Prediction of metals distribution in mill processes, Part 1: Metals equilibrium model

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ABSTRACT: In this paper, a general equilibrium calculation program for aqueous multicomponent and multiphase systems, SOLGASWATER, is adapted to metals equilibrium calculation for pulp slurries. Sodium, calcium, magnesium, potassium, and manganese are currently included in the model. A set of pulp-bound metals measurements at different pHs are used to determine the interactions of pulp-binding ligands with metals. The effect of diaminetriethylenepentaacetic acid (DTPA) on metals equilibrium is included in the model. We examine the effects of dissolved organics and temperature and present the related models.

This paper provides the basic equilibrium models for metals profile prediction in kraft pulp mills. Part 2 of this series demonstrates that metals profiles in fiber lines can be predicted by combining this equilibrium engine with existing process simulators. Part 3 of this series shows how nonprocess metals can be calculated and controlled in kraft mill chemical recovery systems.

Application: By combining equilibrium calculations with mill measurements, simulation can help to address practical mill issues and help us to understand metals distribution at real mill conditions.

In response to environmental regulations, pulp mills are using more environmentally friendly technologies, such as peroxide-based bleaching and mill closure. Because transition metals, such as manganese (Mn), catalyze peroxide decomposition, these metals have to be removed before peroxide-based bleaching stages. The reduction of mill water usage and filtrate discharge also increases the possibility of scale, such as calcium oxalate, forming in mill processes. Nonprocess metals management is becoming an important issue in mill operation.

The major source of nonprocess metals is wood chips [1]. A significant amount of magnesium (Mg) is added as a fiber protector when oxygen delignification and peroxide bleaching are used. During cooking, metals from the wood dissolve into the spent cooking liquor. The amount of metals separated from the fiber during cooking depends on cooking conditions and how much black liquor can be extracted. Nonprocess metals left in washed brownstock are almost totally purged at the chlorine (Cl_2) or chlorine dioxide (ClO_2 [D_0]) stages if good washing is available for these stages. In totally chlorine free (TCF) sequences, Mn is purged at a chelation stage, while a significant amount of calcium (Ca) and Mg are left in bleached pulp. Part 2 of this series [1] presents these data from mill measurements and simulation.

Most nonprocess metals left in black liquor are precipitated in green liquor and white liquor. How these precipitants are purged from chemical recovery depends on the operation of the green liquor and white liquor clarifiers. Part 3 of this series [2] presents a good example. Thermomechanical pulp (TMP) mills also have metals related scale issues, as described in Part 2.

Mill process and operating conditions have a significant role in determining how metals are distributed and purged from the processes. To predict metals distribution in mill processes, we need to understand the fundamentals, such as metals binding to pulp and metals solubility in green liquor, and the process effects. Our experiences in volatile organic compound (VOC) air emissions [3] and bleaching [4] have shown that the effects of the process details can be modeled by an existing modular simulator (WinGEMS) if fundamental models are carefully included in the simulation. This paper presents the basic equilibrium model needed for the prediction of metals in mill processes. Part 2 of this series [1] demonstrates how this metals equilibrium model is combined with WinGEMS to predict metals profiles in fiber lines. Part 3 of this series [2] is about nonprocess metals management in kraft chemical recovery systems.

MODELING METALS DISTRIBUTION: BACKGROUND

Metals equilibrium vs. process measurements

We based the proposed approach to predicting metals distribution in mill processes on combining mass and energy balances with metals equilibrium calculations. This approach assumes that there is enough time for metals to reach equilibrium at mill conditions. This assumption is validated below.

In laboratory diaminetriethylenepentaacetic acid (DTPA) chelation experiments [5], Mn concentration reaches 91% equilibrium in 2 min and 96% in 5 min (75°C). High temperature decreases the time needed. The time needed to reach equilibrium is very short even for a significant shift of equilibrium concentrations. For example, in the DTPA chelation experiments [5], the initial Mn on pulp is 25 ppm and the Mn equilibrium concentration on pulp is 0.9 ppm.

Table I compares Mn measured from mill samples and predicted from equilibrium calculation. We obtained the mill measurements during a mill trial that used Eop-filtrate on the chelation stage (Q-stage) washer shower (**Fig. 1**)[5]. The tower has 30 min residence time and the washer is a vacuum drum washer. The tower was operated at pH 5.5. Before the trial, fresh water was used as the washer shower. During the trial, part of the fresh

water was replaced by Eop-filtrate (pH 10.5). Because of the high pH of Eop-filtrate, the application of Eop-filtrate caused a pH increase in the washer vat and mat. Although Q-filtrate was used for Q-stage incoming pulp dilution, the tower was held at pH 5.5 by adjusting the addition of sulfuric acid (H_2SO_4). Therefore, the pH change occurred at washer vat dilution. The time from the vat dilution to the vat sampling point (inside the hood) and the mat sampling point (before repulping) is very short. Manganese content in vat samples reflects the pH shift from the tower pH 5.5 to the vat pH. Table I shows that the predicted Mn concentrations, assuming equilibrium at vat pH, are very close to mill measurements.

