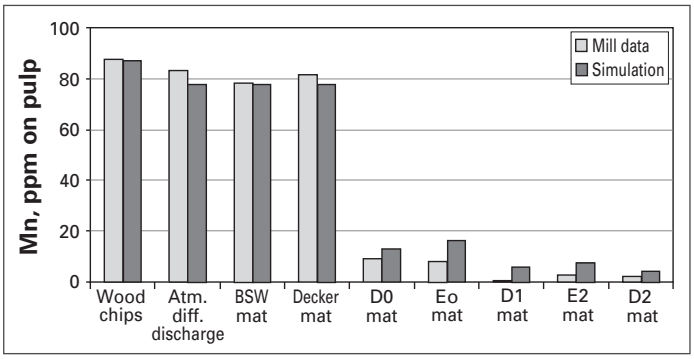
7. Comparison of simulation with mill measurements: calcium.



8. Comparison of simulation with mill measurements: barium.



9. Comparison of simulation with mill measurements: potassium.



10 . Comparison of simulation with mill measurements: manganese.

	Digester Extraction		Blowline Carryover		BP Acid Sewer	
	Mill Data	Sim.	Mill Data	Sim.	Mill Data	Sim.
K	33.7	87.6	153.3	97.7	1.9	2.3
Ca	41.3	45.6	41.3	43.9	50.0	33.5
Mg	16.0	22.9	11.8	10.4	13.0	13.9
Ba	0.83	0.86	0.47	0.11	0.30	0.38
Mn	14.0	13.5	8.0	0.3	3.7	3.6

VI. Comparison of simulation with ECF mill measurements: metals in liquors (ppm in liquor).

	Digester Extraction, %	WBL Bypass, %	Acid Sewer, %	Alkaline Sewer, %	Bleached Pulp, %
K	69	27	4	0	0
Ca	26	15	47	4	8
Mg	36	6	53	1	4
Ba	46	1	49	0	4
Mn	60	0	38	0	2

VII. Model predicted metals purge in ECF fiber line.

approach. The separation of Mn from fiber is mainly determined by cooking operations. New cooking technologies, such as Lo-Solids™ cooking, purge more Mn into black liquor than does conventional cooking. At 9.2 mg/L Mn in white liquor, Mn input from white liquor accounts for about 45% of total Mn input into fiber line (Table IV). Better Mn management in chemical recovery reduces Mn in white liquor to 2 mg/L [12]. Figure 6 shows the affect of lower Mn in white liquor on Mn in the fiber line.

Case B: ECF fiber line

Case B is for a kraft pulp mill that produces bleached market pulp from softwood and hardwood. A two-vessel Lo-Solids™, Kamyr continuous digester is used for cooking. Brownstock washing includes a pressurized diffuser, a two-stage atmospheric diffuser, a vacuum drum washer, and a decker. The bleach plant is a typical 5-stage ECF DEoDED sequence. We conducted mill sampling and full mill process simulation to understand metals distribution in its fiber line and chemical recovery system. The data and simulation presented in this section is only for softwood.

Table V shows the species and formation constants for the equilibrium model used in the simulation. The model includes 14 components, 40 formed species, and three precipitants—calcium oxalate (CaC_2O_4), calcite/limestone ($CaCO_3$), and barium sulfate ($BaSO_4$). Compared to the equilibrium model used in Case A, this model focuses more on solids precipitation. Most of the formation constants in Table V are identified from modeling pulp's metal binding ability, as presented in Part 1 of this series [9].

Figures 7-10 show the comparisons of metals simulation results with mill measurements for softwood. Metals shown in these figures are total metals (pulp-bound metals and metals in liquor) for oven dry pulp. The simulation shows no CaC_2O_4 and $BaSO_4$ precipitation. However, $CaCO_3$ precipitation is found in the simulation. In current calculation, all precipitated $CaCO_3$ is treated as suspended solids. Further study is needed to understand the behaviors of model predicted precipitants in real mill processes.

The major source of nonprocess metals is wood chips. Figures 7-10 show that metals content in bleached pulp is very low. Therefore, the metals from wood chips are purged mainly in the liquors. The major purge liquors in the fiber line are digester extraction liquor, bypass weak black liquor, bleach plant acid sewerage, and bleach plant alkaline sewerage

