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# Multi-phase thermodynamic modelling of pulp suspensions: Review of the methodology

Petteri Kangas, Risto Pajarre, Marja Nappa and Pertti Koukkari

**KEYWORDS:** Gibbs free energy, Constrained equilibrium, Meta-model, Papermaking chemistry

**SUMMARY:** Thermodynamic models have been increasingly applied to describe the multi-component chemistry of pulp suspensions. Their advantage is the inclusion of a great number of phases and chemical species in fibre line and paper-making furnish. The equilibrium models may consider both non-selective ion-exchange (Donnan equilibrium) and ion-specific complex formation in order to predict the distribution of ions between the fibre and aqueous phases. In this work, an extended Gibbs free energy method, also combined with reaction kinetics, was used. The Pitzer formalism was introduced to describe the activities of the solution phases. The constructed model was then applied to paper-making applications. Additionally, the multi-phase model was used in creating a neural network-based meta-model of pulp suspension pH. The Gibbsian method appears to be the best option for the calculation of chemical equilibrium in the multi-phase pulp suspension. The meta-models can be further used for ad-hoc applications, such as soft sensors.

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During the last decade, a number of studies have been published on the use of the thermodynamic approach for the modelling of pulp suspensions. These studies aimed to support industry in several issues, such as (i) metal management in fibre line (e.g. Lindgren et al. 2001; Räsänen 2003; Gu et al. 2004a; Sundman et al. 2008), (ii) development of bleaching chemistry (Tarvo et al. 2008), (iii) closure of the mill-water cycles (e.g. Gu et al. 2004b), (iv) chelation (e.g. Nordberg et al. 2001; Gu et al. 2004b; Pajarre et al. 2006), (v) pulp acidification and pH buffering (e.g. Pakarinen, Leino 2000; Kalliola, Pakarinen (2002), and (vi) introduction of the usage of calcium carbonate into wood containing paper grades (e.g. Ylén 2001; Viitikko, Kalliola 2002; Koukkari et al. 2004).

The increased interest in the multi-component thermodynamics of pulps descends from the original publication by Towers and Scallan (1996), who introduced a Donnan equilibrium between the bulk aqueous phase and the aqueous phase inside the fibre. Another important step in this field was the development

of a titration method to measure the amount of carboxylic and phenolic acid groups in fibres (Laine et al. 1994; Lindgren et al. 2001; Räsänen et al. 2001). A third advantage has been the development of effective computational tools, such as SOLGASWATER (Eriksson 1979) and ChemSheet (Koukkari et al. 2000).

During the early years of pulp suspension modelling, the Donnan equilibrium model was developed further by several research groups. Räsänen et al. (2001) focused on pulp bleaching and washing applications and developed the Donnan ion-exchange method for solutions containing multiple anions and cations. At same time, Lindgren et al. (2001) studied metals management and applied the theory in terms of non-selective surface reactions at elevated temperatures. Koukkari et al. (2002) demonstrated the Donnan effect of different pulp species using a Gibbs energy minimisation method. In general, the non-selective Donnan model usually gave a reasonable agreement for the predicted and measured cation concentrations in the external filtrate and fibre phases.

When pulp suspensions with excess metal ions were studied, it was noticed that additional ion-specific interactions with fibres must be considered. Gu et al. (2004a) evaded this phenomenon by applying the measurable formation reaction constants of each notable reaction. Rudie et al. (2006) defined selectivity coefficients to predict the non-ideal partition of metal ions. The importance of specific interactions was confirmed by Södö et al. (2007). Their study showed a significant difference in the metal ion affinity of various ions. Sundman et al. (2008) noted that with an excess quantity of  $\text{Na}^+$  ions, the unspecific Donnan equilibrium is not valid. They introduced specific ion-fibre complexes to cope with the inadequacy of the Donnan model. In addition, competitive adsorption models (NICA-Donnan) have been developed (Li, Englezos 2005). These models, however, have not been applied for multi-phase suspensions and thus will not be considered here.

Once the use of calcium carbonate as a filler and coating pigment became more common in the production of mechanical pulp dominated grades, the importance of pH and calcium chemistry control in paper-making was increased (Kalliola, Pakarinen 2002; Pajarre et al. 2006). At that time, the non-specific ion-exchange of pulp fibres was combined with the equilibrium state calculation of an aqueous-gaseous-solid phase system through a Gibbsian approach (Koukkari et al. 2002). The gas phase was seen as a critical feature in, for example, models describing industrial applications such as pulp pH buffering and acidification done with carbon dioxide (Pakarinen, Leino 2000). Thereafter, unit operation studies were performed for several paper mills. The off-line simulations developed by these studies could be extensively applied to the comparison of acidifying techniques, the

determination of chemical dosages and broke circulation ratios, and the investigation of the bleaching and washing of pulp suspensions (Räsänen 2003). Furthermore, the extension of the multi-phase chemistry model within the calculation framework of a process simulator has enabled the monitoring of the chemistry of large process integrates (Gu et al. 2004b; Dionísio De Oliveira et al. 2010; Kalliola et al., 2012).