The rebalance of metal concentration between pulp and liquor is very fast. At vat pH 7.8 in Table I, measured Mn bound on vat pulp was 15.1 ppm, while Mn-bound pulp at the Q tower (pH 5.5) is below 1.6 ppm. Table I shows that even for the fast pH change situation, equilibrium-based calculation can predict metals content in mill processes. For most process situations, equilibrium shift is not as dramatic as the situation in Fig. 1 and time for the shift normally is much longer. Therefore, it is reasonable to predict metals profiles in mill processes from equilibrium calculations.

Equilibrium calculation engine: SOLGASWATER

Understanding metals behaviors in pulp and paper mills is a complex and on-going task. A general equilibrium calculation program with the details of the equilibrium system supplied as model inputs is desirable. Ultimately, only these model inputs are changed and no modification is needed for the calculation program. SOLGASWATER [6] is one of the available equilibrium calculation programs.

SOLGASWATER [6] is a general computer program for aqueous multicomponent, multiphase equilibrium calculation. It was developed in the late 1970s in Sweden. In addition to multiple liquid phases, gas and solids can also be included.

In SOLGASWATER, components are the basic units. Formed species are derived from components. Species refers to both components and formed species. The following items are needed to define a system for equilibrium calculation:

1. All species involved, and their stoichiometric coefficients for all components.
2. Formation constants for all species.
3. Component concentrations.
4. For non-ideal systems, species activity coefficients.

SOLGASWATER details are available in the original publication [6].

The mathematical approach to equilibrium calculation is general, stable, and available. The calculation of equilibrium by SOLGASWATER is mainly about defining the system, i.e. preparing the four items listed above. SOLGASWATER takes these inputs, performs the mathematical calculations, and delivers the equilibrium concentrations for all species in the system as the calculation results. This paper shows how SOLGASWATER is used to describe metal equilibrium calculation for pulp slurries. Metals precipitation in the fiber line and chemical recovery is also calculated in Parts 2 and 3 of this series.

Vat pH	Mn Bound on Vat Pulp[1]		Total Mn in Mat[2]	
	Measured[3]	EQ Predicted[4]	Measured[5]	EQ Predicted[6]
	ppm	ppm	ppm	ppm
5.5		0.4		0.7
6.0	1.6	0.6	1.4	1.0
6.5	4.5	2.2	2.2	2.6
6.6	3.0	2.9	2.9	3.2
7.0	5.1	7.1	4.4	7.1
7.8	15.1	18.2	14.0	18.4

1. Pulp bound Mn only (exclude Mn in liquor); 2. Total Mn (include Mn bound on pulp and Mn in mat liquor); 3. Calculated from vat sample Mn, Mn in vat liquor, vat sample consistency; and vat consistency; 4. From equilibrium calculations at vat pH (WinGEMS); 5. Reported mat measruements (Mn on pulp and in liquor); 6. Based on equilibrium calculation and washing calculation in WinGEMS.

I. Mill measured and equilibrium predicted Mn in Q washer samples.

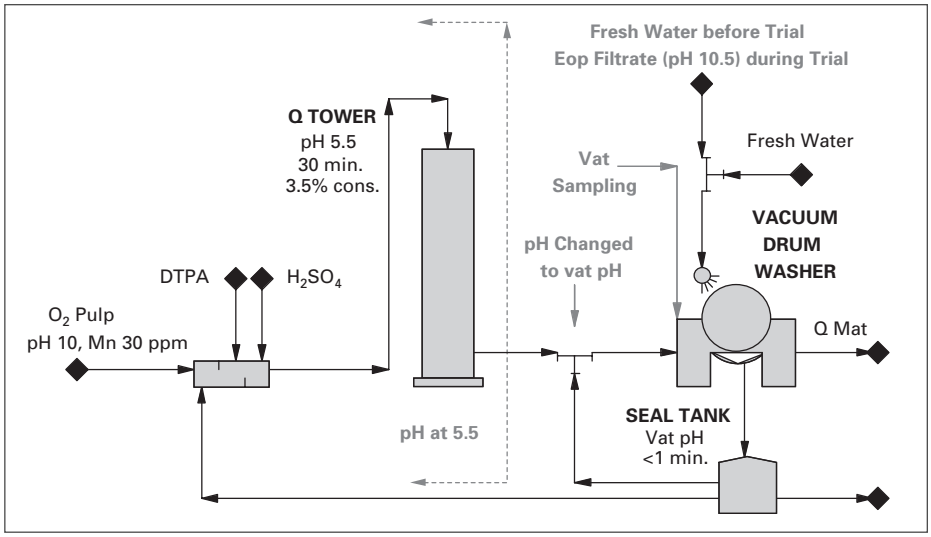
To effectively use equilibrium calculations in process simulation, we integrated SOLGASWATER into a modular process simulation as a single modular. The details about this integration are contained in Part 2 of this series.