Components							
Serial No.	Component	Description		Serial No.	Component	Description	
1	H^+	Proton		6	OX^{2-}	Oxalate	
2	Na^+	Sodium		7	Lf	Long Fibers	
3	Ca^{2+}	Calcium		8	F^-	Fines	
4	Al^{3+}	Aluminum		9	Co^-	Colloids	
5	CO_3^{2-}	Carbonate		10	W^-	Dissolved wood solids	
Formed Species							
Serial No.	Species	Formation Reaction	Constant [1]	Serial No.	Species	Formation Reaction	Constant [1]
1	HLf	$H^+ + Lf^- === HLf$	6.0	13	$AlLf^{2+}$	$Al^{3+} + Lf^- === AlLf^{2+}$	3.0
2	HF	$H^+ + F^- === HF$	6.0	14	AlF^{2+}	$Al^{3+} + F^- === AlF^{2+}$	3.0
3	HCo	$H^+ + Co^- === HCo$	6.0	15	$AlCo^{2+}$	$Al^{3+} + Co^- === AlCo^{2+}$	3.0
4	NaLf	$Na^+ + Lf^- === NaLf$	0.8	16	HOX^-	$H^+ + OX^{2-} === HOX^-$	3.55
5	NaF	$Na^+ + F^- === NaF$	0.8	17	H_2OX	$2H^+ + OX^{2-} === H_2OX$	4.59
6	NaCo	$Na^+ + Co^- === NaCo$	0.8	18	HCO_3^-	$H^+ + CO_3^{2-} === HCO_3^-$	10.34
7	NaW	$Na^+ + W^- === NaW$	-1.1	19	H_2CO_3	$2H^+ + CO_3^{2-} === H_2CO_3$	16.64
8	$CaLf^+$	$Ca^{2+} + Lf^- === CaLf^+$	3.4	20	CaOX(a)	$Ca^{2+} + OX^{2-} === CaOX(a)$	1.66
9	CaF^+	$Ca^{2+} + F^- === CaF^+$	3.4	21	$CaCO_3(a)$	$Ca^{2+} + CO_3^{2-} === CaCO_3(a)$	2.00
10	$CaCo^+$	$Ca^{2+} + Co^- === CaCo^+$	3.4	22	CaOX(s)	$Ca^{2+} + OX^{2-} === CaOX(s)$	6.90
11	CaW^+	$Ca^{2+} + W^- === CaW^+$	-0.9	23	$CaCO_3(s)$	$Ca^{2+} + CO_3^{2-} === CaCO_3(s)$	1.66
12	AlW^{2+}	$Al^{3+} + W^- === AlW^{2+}$	-0.9	24			

Note: 1. Formation constants, pKf

VIII. Equilibrium model for TMP plant simulation.

Stream	Oxalate, kg/h	Calcium, kg/h
Chips	7.10	17.29
PM WW	38.25	21.25
Generation	12.60	
Total Input	**57.95**	**38.54**
Pulp	27.75	31.64
Sewer	3.09	0.06
Chip washer effluent	1.29	0.31
WW overflow	25.76	6.35
Total output	**57.89**	**38.37**

IX. TMP plant overall oxalate and calcium balances.

Table VI compares the metals content in these liquors with mill measurements. In Table VI, the blow line carryover is a substitute for the weak black liquor that was not measured. The simulation can reasonably predict metals on fiber and in liquors.

The potassium profile in the fiber line (Fig. 9) is very different from the calcium, barium, and manganese profiles. Pulp bound K is much lower in comparison to the other metals. Therefore, K is removed during brownstock washing, while other pulp bound metals are not removed. Compared to K in wood chips, K carryover to the bleach plant is negligible. Therefore, all K in wood chips will end up in the chemical recovery system. Figures 7, 8, and 10 show that almost all metals in the brownstock are purged at the D_0 stage in the ECF bleach plant. At pH 2-3, almost all metals are dissolved and in solution after the D_0 tower. Good washing at the D_0 stage purges non-process metals into the bleach plant acid sewer.

Table VII shows where metals are purged from an ECF fiber line. Table VII clearly shows that the most effective approach to lower metals in brownstock is to improve digester extraction. In the ECF bleach plant, D_0 stage washing determines metals content in the bleach plant if the D_0 stage pH is well controlled.

Case C: TMP plant calcium oxalate precipitation

A newsprint mill had calcium oxalate scale related problems in its TMP plant and paper machine. A significant amount of CaC_2O_4 scale was found in the bottom of the TMP pressate tank. When the mill converted the paper machine to alkaline paper making to make use of $CaCO_3$ as filler, CaC_2O_4 scale became a serious issue. A campaign was conducted to solve the CaC_2O_4 scale problem. The following analysis focuses on the TMP plant. Mill measurements and simulation were conducted to understand Ca, CaC_2O_4 distribution and oxalate generation.

After the primary refiners, fibers are bleached by 2.5% hydrogen peroxide in a high consistency tower to produce high brightness newsprint products. Oxalate is generated during peroxide bleaching. The pulp is diluted to 5% at the bottom of the bleaching tower. Before the secondary refiners, pulp consistency is raised to above 35% by presses. Pressate is used in the bottom dilution of the bleaching tower. CaC_2O_4 scale was found in the pressate tank.

We performed a TMP plant simulation, including metals equilibrium calculation. **Table VIII** shows the components and species included in the equilibrium model. Matching oxalate measurements by simulation, we found that 0.23 kg oxalate per ton of pulp is formed during peroxide bleaching. Peroxide is added at the discharge of the primary refiners. Before the pulp reaches the bleaching tower (2-3 minutes on a conveyer), 0.2 kg/ton of pulp of oxalate forms. The oxalate generation in the bleaching tower is only 0.03 kg/ton of pulp. The simulation and measurements show that CaC_2O_4 precipitate exists in the whole TMP process (**Figs. 11** and **12**). We found CaC_2O_4 in all pulp samples.

