

Erkki Räsänen

## Modelling ion exchange and flow in pulp suspensions



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# **Modelling ion exchange and flow in pulp suspensions**

Erkki Räsänen

VTT Processes

Helsinki University of Technology  
Laboratory of Forest Products Chemistry  
P.O.Box 6300, 02015 HUT, FINLAND

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puh. vaihde (09) 4561, faksi (09) 456 4374

VTT, Bergsmansvägen 5, PB 2000, 02044 VTT

tel. växel (09) 4561, fax (09) 456 4374

VTT Technical Research Centre of Finland, Vuorimiehentie 5, P.O.Box 2000, FIN-02044 VTT, Finland

phone internat. + 358 9 4561, fax + 358 9 456 4374

VTT Prosessit, Biologinkuja 7, PL 1602, 02044 VTT

puh. vaihde (09) 4561, faksi (09) 456 6390

VTT Processer, Biologgränden 7, PB 1602, 02044 VTT

tel. växel (09) 4561, fax (09) 456 6390

VTT Processes, Biologinkuja 7, P.O.Box 1602, FIN-02044 VTT, Finland

phone internat. + 358 9 4561, fax + 358 9 456 6390

*Dedicated to Ville*



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## Abstract

This thesis summarizes the results of four papers dealing with modelling of ion exchange between cellulosic fibers and their surrounding aqueous solution.

Transition metals, in particular manganese, iron and copper, induce fiber-deteriorating radical reactions in oxygen-chemical-based bleaching, while magnesium inhibits such reactions. Thus the removal of the harmful transition metals from a pulp is required while the beneficial magnesium should be retained in a pulp. Selective control of metal contents of pulps is a key factor in the control of bleaching chemistry. Thus, ability to predict the extent of ion exchange and amounts of metals are of great practical interest.

An ion exchange model to describe interaction of ionic species with kraft pulps has been developed in the present work. The model can be applied in pulp washing and chelation. The present model takes into account overall ionic composition of pulp suspensions, i.e. the cations and simple anions as well as the ligands and the complexes. The model facilitates calculation of pH, complexation and distribution of ionic species between the aqueous phase confined to fibers and the external solution. The present model also accounts for the ion exchange kinetics and flow of water through the immobile fiber network, i.e. the "pulp bed".

The present model is based on the formerly developed ion exchange model, which is based on so-called Donnan equilibrium theory. The development of the new model required the inclusion of the different anionic species to model and the combination of the Donnan model with a complexation model. The ion exchange kinetics is described as a two-step phenomenon. The first rate-limiting step can be due to the dissolution of solid metal compounds in the fiber phase as

well as the diffusion of ions in the fiber wall, while the second step is the transfer of the ionic species between the fiber phase and the external solution, which is governed by the concentration gradient between the phases. In the model, the transfer of ions between the phases is directly related to the Donnan theory.

In the testing of the elements of the ion exchange model, it was found that the combination of the Donnan model with a complexation model quantitatively predicts the pH, the ionic distribution as well as the complexation equilibria in batch-type systems when the time to achieve full equilibrium is not limited. In the pulp beds subject to flow the ion exchange kinetics reduces the metal removal efficiency and selectivity. This can be considered to be due to the repulsion of anionic species (simple anions, ligands and complexes) from the negatively charged fiber phase. It can also be considered that the rate of change of fiber charge determines the overall ion exchange kinetics.

It was found in the experiments that a low pH of displacement solution favors rapid metal removal from pulp beds. However, a low pH reduces the metal removal selectivity, i.e. harmful manganese and the beneficial magnesium is also removed from the pulp. The metal removal process in laboratory or in industrial scale could be optimized in terms of chemical concentrations, pH, reaction time and wash flow conditions. The present model facilitates realistic modelling of these conditions.

# Preface

I am grateful to my supervisor, Professor Emeritus Per Stenius for his support, guidance and patience during this study. I am also grateful to Professor Tapani Vuorinen and to Professor Emeritus Johan Gullichsen, at the Helsinki University of Technology, to Professor Adriaan van Heiningen, at the University of Maine, and to Dr. Pertti Koukkari, at the Technical Research Centre of Finland, for sharing their enthusiastic attitude towards scientific work. I wish to express my gratitude to all of my co-authors who have contributed this work. I am especially grateful to Mr. Pekka Tervola for his help in mathematics.

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I am greatly indebted to my mother Kyllikki and to my son Ville; I hope that I will be able to repay my absence and your patience during these years.

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Espoo, May 2003

Erkki Räsänen

## List of original publications

This thesis is mainly based on the papers listed below:

- I. Räsänen, E. Tervola, P. and Stenius, P. 'Model describing Donnan equilibrium, pH and complexation equilibria in fibre suspensions', *Nordic Pulp and Paper Research Journal* 16(2001)2:130–139.
- II. Räsänen, E. and Kärkkäinen, L. 'Modelling of complexation of metal ions in pulp suspensions', Accepted for publication in *Journal of Pulp and Paper Science*, June 2003.
- III. Räsänen, E. van Heiningen, A.R.P. Koukkari, P. Pajarre, R. and Aksela, R. 'Modelling Displacement Flow and Ionic Equilibria in Pulp Beds, Part 1 – Laboratory Experiments' Manuscript submitted for *Paperi and Puu*.
- IV. Räsänen, E. van Heiningen, A.R.P. Koukkari, P. Pajarre, R. and Aksela, R. 'Modelling Displacement Flow and Ionic Equilibria in Pulp Beds, Part 2 – Mathematical Model' Manuscript submitted for *Paperi and Puu*.