Modeling pulp-bound metals

Sodium (Na) binds to brown stock and causes sodium loss in kraft mill fiber lines (i.e. saltcake loss) [7]. The amount of pulp-bound sodium is affected by the Na concentration in filtrates. The pH also has a large effect on total binding capacity of pulp [8, 9]. Although other metals are present at much lower concentrations than Na, pulp-bound calcium and magnesium concentrations can be much higher than sodium. Because Na is a cooking chemical, early work focused on sodium loss from pulp-bound Na. The Langmiur isotherm is used to predict pulp-bound sodium at different sodium concentrations in filtrate. Because pH at the end of brownstock washing is similar from mill to mill, the effect of pH on pulp-bound sodium was not initially included in the modeling.

In the 1990s, the issue shifted from controlling sodium loss to metals management. New theories have been developed to explain and model pulp-bound metals. There are two very different approaches to describe metals equilibrium in pulp slurries [10, 11]. Towers and Scallan's [10] model is based on Donnan theory (i.e., how the anion charges on the fiber phase attract metals cations in the liquor phase). The model was tested for Na, Mg, Ca, and Mn from pH 2 to pH 10. Except for high and low pH, the model can predict lab data very well without using data regression. The research activity in this area is active [12-15]. These works provide one way to understand how metals are "bound" to pulp. Published models are also academically interesting. However, Donnan theory based models may not be the right choice for engineering calculation tools. The Donnan theory only governs the concentrations of soluble ionic species. The real metals species in a mill process are not well defined. For more complicated systems, equilibrium equations are still needed for the formation of complexes and precipitates. So far, no publication has shown how the effect of dissolved wood solids can be handled in Donnan theory based models. It also may be quite difficult to apply a Donnan model developed for kraft pulp to TMP fibers.

The purpose of this series of papers is to develop a practical engineering calculation tool. For this purpose, it is more convenient to develop models that are based ion exchange [11]. Ion exchange models assume that there is chemical equilibrium



1. Flow diagram for applying Eop-filtrate on Q washer shower.

COMPONENTS					
Serial No.	Component	Description	Serial No.	Component	Description
1	H^+	Proton	7	Mg^{2+}	Magnesium
2	C_{HP}^-	Carboxylic on xylan	8	K^+	Potasium
3	C_{LP}^-	Carboxylic on lignin backbone	9	Mn^{2+}	Manganese
4	P_P^-	Phenol on lignin	10	Y^{5-}	$DTPA^{5-}$
5	Na^+	Sodium	11	W^-	Dissolved Wood Solids
6	Ca^{2+}	Calcium			