After these steady-state calculation methods were proven to work well, the research focus was transferred to dynamic modelling of the pulp suspension processes while maintaining a multi-phase thermodynamic approach. The aim has been to model the transient phenomena, such as the release of carbon dioxide and precipitation of calcium carbonate. The time constants of these events have appeared relevant when the operation of a paper machine is considered. This unique feature by Koukkari et al. (2004) was to include the reaction kinetics in the thermodynamic multi-phase model of pulp suspension. Thus, a more realistic model was achieved for industrial applications.

The results were promising but the calculation speed often seemed inadequate for larger scale process simulations, particularly when considering real-time dynamic processes. For this reason, a much faster meta-modelling approach, neural networks, has been evaluated as a possible tool for modelling the chemistry of pulp suspensions (Kangas, Ylén 2005).

In this paper, we focus on the main features of the methodology of the multi-component thermodynamics of pulp suspensions. The non-specific Donnan equilibrium is applied here. Three example cases are presented. The first example explains the kinetics of calcium carbonate. The second example demonstrates the effect of the presence of a gaseous phase. The third example reports the use of a fast meta-modelling technique using neural networks.

## Methods

### The pulp suspension as a multi-phase system

A pulp suspension contains gaseous, aqueous and fibre phases as well as several solid phases. A simplified illustration is given in Fig 1. The gaseous, aqueous and fibre phases include several compounds and ions, which are here called constituents. The solid phases are assumed to be pure stoichiometric phases comprising single constituents. The solid phases may form, disappear and re-form based on the process conditions (temperature, pressure and composition of the system).

The ideal gas assumption is applied to the gaseous phase as the pressure levels applicable to pulp processing are commonly low. The aqueous and fibre phases are both modelled as electrolyte solutions with water as the solvent, with the difference that the fibre itself is negatively charged and the fibre phase has a surplus of cations. Electro-neutrality is applied to both fibre and aqueous phases.

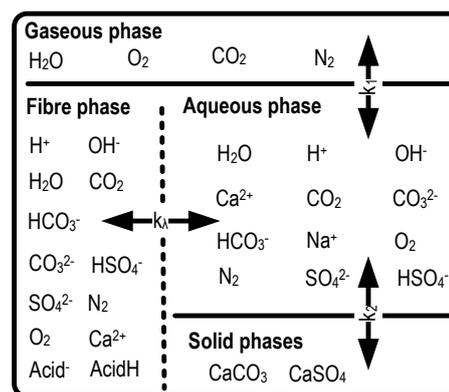


Fig 1. A typical multi-phase system with five separate phase types and multiple constituents.  $k_1$  is the mass transfer speed between the gaseous phase and aqueous phase,  $k_2$  between the aqueous and solid phases and  $k_A$  between the aqueous phase and fibre phase.

### The Gibbs free energy method

The chemical equilibrium state of the pulp suspension is obtained by minimising the Gibbs free energy of the multi-phase system:

$$G = \sum_{i=1}^I \sum_{j=1}^{J_i} n_j^i \mu_j^i = \sum_{k=1}^K n_k \mu_k \quad [1]$$

where  $i$  refers to the phases and  $j$  refers to the constituents of each phase. Similarly,  $k$  refers to each constituent in the multi-phase system,  $n$  to the molar amount of constituents, and  $\mu$  to the chemical potential of the constituents.  $I$  is the number of phases in the system,  $J_i$  is the number of constituents in phase  $i$ , and  $K$  is the number of constituents in the whole system.

The main benefit of this approach is that individual reactions do not need to be defined separately. (Each reaction must, of course, be separately written if equilibrium constants are used). Instead, the multi-phase system is treated as a whole assembly of its phases and constituents (cf. Fig 1.) and becomes defined by the stoichiometric matrix  $N$ :

$$N = \begin{bmatrix} v_{11} & v_{12} & \cdot & \cdot & v_{1L} \\ v_{21} & v_{22} & \cdot & \cdot & v_{2L} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ v_{k1} & v_{k2} & \cdot & \cdot & v_{kL} \end{bmatrix} \quad [2]$$

where  $v_{kl}$  is the stoichiometric factor of the  $l$ :th component of constituent  $k$ , and  $L$  is the total number of components.

Elements are often used as system components. The multi-phase system still contains electrically charged anions and cations. In order to fulfil the electro-neutrality of a single phase, an additional component, an electron, is introduced as a system component. A typical stoichiometric matrix for a multi-component aqueous system is shown in Table A1. To reach thermodynamic equilibrium, the Gibbs energy of this closed isothermal system is minimised using the Lagrange method of

undetermined multipliers. A brief outline of the method is given in Appendix 1. A detailed description of the Gibbs energy minimisation method is presented, for example, by Smith and Missen (1991).

Commercial software such as ChemSheet (Koukkari et al. 2000; Koukkari et al. 2001) or SOLGASWATER (Eriksson 1979) can be used for the Gibbs energy minimisation calculations presented in this study.

### Inclusion of the Donnan effect for modelling the fibre phase

For the pulp suspension systems, a second aqueous solution phase, the fibre phase, must be introduced to the Gibbsian system. This phase represents the water and the constituents inside the fibres. For the introduction of the secondary aqueous phase, an immaterial component ( $s$  in *Table A2*) has been applied, so as to hold the amount of fibre-bound water constant in the calculation. The water retention value (WRV) has been used for the modelling volume of this phase. The volume of the fibre phase is affected by pH and ionic strength. However, it has been found that for practical applications, a constant WRV can be assumed. The same assumption is used by Lindgren et al. (2001). WRV data for each fibre furnish is obtained by a standard measurement method (Gringon, Scallan 1980).