Table IX summarizes the overall calcium balance for the TMP plant derived from the simulation. The major source of Ca (70%) is wood chips and 90% of Ca from wood ends up in the pulp to the paper machine. These data show that it is better to focus on oxalate, rather than calcium, in the TMP plant to attack CaC_2O_4 scale problems. **Figures 13** and **14** show the comparisons of mill measurements for Ca and Na with simulation results.

CONCLUSIONS

This paper demonstrates the utility of integrating an equilibrium calculation scheme into a general pulp and paper simulator (WinGEMS). Calculated fiber line metals profiles match actual mill data for TCF, ECF, and TMP mills.

After validating the simulation using mill measurements, the following predictions illustrate practical applications of this powerful new simulation tool to mill issues:

TCF mill

A 25% reduction in post-chelation washer shower flow doubles the manganese level in the washer mat.

ECF mill

Almost no potassium is purged in the bleach plant acid sewer. This affects the recovery boiler dust stickiness.

TMP mill

Controlling paper machine calcium oxalate scale is best addressed by managing the oxalate rather than the calcium. **TJ**

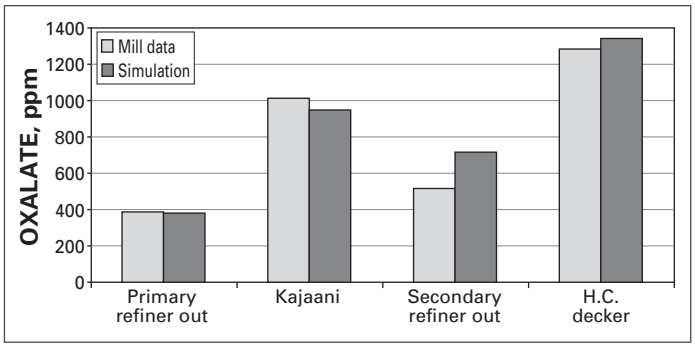
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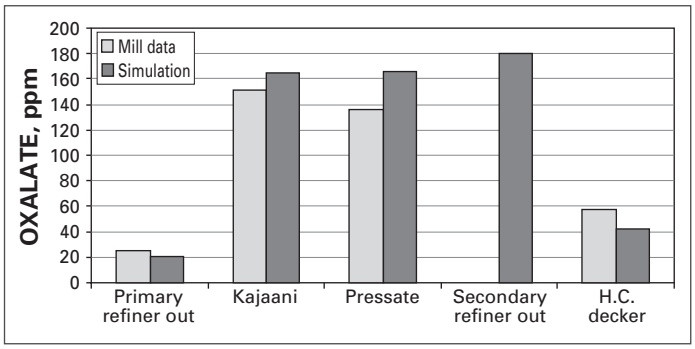
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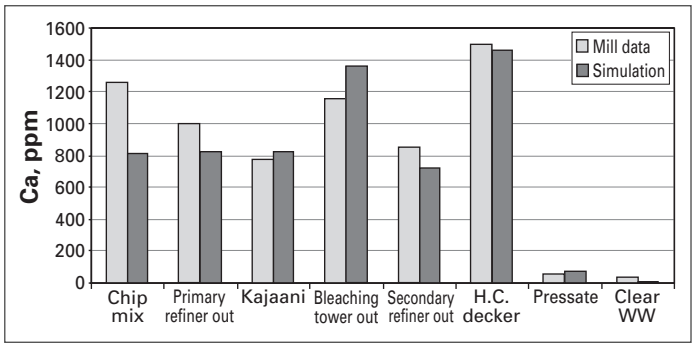
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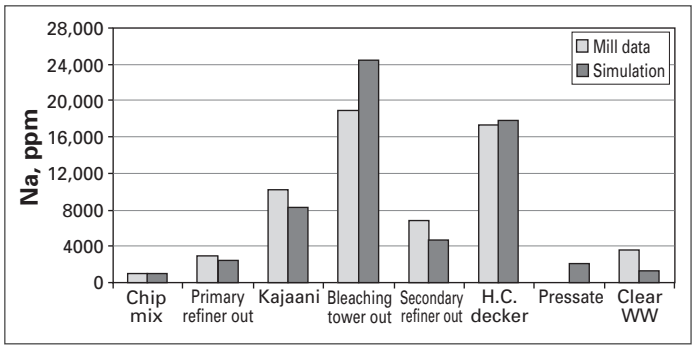
11. Comparison of simulation with TMP mill measurements: total oxalate.



12. Comparison of simulation with TMP mill measurements: oxalate in liquor.



13. Comparison of simulation with TMP mill measurements: total calcium.



14. Comparison of simulation with TMP mill measurements: total sodium.

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INSIGHTS FROM THE AUTHORS

We chose this field of research because we feel that the industry needs tools to manage non-process metals in kraft mills. This work adds multi-component, multi-phase chemical equilibrium calculations to the WinGEMS modular mass and energy balance software already available.

Validation of the computations was the most difficult task of this research. It required collection of mill data over several years.

Mills can use the information in this research when designing programs for bleach plant scale prevention. It will also be useful for mills that want lower hydrogen peroxide decomposition in bleach plants. The next step in the research will be mill applications and model improvements.

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