FORMED SPECIES							
Serial No.	Species	Formation Reaction	Constant [1]	Serial No.	Species	Formation Reaction	Constant [1]
1	HC_{HP}	$H^+ + C_{HP}^- === HC_{HP}$	3.4 [2]	18	KaC_{HP}	$K^+ + C_{HP}^- === KC_{HP}$	2.5
2	HC_{LP}	$H^+ + C_{LP}^- === HC_{LP}$	5.5 [2]	19	KC_{LP}	$K^+ + C_{LP}^- === KC_{LP}$	1.5
3	HP_P	$H^+ + P_P^- === HP_P$	10.0	20	KP_P	$K^+ + P_P^- === KP_P$	2.0
4	NaC_{HP}	$Na^+ + C_{HP}^- === NaC_{HP}$	2.2	21	KW	$K^+ + W^- === KW$	-1.1
5	NaC_{LP}	$Na^+ + C_{LP}^- === NaC_{LP}$	3.0	22	MnC_{HP}^+	$Mn^{2+} + C_{HP}^- === MnC_{HP}^+$	3.2
6	NaP_P	$Na^+ + P_P^- === NaP_P$	2.5	23	MnC_{LP}^+	$Mn^{2+} + C_{LP}^- === MnC_{LP}^+$	3.2
7	NaW	$Na^+ + W^- === NaW$	-1.1	24	MnP_P^+	$Mn^{2+} + P_P^- === MnP_P^+$	2.0
8	CaC_{HP}^+	$Ca^{2+} + C_{HP}^- === CaC_{HP}^+$	4.0	25	MnY^{3-}	$Mn^{2+} + Y^{5-} === MnY^{3-}$	15.1
9	CaC_{LP}^+	$Ca^{2+} + C_{LP}^- === CaC_{LP}^+$	3.5	26	$Mn(OH)C_{HP2}^-$	$Mn^{2+} + OH^- + 2C_{HP}^- === Mn(OH)C_{HP2}^-$	2.0
10	CaP_P^+	$Ca^{2+} + P_P^- === CaP_P^+$	2.0	27	$Mn(OH)C_{LP2}^-$	$Mn^{2+} + OH^- + 2C_{LP}^- === Mn(OH)C_{LP2}^-$	2.0
11	CaY^{3-}	$Ca^{2+} + Y^{5-} === CaY^{3-}$	10.7	28	$Mn(OH)W_2^-$	$Mn^{2+} + OH^- + 2W^- === Mn(OH)W_2^-$	-4.6
12	CaW^+	$Ca^{2+} + W^- === CaW^+$	-0.9	29	HY^{4-}	$H^+ + Y^{5-} === HY^{4-}$	10.42 [3]
13	MgC_{HP}^+	$Mg^{2+} + C_{HP}^- === MgC_{HP}^+$	3.5	30	H_2Y^{3-}	$2H^+ + Y^{5-} === H_2Y^{3-}$	19.18 [3]
14	MgC_{LP}^+	$Mg^{2+} + C_{LP}^- === MgC_{LP}^+$	4.5	31	H_3Y^{2-}	$3H^+ + Y^{5-} === H_3Y^{2-}$	23.6 [3]
15	MgP_P^+	$Mg^{2+} + P_P^- === MgP_P^+$	4.0	32	H_4Y^-	$4H^+ + Y^{5-} === H_4Y^-$	26.16 [3]
16	MgY^{3-}	$Mg^{2+} + Y^{5-} === MgY^{3-}$	9.0	33	H_5Y	$5H^+ + Y^{5-} === H_5Y$	27.95 [3]
17	MgW^+	$Mg^{2+} + W^- === MgW^+$	-0.9	34	HW	$H^+ + W^- === HW$	6.0

1. Formation constants, pKf; 2. From Laine et al (17); 3. Converted from DTPA equilibrium constants.

II. Metals equilibrium model for fiber line simulation.

among metal ions and pulp binding ligands. Since several metals compete for the same binding sites on pulp, it is necessary to solve a set of equilibrium equations and mass balance equations simultaneously in order to calculate equilibrium concentrations from total concentrations. The mathematical approach used by Bryant and Edwards [11] is not very successful when many species or precipitation are involved.

In this paper, while the concept of metals ion exchange on pulp binding sites is still used, a totally different mathematical approach is used. We use a general equilibrium calculation approach, i.e. free energy minimization, to calculate metals equilibrium concentrations in pulp slurries from total metals concentrations. A general equilibrium calculation program, SOLGASWATER [6], is used to perform the computation. This paper shows how this general equilibrium calculation program is used to address metals equilibrium calculations for pulp slurries. Although Donnan effect can be added into the current modeling approach [12, 16], it is not included in the version of the current model presented in this paper.

SOLGASWATER EQUILIBRIUM MODEL FOR PULP SLURRIES

Components and species

Fiber and dissolved components are treated as pseudo-homogeneous. Fiber is treated as another anionic species in the model. Metal ions are attached to pulp fiber through ion exchange. There are at least three kinds of binding sites on unbleached kraft pulp. In the pH range 2.5-7.5, potentiometric titration [17] has identified two kinds of acid groups, one with pK around 3.4 and another with pK around 5.5. It is very likely that the stronger acid is bound to xylan, while the weaker acid is bound to a lignin backbone. Another binding group is phenol on lignin with pK around 10.