The fibre phase includes the same constituents as the aqueous phase. Additional constituents are defined to describe the acidic groups of the fibres. These acidic groups cause a difference in the ion distribution between the external aqueous and fibre phases. This effect is sometimes also referred to as sorption. The respective distribution coefficient  $\lambda$  is described by the Donnan theory as follows:

$$\lambda^{z_k} = \frac{a_{k, \text{fibre}}}{a_{k, \text{aqueous}}} \quad [3]$$

where  $z_k$  is the charge of constituent  $k$ . The acidic groups are quantified using their  $pK_a$  values, which can be measured by conductometric or potentiometric titration. Thus, it is not necessary to describe the exact chemical composition of the acid groups or to specify their complexation with individual ionic species. A single acidic group pair (Acid<sup>-</sup> + H<sup>+</sup> and AcidH) is used in this example (see *Fig 1*.) The same approach has been used by Lindgren et al. (2001). If needed, several acidic groups with different  $pK_a$  values can be defined in the fibre phase. Based on their  $pK_a$  values, the Gibbs energy and chemical potential of the acidic groups can be defined:

$$\ln K_a = -\frac{\Delta G^\circ}{RT} \quad [4]$$

where  $R$  is the gas constant and  $T$  is the temperature. A detailed description of the non-specific Donnan effect in a pulp suspension is presented by Towers and Scallan (1996). The inclusion of the Donnan effect in Gibbs energy minimisation is described in detail by Koukkari et al. (2002, 2004) and Pajarre et al. (2006). If process conditions with excess metal ion concentrations are studied (e.g. for pulp washing), the specific ion/fibre interactions or, for example, chelation can be implemented in the multi-phase model. Such an extended multi-phase model could use the ion-acid complexes by

proposed Sundman et al. (2008) or NICA-Donnan type parameterisation, proposed by Li and Englezos (2005). The extended model will, however, increase the necessary furnish-specific measurements.

### Describing the activities of the suspension using Pitzer formalism

In order to describe the effects of different ions and neutral constituents in the aqueous solution, an ionic activity model is needed. The activities of the water solvent and solute constituents are conventionally calculated using the well-known Pitzer formalism, which is also briefly presented in Appendix 1. In this work, the Pitzer model was used for both the aqueous and fibre phases. The Pitzer parameters used to describe the activities of the aqueous phase constituents were obtained from the literature (Pitzer 1995).

### Constraining kinetic reactions

When a pulp suspension is considered, there are often kinetically constrained reactions present. For example, the precipitation of calcium carbonate as a solid phase and its respective dissolution to aqueous solutes are both slow compared with the reactions in the homogeneous solution phase. Equally, the dissolution of carbon dioxide into the aqueous phase or, conversely, its release into the ambient air appears as kinetically constrained reactions in the suspension system. Thus, additional constraints need to be defined to include such kinetically controlled reactions in the Gibbs energy model.

The net reaction rate,  $r$ , in general form is a function of the molar amounts of the reactants and products, as well as of the temperature and pressure:

$$r = \frac{dn_k}{dt} = f(n_1, \dots, n_K, T, P) \quad [5]$$

The combination of reaction kinetics with the Gibbs energy calculation can be performed by the differential-algebraic (DAE) technique, which applies additional constraining elements in the stoichiometric matrix. Such constraints have been applied, for example, by Alberty (1989) as a conservation property, further developed for reaction kinetics by Koukkari (1993), and applied in pulp and paper processes by Koukkari and Pajarre (2006). The structure of the DAE method is briefly given in Appendix 1. For a more detailed description, see (Koukkari, Pajarre 2006; Koukkari et al. 2011).

*Table 1* describes the stoichiometric matrix of the presented example system. Gaseous, aqueous and fibre phases as well as two solid phases are included. A non-specific Donnan equilibrium is assumed. Reaction kinetics is implemented for the release of CO<sub>2</sub> and precipitation and dissolution for CaCO<sub>3</sub>. Similar multi-phases systems are used for examples 1-3.

### Meta-modelling the chemistry using neural networks

Meta-modelling was evaluated in order to reduce the complexity of a rigorous multi-phase model of pulp suspension. The reduced surrogate model could be feasible for any computational purpose requiring a fast calculation procedure, such as soft-sensor development, process simulation and control, or optimisation.

A neural network approach was chosen for meta-modelling the system presented in the previous sections. Neural networks were considered as a fast alternative for multi-phase chemistry calculation with additional kinetic constraints. A multi-phase model, presented above, was then used to generate training, evaluation and validation data for the neural networks. A brief description of neural networks is in Appendix 1.