Pulp is treated as an anionic species that can associate with H^+ and metal cations. The concentration of pulp is represented by equivalent ligand concentrations that can be measured experimentally. The equivalent ligands vary according to pulp species and may be affected by kappa number. In the model, the following reactions are included to represent the binding of H^+ with pulp ligands with the association constant as the formation constant:

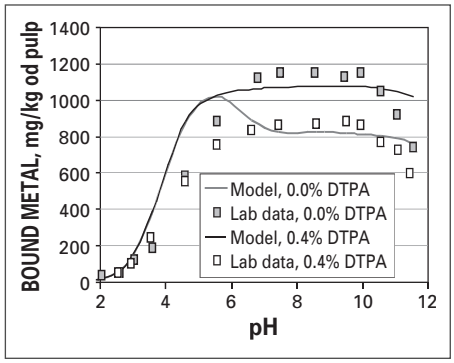
$$C_{HP}^- + H^+ \Leftrightarrow HC_{HP}$$
$$C_{LP}^- + H^+ \Leftrightarrow HC_{LP}$$
$$P_P^- + H^+ \Leftrightarrow HP_P$$

C_{HP}^- represents carboxylic groups on xylan, C_{LP}^- represents carboxylic groups on the lignin backbone and P_P^- represents phenol on lignin.

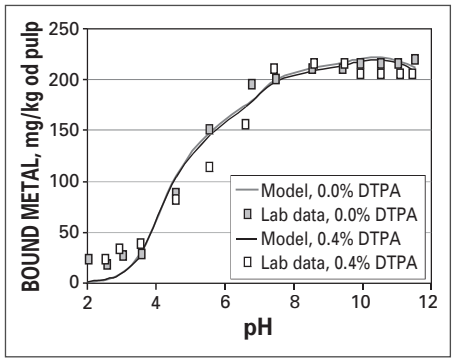
Similar to H^+, metals ions bind to the above pulp ligands. In the model, the following reactions represent the formation of fiber bound metals:

$$C_{HP}^- + M_1^+ \Leftrightarrow M_1C_{HP}$$
$$C_{HP}^- + M_2^{2+} \Leftrightarrow M_2C_{HP}^+$$

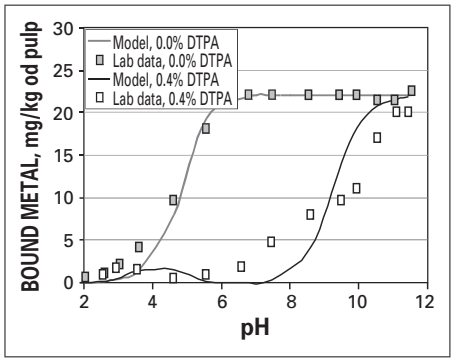
in which, M_1^+ represents univalent metal ions and M_2^{2+} represents bivalent metal ions. Similarly, metal ions bind to C_{LP}^- and



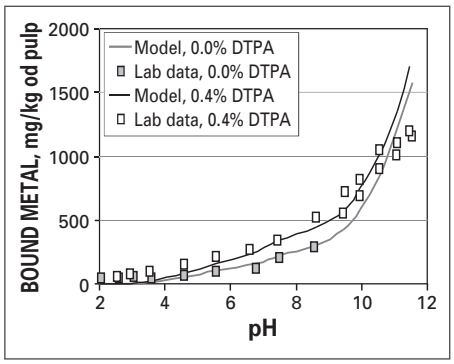
2. Comparison of model prediction with measurements: pulp-bound calcium.



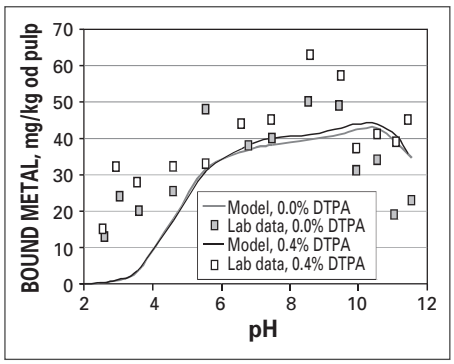
3. Comparison of model prediction with measurements: pulp-bound magnesium.



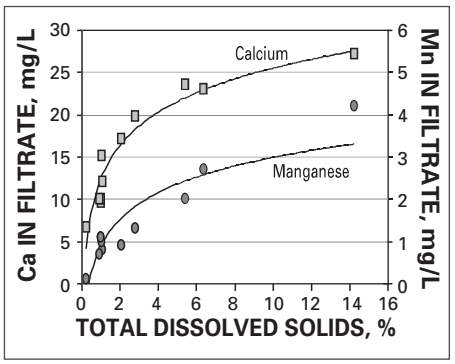
4. Comparison of model prediction with measurements: pulp-bound manganese.