Table 1. The stoichiometric matrix of the pulp suspension, including gaseous, aqueous and fibre phases as well as solid phases. The Donnan effect and kinetics constraints are included in the matrix.

	k		C	O	H	S	Ca	Na	N	e-	s	q	a	R1	R2	
Gas phase	1	H <sub>2</sub> O		1	2											
	2	O <sub>2</sub>		2												
	3	CO <sub>2</sub>	1	2										1		
	4	N <sub>2</sub>							2							
Aq. phase	5	H <sub>2</sub> O		1	2											
	6	O <sub>2</sub>		2												
	7	CO <sub>2</sub>	1	2												
	8	N <sub>2</sub>							2							
	9	H <sup>+</sup>			1						-1					
	10	OH <sup>-</sup>		1	1							1				
	11	HCO <sub>3</sub> <sup>-</sup>	1	3	1								1			
	12	CO <sub>3</sub> <sup>2-</sup>	1	3										2		
	13	SO <sub>4</sub> <sup>2-</sup>		4		1								2		
	14	HSO <sub>4</sub> <sup>-</sup>		4	1	1								1		
	15	Ca <sup>2+</sup>						1							-2	
	16	Na <sup>+</sup>							1						-1	
Fibre phase	17	H <sub>2</sub> O		1	2									1		
	18	O <sub>2</sub>		2												
	19	CO <sub>2</sub>	1	2												
	20	N <sub>2</sub>							2							
	21	H <sup>+</sup>			1						-1		1			
	22	OH <sup>-</sup>		1	1							1	-1			
	23	HCO <sub>3</sub> <sup>-</sup>	1	3	1								1	-1		
	24	CO <sub>3</sub> <sup>2-</sup>	1	3										2	-2	
	25	SO <sub>4</sub> <sup>2-</sup>		4		1								2	-2	
	26	HSO <sub>4</sub> <sup>-</sup>		4	1	1								1	-1	
	27	Ca <sup>2+</sup>						1							-2	2
	28	Na <sup>+</sup>							1						-1	1
	29	Acid <sup>-</sup>												1	-1	1
	30	AcidH		1												1
CaCO <sub>3</sub>	31	CaCO <sub>3</sub>	1	3			1									
CaSO <sub>4</sub>	32	CaSO <sub>4</sub>		4		1	1									
R1+	33	R1+												1		
R1-	34	R1-												-1		
R2+	35	R2+													1	
R2-	36	R2-													-1	

## Results and discussion

### Example 1 – Kinetically constrained thermodynamic system

In the first example, the aim was to calculate the constrained thermodynamic equilibrium suspension. A detailed description of the experimental setup is given in (Koukkari et al. 2001). The dissolution of calcium carbonate to Ca<sup>2+</sup> ions and the release of carbon dioxide from the solution to the ambient air were constrained in the Gibbsian calculation. For the reaction kinetics of these constituents, the following differential equations were used

$$\frac{d[Ca^{2+}]}{dt} = k_1[H^+] + k_2 \quad [6]$$

$$\frac{d[CO_2]}{dt} = k_3(a_{CO_2^g}^* - a_{CO_2^g}) \quad [7]$$

where  $k_1 = 2.925 \text{ min}^{-1}$ ,  $k_2 = 0.000225 \text{ mol} \cdot (\text{l} \cdot \text{min})^{-1}$ ,  $k_3 = 0.0047 \text{ mol} \cdot (\text{l} \cdot \text{min})^{-1}$ ,  $a_{CO_2}^*$  is activity over saturated carbon dioxide in an aqueous solution, and  $a_{CO_2g}$  is activity of carbon dioxide in the gas phase. The result of this constrained thermodynamic equilibrium model and the validation data is shown in Fig 2.

### Example 2 – Thermodynamic system with open and closed gas phase

The second example illustrates the effect of the gas phase on the thermodynamic equilibrium. A closed gas phase with increasing CO<sub>2</sub> content and constant pressure was compared to an open gas phase with constant CO<sub>2</sub> content and constant pressure.

Coated broke from an LWC mill was used as furnish. Acidic groups in fibres were determined by potentiometric titration (Räsänen et al. 2001). Broke was diluted to 3% by white water from the mill. Experiments were run in a stirred reactor and pH was monitored. 1M H<sub>2</sub>SO<sub>4</sub> was added to the reactor to control the pH drop and illustrate the kinetics of broke suspension. Reaction kinetics was included with the following equations:

$$\frac{d[CaCO_3]}{dt} = -k_1 \cdot m_{CaCO_3} \cdot \left( K_{sp}^{1/2} - a_{Ca^{2+}}^{1/2} \cdot a_{CO_3^{2-}}^{1/2} \right) \quad [8]$$

$$\frac{d[CO_2^g]}{dt} = k_2 \cdot m_{H_2O} \cdot a_{CO_2} \cdot \left( 1 - \frac{a_{CO_2^g}}{a_{CO_2} \cdot K_{eq}} \right) \quad [9]$$

where  $k_1 = 6000 \text{ mol/min}$  and  $k_2 = 0.5 \text{ mol/min}$ ,  $m_k$  is the mass of constituent  $k$ ,  $a_k$  is the activity of constituent  $k$ ,  $K_{sp}$  is the solubility product of CaCO<sub>3</sub> ( $2.9 \cdot 10^{-9}$  at 40°C) and  $K_{eq}$  is the equilibrium constant for CO<sub>2</sub> dissolution (42.0 at 40°C).