5. Comparison of model prediction with measurements: pulp-bound sodium.



6. Comparison of model prediction with measurements: pulp-bound potassium.



7. Mill measurements of metals contents in washer filtrates [22].

P_p. **Table II** shows a complete species list for the current model.

Because of the competition among different metals species for binding sites on pulp, we must include all major metals in the model. As the cooking chemical, sodium is the most abundant metal in the system. Although data show that the binding between and Na and pulp is not as strong as that of divalent metals, such as Ca, the high Na concentration still makes Na a major competitor for binding to pulp. Calcium is the dominant metal in wood and the major cation species involved in scale formation. Magnesium is abundant enough to affect other metals when magnesium sulfate ($MgSO_4$) is used in oxygen delignification. Although minor metals also compete with major metals for binding to pulp, the existence of minor metals has little effect on the binding of major metals species. However, some minor metals are important for other reasons. Potassium is important for recovery boiler plugging [18] and manganese is important for peroxide related bleaching. Both metals are included in the current model.

Similar to binding competition among cations, anions also compete with each other for cations. DTPA is a commonly used chelant in the industry to control Mn for peroxide bleaching. When DTPA exists, DTPA competes with pulp ligands for metals and keeps metals in the liquor. In the model, the DTPA effect is included according to the following reaction:

$$Y^{5-} + M_2^{2+} \Leftrightarrow M_2Y^{3+}$$

DTPA only acts with bivalent metal ions, such as Mn^{2+} and does not bind with univalent metal ions, such as Na^+. Because the strength of metal binding with DTPA is different for each bivalent metal, the effect of DTPA on removal of each metal from pulp is unique (**Figures 2** to **4**). Table II lists all species in the current fiber line model.

Temperature, °C	50	50	20
Ion strength, mol/l	2.0	0.1	2.0
Formation constant, K_f	$3.39x10^4$	$6.03x10^4$	$2.75x10^4$
K_f change, %*	0.0	78.0	-19.0

* Compared to Temp.= 50°C and I = 2.0 mol/L.

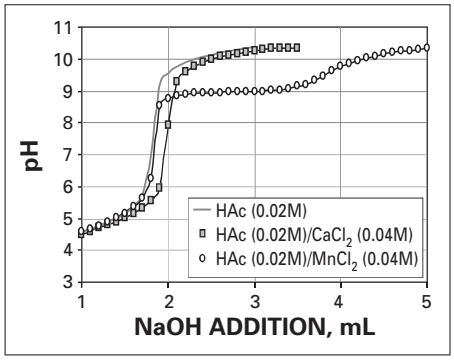
III. Ion strength and temperature effects on acetic acid formation constants [19].

Liquor Sample	Equivalent Monocarboxylic Group, mol/L	
	Conventional Cooking	Lo-Solids Cooking
UCC		0.38
LCC	0.36	0.33
Main Extraction	0.41	0.43
#1 BSW Filtrate	0.20	0.22
#2 BSW Filtrate	0.15	

IV. Equivalent mono-carboxylic groups in kraft cooking liquors.

Formation constants

The formation constants for all components are zero by definition. The formation constants for all formed species have to be determined before SOLGASWATER can perform any calculation. For formed species listed in Table II, not all formation constants can be identified individually from measurements. Particularly, metals bound on different pulp binding ligands



8. Titration of acetic acid: metals effect [19].

COMPONENTS					
Serial No.	Component	Description	Serial No.	Component	Description
1	Ba^{2+}	Barium	3	CO_3^{2-}	Carbonate
2	$C_2O_4^{2-}$	Oxalate	4	SO_4^{2-}	Sulfate

FORMED SPECIES							
Serial No.	Species	Formation Reaction	Constant (1)	Serial No.	Species	Formation Reaction	Constant (1)
1	$HC_2O_4^-$	$H^+ + C_2O_4^{2-} === HC_2O_4^-$	3.55	6	CaC_2O_4 (s)	$Ca^{2+} + C_2O_4^{2-} === CaC_2O_4$ (s)	6.90
2	$H_2C_2O_4$	$2H^+ + C_2O_4^{2-} === H_2C_2O_4$	4.59	7	$CaCO_3$ (a)	$Ca^{2+} + CO_3^{2-} === CaCO_3$ (a)	1.20
3	HCO_3^-	$H^+ + CO_3^{2-} === HCO_3^-$	10.34	8	$CaCO_3$ (s)	$Ca^{2+} + CO_3^{2-} === CaCO_3$ (s)	8.06
4	H_2CO_3	$2H^+ + CO_3^{2-} === H_2CO_3$	16.64	9	$BaSO_4$ (a)	$Ba^{2+} + SO_4^{2-} === BaSO_4$ (a)	1.10
5	CaC_2O_4 (a)	$Ca^{2+} + C_2O_4^{2-} === CaC_2O_4$ (a)	1.66	10	$BaSO_4$ (s)	$Ba^{2+} + SO_4^{2-} === BaSO_4$ (s)	5.00

1. Formation constants, pK_1

V. Species added to Table II for metals equilibrium model with fiber line precipitation prediction.

cannot be measured individually. In Table II, literature data are used if the formation constants or equilibrium constants, such as DTPA related species, are available. The other formation constants in Table II are determined by fitting the model to various laboratory and mill measurements as illustrated above.

The main purpose for the model shown in Table II is for simulation of a TCF fiber line metals profile [1]. In this TCF fiber line, Mn is removed through DTPA chelation (Q-stage) at a pH around 5 before peroxide bleaching. Therefore, mill Q-stage incoming pulp (O_2 pulp) was selected to examine its pulp-bound metals at different pHs with and without DTPA [5]. In the lab, softwood O_2 pulp was diluted to 1% consistency at 75°C and pH was adjusted by H_2SO_4 or sodium hydroxide (NaOH). After reaching equilibrium, pulp was fully washed and metals contents analyzed by ionic coupled plasma (ICP). More details are available [11]. **Figures 2 to 6** show the measured metals contents. Pulp-bound metals are also calculated from SOLGASWATER. The formation constants (Table II) are determined by minimizing the errors between metals measurements and calculations.

The total number of pulp binding sites available determines the total amount of cations (H^+ and metals) that can be bound to pulp. H^+ as a cation also competes with other cations to bind on pulp. However, the source of H^+ in aqueous solution is not limited. pH is an indicator for available H^+ after H^+ binds with anions. At low pH (<3), most pulp ligands associate with H^+ because of high H^+ concentration. Therefore, at low pH, almost no metals attach to pulp and are therefore washable. As pH increases, pulp ligand begins to dissociate from H^+ and metals bind to pulp. More metals binds to pulp at high pH because of limited competition from H^+, as shown in Figs. 2 to 6.

DTPA (H_5Y) exists as Y^{5-} at high pH and only Y^{5-} interacts with metal ions. At the same time, metals bind to pulp at high pH. Therefore, there is an optimum pH to use DTPA to selectively remove metals from pulp. Figure 4 shows that MnY^{3-} is formed at pH higher than 3. From pH 3 to 7, Mn prefers to form MnY^{3-} and almost all Mn is in the filtrate. At pH higher than 7, pulp's binding competition for Mn increases and more Mn binds to pulp at higher pH in the presence of DTPA. Because MnY^{3-} has a higher formation constant than CaY^{3-} and MgY^{3-}, DTPA is most effective at removing Mn from pulp. MgY^{3-} has the lowest formation constant, the effect of DTPA on Mg removal is negligible in the model prediction and in the measurements. Because DTPA was added as sodium salt, the addition of DTPA increases the total concentration of Na. Therefore, more bound sodium was found in pulp with DTPA while DTPA has no ability to bind Na.

ADDITIONAL ISSUES FOR METALS EQUILIBRIUM CALCULATION

Ion strength and temperature

Table III shows the effect of ion strength and temperature on acetic acid formation constants determined by conductometric titration [19]. The acetic acid formation constant decreases as ion strength increases. Increasing temperature causes an increase in the formation constant. We observed the same effects for other organic acids, such as formic acid and lactic acid [19]. While ion strength in the digester is around 2 mol/L, the ion strength in the brown stock washing filtrates can be less than 0.1 mol/L. Therefore, it is helpful to consider ion strength corrections during process simulation. Several methods for ion strength correction are available and have been incorporated into current simulation tools [20, 21]. Comprehensive modeling work on ionic strength correction of formation constants is coming in a Ph.D. dissertation [16]. For the temperature correction, the van't Hoff equation is used.

Dissolved organics

Figure 7 shows mill measurements of Ca and Mn in the filtrates of brown stock washing and post oxygen delignification washing [22]. The temperatures for all these filtrates are similar. The ion strength effect will not change metals concentrations in filtrates by such a large amount. If Ca and Mn do not bind to species in liquor, almost all Ca and Mn bind to pulp at high pH, which is the case in Figs. 2 and 4 (no DTPA). Only binding competition from the liquor side, such as DTPA in Fig. 2, can keep high Ca and Mn concentrations in filtrates. In Fig. 7, there are relationships between metals in filtrate and total dissolved solids. Metals do not relate to dissolved inorganics if there is no precipitation. Therefore, dissolved organics are responsible for the high metals concentrations in the washer filtrates shown in Fig. 7.