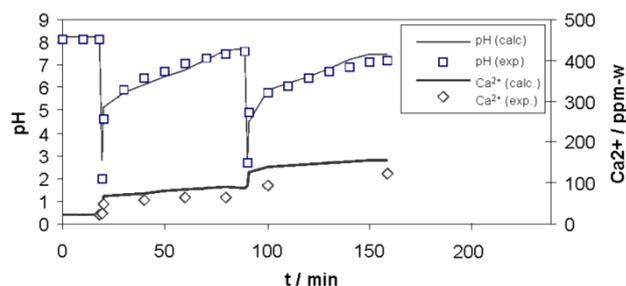


Fig 2. A dynamic constrained multi-phase thermodynamic equilibrium. The concentration of dissolved calcium is measured with ion selective electrodes and AAS (dark dots). The repeated pH drop is affected by controlled acidification with sulphuric acid.

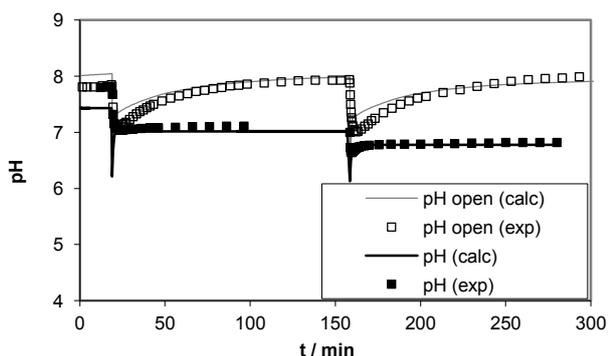


Fig 3. A constrained multi-phase thermodynamic equilibrium with open and closed gas phases. The repeated pH drop is affected by controlled acidification with sulphuric acid.

Results for open and closed gas phase systems are shown in Fig 3. Validation data is included. In the open system, the gas phase is assumed to be ideally mixed and the  $\text{CO}_2$  concentration remains at its initial value 350 ppm. In the closed system, the concentration of  $\text{CO}_2$  increases in the gas phase during the experiment.

### Example 3 – Meta-model for estimating the pH of a pulp suspension

In the third example, a meta-model was used to estimate the pH of the solution. A neural network, as illustrated in Fig 4, was chosen as the surrogate technique. Training data for the pH meta-model was generated using the same rigorous multi-phase model as explained above and ChemSheet as the software.

The equilibrium composition was solved for the estimated pH and equilibrium constants. The slow phenomena were taken into account as presented in Eqs 6 and 7.

The aim of using neural networks was to remove time-consuming iterations from the computer solutions. However, the somewhat simplified example system presented in Table 1 introduces 32 constituents describing the physico-chemical conditions in a typical pulp suspension. A more realistic description (e.g. Kangas 2009) would increase the number of constituents. These large systems appeared too extensive for the teaching process of the neural networks.

Removing the pulp phase gives a simplified system, which was applicable as a data source for the meta-model. This model was verified against a parallel model,

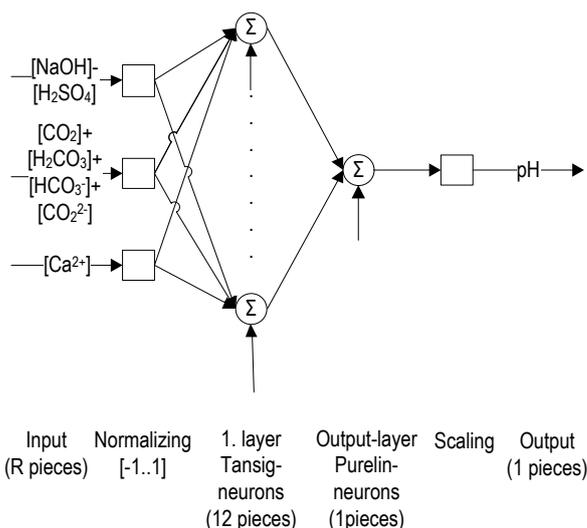


Fig 4. Schematic of the applied neural network.

explained in more detail by Ylén (2001). The results of the two calculations can be seen in Fig 5. The small differences in results are due to the method used for pH estimation: Ylén (2001) used an iterative approach based on the equilibrium constants.

## Conclusions

During the last decade, the understanding of the chemistry of fibre suspensions has dramatically increased. Of no little importance in this development has been the possibility to use computational equilibrium chemistry to quantify the multi-component, multi-phase effects in aqueous pulps suspensions. The use of these models has proven to be successful for the chemistry of fibre suspensions, and feasibly such models may be said to be a unique technique to match also the wide range of pH and alkalinity in industrial pulp suspensions. The salient assumption in these models has been to regard the fibres as an additional chemical entity in the system, for which then the chemically active groups are described in terms of the ion exchange or complex formation equilibria.

The thermodynamic models used in this study are based on the extended Gibbs free energy method. The non-specific Donnan effect was included in the model to describe the ionic distribution between the external solution and the fibre phase and the respective effects of acidic groups. The constructed model was applied in paper-making applications where an assumption of non-specific ion interactions seems valid. The Donnan approach is non-selective as regards the distribution of charged species between the pulp and filtrate, and thus does not require specific input parameters for the absorption of ions. Standard laboratory methods to identify the charged groups in the pulp in terms of their protonation constants ( $pK_a$  values) remain the necessary model parameters, to be used in accordance with the thermodynamic data of the other (conventional) solute species. For pulp mill applications with higher metal ion concentrations, specific interactions may be needed. This approach often gives more detailed information on the

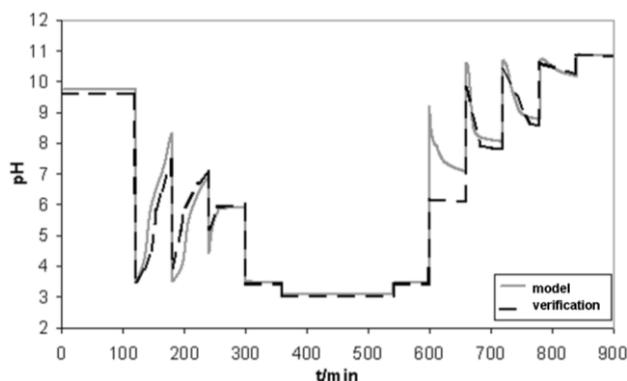


Fig 5. A dynamic model of the multi-phase chemistry of a pulp suspension. The model is based on neural networks and equilibrium constants (Kangas, Ylén 2005) and verified against the results by Ylén (2001).

distribution of individual ions but also requires a large number of measurements to describe the equilibrium chemistry of individual surface complexes.

The Pitzer formalism was introduced to describe the activities of the solute species in both the aqueous and fibre phases. Reaction rate constraint has been demonstrated using the differential-algebraic technique in Gibbs energy minimisation and was found to be of importance in cases where a kinetically slow chemical reaction was combined with a phase change (precipitation or dissolution).

Surrogate models, neural networks here, were applicable when a simplified model of the solution was considered and the fibre phase could be neglected. When more comprehensive models were introduced, the training of neural networks appeared to be too laborious. Meta-models, such as neural networks, could provide an alternative solution for more rapid calculations, such as soft-sensors.

In some cases it is viable to simplify the multi-phase system by excluding the effect of the fibre phase, but if a reliable pH and solubility model of an arbitrary pulp suspension is needed, this simplification is not applicable. It is concluded that Gibbs energy minimisation provides a general and robust method for calculation of the multi-phase chemistry of pulp suspensions.

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## Appendix 1. The Gibbs free energy method

### Lagrange method for Gibbs energy minimising

The Lagrange method of undetermined multipliers is used for minimising the Gibbs energy of this closed isothermal system (Smith, Missen 1991).

$$L = G - \pi\Psi = \sum_{k=1}^K n_k \mu_k - \sum_{l=1}^L \pi_l \left( \sum_{k=1}^K \nu_{kl} n_k - b_l \right) \quad [A1]$$

where  $\pi$  is the Lagrange multiplier,  $\Psi$  is the mass balance of the different components of each constituent,  $\pi_l$  is the Lagrange multiplier of component  $l$ , and  $b_l$  is the total amount of component  $l$  in the system.

The minimum of the Lagrangian function is obtained when its partial derivatives are zero.

$$\left( \frac{\partial L}{\partial n_k} \right)_{n_{n \neq k}} = \mu_k - \sum_{l=1}^L \pi_l \nu_{kl} = 0 \quad [A2]$$

$$\left( \frac{\partial L}{\partial \pi_l} \right)_{\pi_{n \neq l}} = \sum_{k=1}^K \nu_{kl} n_k - b_l = 0 \quad [A3]$$

Eq A2 defines the chemical potential of each component as a Lagrange multiplier, and Eq A3 represents the mass balance of the system in terms of the amounts of

components. The chemical potential of constituent  $k$  is further defined as

$$\mu_k = \mu_{k,id} + \mu_{k,ex} \quad [A4]$$

where  $\mu_{k,id}$  is the ideal term of the chemical potential of constituent  $k$ , and  $\mu_{k,ex}$  is the excess term of the chemical potential of constituent  $k$ .

The chemical potential of each constituent in the gaseous phase, which is considered to be an ideal gas, is presented as

$$\mu_{k,gaseous} = \mu_k^o + RT \cdot \ln \left( \frac{P}{P^o} \right) + RT \cdot \ln \left( \frac{n_k}{N} \right) \quad [A5]$$

where  $\mu_k^o$  is the chemical potential in the standard state,  $P$  is the pressure,  $P^o$  is the pressure in the reference state (1 bar),  $R$  is the gas constant,  $n_k$  to the molar amount of constituents  $k$ , and  $N$  is the total mole amount of gaseous constituents.

The chemical potentials of the pure stoichiometric solid phases are defined as

$$\mu_{k,solid} = \mu_k^o \quad [A6]$$

For the aqueous phase, the chemical potential is

$$\mu_{k,aqueous} = \mu_k^o + RT \ln a_k \quad [A7]$$

where  $a_k$  is the activity of constituent  $k$  in the aqueous phase. To solve the minimisation problem, Eqs A5 and A7 are linearised and Eqs A2 and A3 are arranged in matrix form. The set of equations thus obtained is iteratively solved until convergence is reached (Eriksson 1971; Weber 1998).

At this stage, when the fibre phase is still neglected, the stoichiometric matrix of the multi-phase system is shown in Table A1.