In **Fig. 8**, a set of conductometric titration curves show the interactions of acetic acid with Ca and Mn [19]. The titration curves of acetic acid with metals are different from those without metals. This demonstrates the interaction among metals and acetate. The existence of calcium acetate lowers the solution pH (more NaOH is needed to reach the same

pH) in the pH range 5 to 10. The interaction between Mn^{2+} and acetate is weaker than Ca^{2+}. However, there is a transition area in the titration curve for the Mn solution at pH higher than 8.5. This indicates that some unidentified Mn species, other than Mn^{2+} and manganese acetate, exist in this area.

Figure 8 demonstrates the important role of dissolved organics in metals equilibrium. However, it is difficult to characterize dissolved organics in pulp mills. In our model, we treat dissolved organics as one univalent component. We use conductometric titration to determine the collective liquor binding ability. **Table IV** shows equivalent mono-carboxylic groups in mill kraft cooking liquors. To determine the formation constants of dissolved organics with various metals is even more difficult. The current formation constants with metals, listed in Table II, were determined by tuning the model to match mill measurements.

Precipitation prediction

Scaling is a major issue related to nonprocess metals in pulp and paper mills. The commonly encountered scales are calcium oxalate (CaC_2O_4), calcium carbonate ($CaCO_3$), and barium sulfate ($BaSO_4$). Part of the equilibrium model involving these precipitants is shown in **Table V**. Metals precipitation is related to free metals concentration in solution. Therefore, precipitation is affected by bound metals on fiber and on other anions, such as dissolved organics, in solution. Most species in Table II are still needed for precipitation prediction, although minor metals, such as Mn, have little impact. An equilibrium model including CaC_2O_4, $CaCO_3$, and $BaSO_4$ precipitation is demonstrated in an ECF fiber line simulation in Part 2 of this series [1]. A simplified equilibrium model for nonprocess metals in kraft chemical recovery systems has also been proposed and is validated by mill measurements [2].

APPLICATIONS

SOLGASWATER is a stand-alone computer program that only performs equilibrium calculations. For industry applications, it is more important to determine metals concentrations in actual mill processes. In order to do this, the free-energy minimization engine used in SOLGASWATER has been integrated into an existing process simulator, WinGEMS, as an individual calculation block [1]. Now, equilibrium concentrations can be routinely calculated as part of the full mill process simulation if we know how to define the equilibrium chemistry. Metals profiles in mill processes can be predicted by simulation, as shown in Part 2 of this series [1].

In our typical metals equilibrium calculations, pH, i.e. H^+ concentration, is specified as a SOLGASWATER input. Instead of specifying H^+, total component H (H^+ and H existing in other species) concentration can be specified as input and H^+, i.e. pH, can be calculated from SOLGASWATER. The pH prediction based on this equilibrium calculation approach has been used in mill simulation [23].

The equilibrium model in Table II is mainly developed for a TCF fiber line metals simulation (1). Precipitation in a fiber line can be calculated by combining information from Tables II and V. Through changing input data, i.e. defining different systems, the same computer program, SOLGASWATER, is used to address very different issues. This significantly simplifies the effort needed for simulation tool development when our understanding about metals behavior in mill processes is still evolving. This tool can apply our understanding of equilibrium directly into mill processes. We can also use equilibrium models to interpret mill measurements. Such calculations unite basic research and mill applications.

CONCLUSIONS

The minimization of free-energy method has been successfully applied to metals equilibrium calculations for pulp slurries. Pulp-bound metals, including Ca, Mg, Mn, Na, and K, can be calculated by a free-energy minimization program, SOLGASWATER, from the proposed equilibrium models for pulp slurries, i.e. species and their formation constants in Table II. The effects of pH and DTPA on pulp-bound metals are also predicted.

Temperature and ionic strength affect formation constants. For metals profile prediction in mill process, dissolved organics from kraft cooking have a significant role in keeping metals in the liquor. Unfortunately, the composition of dissolved organics from kraft cooking is very complicated and further study is needed to define species formed from metals and dissolved organics. In the current model, dissolved organics are represented by an equivalent univalent component.

This series of papers shows that using a general free-energy minimization program with easily definable input data is a practical way to develop simulation tools that address today's mill issues. **TJ**

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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. The fact that the time constant for changes in NPE metals in kraft mills is several weeks was one of the most interesting findings we made.

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 and drier lime mud to the kiln. The next step in the research will be mill applications and model improvements.

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