### Donnan effect

A second aqueous solution phase, the fibre phase, is introduced into the system. The chemical potential of the aqueous phases, Eq A8, is expanded to give the electrochemical potential:

$$\mu_{k, \text{aqueous}} = \mu_k^o + RT \ln a_k + z_i F \psi^D \quad [\text{A8}]$$

where  $F$  is Faraday's constant and  $\psi^D$  is the electrical potential.

To include the fibre phase and its apparent charge, three additional system components are needed as constraints in the conservation matrix. The first constraint (component  $s$  in Table A2) is introduced for conserving the water content in the fibre phase. Thus, a constant WRV is assumed.

The second constraint (component  $q$  in Table A2) is for ensuring electro-neutrality in the fibre phase. The third constraint (component  $a$  in Table A2) is used for defining the acidic groups. A single acidic group is given as an example.

### Pitzer formalism

Eq A9 indicates the interaction parameters for the activity of the H<sub>2</sub>O solvent, Eqs A10 and A11 indicate the interaction parameters for the cations and anions, respectively, and Eq A12 indicates the neutral solute species. Activities are presented here in general form as a function of molality, charge, and Pitzer interaction coefficients. A more detailed description of the equations is given, for example, by Harvie et al. (1984).

$$\ln a_{\text{H}_2\text{O}} = f(m_c, m_a, m_n, z_c, z_a, \beta_{ca}^{(0)}, \beta_{ca}^{(1)}, \beta_{ca}^{(2)}, C_{ca}^\phi, \Phi_{cc}^P, \Phi_{aa'}^P, \Psi_{cc'a}^P, \Psi_{aa'c}^P, \lambda_{na}^P, \lambda_{nc}^P) \quad [\text{A9}]$$

$$\ln a_M = f(m_c, m_a, m_n, z_M, \beta_{Ma}^{(0)}, \beta_{Ma}^{(1)}, \beta_{Ma}^{(2)}, C_{Ma}^\phi, C_{ca}^\phi, \Phi_{Mc}^P, \Psi_{Mca}^P, \Psi_{aa'M}^P, \lambda_{nM}^P) \quad [\text{A10}]$$

$$\ln a_X = f(m_c, m_a, m_n, z_X, \beta_{cX}^{(0)}, \beta_{cX}^{(1)}, \beta_{cX}^{(2)}, C_{cX}^\phi, C_{ca}^\phi, \Phi_{Xa}^P, \Psi_{Xac}^P, \Psi_{cc'X}^P, \lambda_{nX}^P) \quad [\text{A11}]$$

$$\ln a_N = f(m_c, m_a, \lambda_{nc}^P, \lambda_{na}^P) \quad [\text{A12}]$$

In Eqs A9 to A12,  $m_k$  is the molality of the cation, anion or neutral species.  $z_k$  is the charge of the cation or anion.  $\beta_{kk'}^{(0)}$ ,  $\beta_{kk'}^{(1)}$ ,  $\beta_{kk'}^{(2)}$  and  $C_{kk'}^\phi$  are the Pitzer coefficients for a cation-anion pair.  $\Phi_{kk'}^P$  is the Pitzer coefficient for a cation-cation or anion-anion pair.  $\Psi_{kk'k''}^P$  is the Pitzer coefficient for an anion-anion-cation or cation-cation-anion triplet.  $\lambda_{kk'}^P$  refers to the Pitzer coefficient of a neutral-cation or neutral-anion pair. The subscript  $M$  refers to an observed cation,  $X$  to an observed anion, and  $N$  to an observed neutral species. The subscript  $c$  refers to

Table A1. Stoichiometric matrix of the aqueous suspension when the fibre phase is neglected. Constituents are shown as rows and system components as columns.

	k	C	O	H	S	Ca	Na	N	e <sup>-</sup>	
Gaseous phase	1	H <sub>2</sub> O	1	2						
	2	O <sub>2</sub>		2						
	3	CO <sub>2</sub>	1	2						
	4	N <sub>2</sub>						2		
Aqueous phase	5	H <sub>2</sub> O	1	2						
	6	O <sub>2</sub>		2						
	7	CO <sub>2</sub>	1	2						
	8	N <sub>2</sub>						2		
	9	H <sup>+</sup>			1				-1	
	10	OH <sup>-</sup>		1	1				1	
	11	HCO <sub>3</sub> <sup>-</sup>	1	3	1				1	
	12	CO <sub>3</sub> <sup>2-</sup>	1	3					2	
	13	SO <sub>4</sub> <sup>2-</sup>		4		1			2	
	14	HSO <sub>4</sub> <sup>-</sup>	4	1	1				1	
	15	Ca <sup>2+</sup>					1		-2	
	16	Na <sup>+</sup>						1	-1	
	CaCO <sub>3</sub>	17	CaCO <sub>3</sub>	1	3		1			
	CaSO <sub>4</sub>	18	CaSO <sub>4</sub>	4		1	1			

each cation,  $a$  to each anion, and  $n$  to each neutral species.

### Constraining kinetic reactions

In order to introduce kinetic reactions into a multi-phase system, new system components, as well as new constituents, are included in the stoichiometric matrix  $N$ :

$$N = \begin{bmatrix} v_{1,L+1} & \cdot & \cdot & v_{1,L+2} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ v_{K+4,L+1} & \cdot & \cdot & v_{K+4,L+2} \end{bmatrix} \quad [\text{A13}]$$

The new system components (columns  $L+1$  and  $L+2$ ) are connected to the new constituents (rows  $K+1$  and  $K+2$  for column  $L+1$ , and  $K+3$  and  $K+4$  for column  $L+2$ , respectively) with non-zero  $v_{k,l}$  values. The positive value 1 is used for forward and the negative value -1 for reverse reaction. The actual constituents are incorporated into the new components based on the reaction stoichiometry. The combined solution of the reaction rate differential equations and the min( $G$ ) system then provides the DAE technique that follows the chemical change of the multicomponent system as a function of the extent of the kinetically constrained reactions. The extended matrix, with two kinetic reactions included, is shown in Table 1.

### Appendix 2. Neural networks

A neural network is a mathematical model mimicking the functions of a biological neural network. The network is constructed from multiple artificial neurons on several layers. A neural network is adaptive and the correct patterns are taught using data. Networks are used to describe complex interactions between various inputs and outputs. An example of a typical neural network used in this study is shown in Fig A1. The first inputs, P<sub>1</sub> to P<sub>R</sub>, of the neural network are normalised between -1 and 1. Each of the neurons is calculated:

$$n_s = w_{s,1}p_1 + \dots + w_{s,R}p_R \quad [A14]$$

where  $n_s$  is the neuron input,  $w_{sr}$  is the weight of the  $s$ :th neuron's  $r$ :th input and  $p_r$  is the  $r$ :th input.  $S$  is the number of neurons and  $R$  is the number of inputs (see Fig A1). The first layer of the neural network is based on Tansig neurons, Eq A15, and the second layer on Purelin neurons, Eq A16. Output, a, is calculated as:

$$a = \frac{2}{1 + e^{-2n}} - 1 \quad [A15]$$

$$a = n \quad [A16]$$

The neural network is taught using a back-propagation algorithm:

$$x_{k+1} = x_k - \alpha_k g_k \quad [A17]$$

where  $x_k$  is a vector of current weights and biases,  $g_k$  is the current gradient, and  $\alpha_k$  is the learning rate. Matlab was used for developing the neural networks. A detailed description is provided by Mathworks (2007).

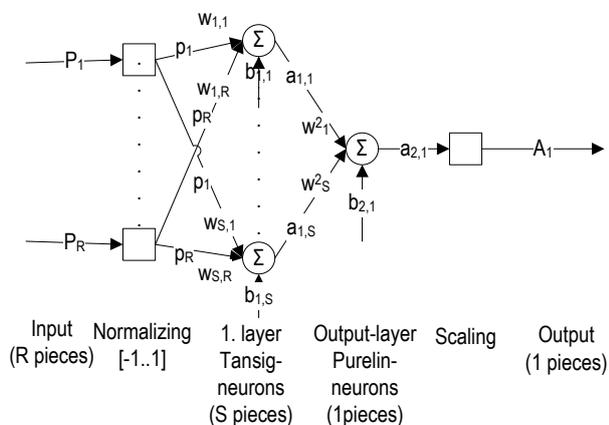


Fig A1. Schematic of a two-layer neural network.

Table A2. Stoichiometric matrix of the aqueous suspension when the fibre phase is included. Constituents are shown as rows and system components as columns.

	k	C	O	H	S	Ca	Na	N	e-	s	q	a
Gaseous phase	1 H <sub>2</sub> O		1	2								
	2 O <sub>2</sub>		2									
	3 CO <sub>2</sub>	1	2									
	4 N <sub>2</sub>							2				
Aqueous phase	5 H <sub>2</sub> O		1	2								
	6 O <sub>2</sub>		2									
	7 CO <sub>2</sub>	1	2									
	8 N <sub>2</sub>							2				
	9 H <sup>+</sup>		1								-1	
	10 OH <sup>-</sup>		1	1							1	
	11 HCO <sub>3</sub> <sup>-</sup>	1	3	1							1	
	12 CO <sub>3</sub> <sup>2-</sup>	1	3								2	
	13 SO <sub>4</sub> <sup>2-</sup>		4	1							2	
	14 HSO <sub>4</sub> <sup>-</sup>		4	1	1						1	
	15 Ca <sup>2+</sup>						1				-2	
	16 Na <sup>+</sup>							1			-1	
Fibre phase	17 H <sub>2</sub> O		1	2								1
	18 O <sub>2</sub>		2									
	19 CO <sub>2</sub>	1	2									
	20 N <sub>2</sub>							2				
	21 H <sup>+</sup>		1								-1	1
	22 OH <sup>-</sup>		1	1							1	-1
	23 HCO <sub>3</sub> <sup>-</sup>	1	3	1							1	-1
	24 CO <sub>3</sub> <sup>2-</sup>	1	3								2	-2
	25 SO <sub>4</sub> <sup>2-</sup>		4	1							2	-2
	26 HSO <sub>4</sub> <sup>-</sup>		4	1	1						1	-1
27 Ca <sup>2+</sup>						1				-2	2	
28 Na <sup>+</sup>							1			-1	1	
29 Acid <sup>-</sup>										1	-1	1
30 AcidH		1										1
CaCO <sub>3</sub>	31 CaCO <sub>3</sub>	1	3			1						
CaSO <sub>4</sub>	32 CaSO <sub>4</sub>		4	1	1							