# Contents

Abstract.....	5
Preface .....	7
List of original publications .....	8
Abbreviations.....	11
Nomenclature.....	12
1 Introduction.....	15
1.1 Towards better understanding of the chemistry of pulp suspensions .....	15
1.2 Hypothesis .....	16
1.3 The objectives of the work.....	17
2 Theory.....	19
2.1 Cellulose fibers in ionic media .....	19
2.2 The Donnan equilibrium model.....	21
2.3 Extensions of equilibrium model to include kinetics.....	27
2.4 Mobile phase model.....	32
2.5 Parallel Plug Flow model.....	34
3 Materials and methods .....	36
3.1 Pulp properties .....	36
3.2 Fiber titrations and equilibrium experiments.....	37
3.3 Determination of ion exchange kinetics .....	38
4 Results and discussion .....	40
4.1 The influence of ionic composition on the Donnan distribution .....	40
4.2 The equilibrium concentrations of metal species in fiber suspensions..	41
4.3 The kinetics of ion exchange .....	43
4.4 Ionic interactions in pulp bed subject to displacement flow .....	44
4.5 Mobile phase model.....	46
4.6 The effect of system properties in modelling .....	50

5 Conclusions.....	53
6 Ideas for future research.....	56
References.....	57
Appendices	
Papers I–IV	

## Abbreviations

<b>BCA6</b>	Bis-N-[2-(1,2-dicarboxylethoxy)]-aspartic acid
<b>BTC</b>	Breakthrough Curve
<b>COD</b>	Chemical Oxygen Demand (required for oxidation of organic carbon)
<b>CTMP</b>	Chemi-Thermo-Mechanical Pulp
<b>CSTR</b>	Continuously Stirred Tank Reactor
<b>D</b>	Chlorine Dioxide Bleaching Stage
<b>DTPA</b>	diethylenetriaminepentaacetic acid
<b>EDTA</b>	ethylenediaminetetraacetic acid
<b>E<sub>OP</sub></b>	Alkaline Extraction Stage with Oxygen and Peroxide
<b>FSP</b>	Fiber Saturation Point
<b>PPF</b>	Parallel Plug Flow
<b>TOC</b>	Total Organic Carbon
<b>WRV</b>	Water Retention Value

# Nomenclature

## Latin letters

$A$	molar amount of acid
$A_f$	molar amount of fiber-bound acid
$\bar{C}_i$	concentration of all species of component $i$
$D$	dispersion coefficient
$eq$	subscript denoting equilibrium
$E(T)$	normalized residence time distribution
$F$	fiber phase volume in $\text{dm}^3 \text{kg}^{-1}$
$f$	subscript denoting fiber phase
$f \leftrightarrow s$	subscript denoting mass transfer region in fiber phase
$f_j$	flow fraction of channel $j$ , dimensionless
$H$	height, m
$in$	subscript denoting input
$j, J$	number of bed channel
$k$	number of protons bound in acid
$K_{A_f}$	dissociation constant of fiber-bound acid
$K_{A_p}$	dissociation constant of $p$ -protic acid
$k_\lambda$	overall ion exchange rate coefficient
$K_\lambda$	overall dimensionless ion exchange rate coefficient
$k_i$	internal ion exchange rate coefficient
$K_i$	internal dimensionless ion exchange rate coefficient
$K_{my}$	metal complex stability constant
$l, L$	number of pulp bed layer
$M$	metal cation

$M'$	uncomplexed metal
$n$	molar amount, mol
$out$	subscript denoting output
$p$	number of protons dissociated from acid
$Pe$	Peclet number
$q$	superficial velocity of fluid, $m\ s^{-1}$
$Q_d$	flow rate through the bed, $dm^3\ kg^{-1}\ s^{-1}$
$Q_j$	flow rate through the channel $j$ , $dm^3\ kg^{-1}\ s^{-1}$
$s$	subscript denoting external phase
$S$	suspension consistency, %
$t$	time, s
$T$	dimensionless time
$\Delta t$	displacement time increment
$\Delta T$	dimensionless displacement time increment
$t_D$	displacement time, s
$t_r$	residence time, s
$\tau$	subscript denoting total concentration in suspension
$V$	total volume of water in pulp bed, $dm^3\ kg^{-1}$
$V_{bed}$	dimensionless volume of external (movable) solution in bed
$V_d$	displacement volume, $dm^3\ kg^{-1}$
$V_D$	dimensionless displacement volume, $dm^3\ kg^{-1}$
$X_i$	molar amount of ion $i$
$Y$	ligand
$Y'$	uncomplexed ligand
$z$	charge (valency) of ion
$\bar{z}_i$	net charge (valency) of ionic component $i$

## Greek letters and symbols

$\lambda$	Donnan distribution coefficient
$\rho_s$	density of fluid
*	superscript denoting non-transferable fraction

# 1 Introduction

## 1.1 Towards better understanding of the chemistry of pulp suspensions

Chemically delignified and fully bleached kraft pulp is the most important raw material of paper and many other fiber products. Due to the quality requirements of pulp, environmental reasons, and the cost of the chemicals, energy and process equipment, it is essential to understand and manage the chemistry of pulping and the fiberline processes as well as the chemistry of papermaking processes. The quality of kraft pulp determines the value and the technical properties of products and the reusability of fiber material.

The chemistry of pulping and bleaching process is highly complex. Due to the heterogenous chemical composition of wood raw material, its reaction products, the chemicals as well as the so-called non-process elements, the many different phenomena related to interactions of these components have been difficult to understand and characterize. Fundamental characterization of the chemical structure of wood material and its reactions with different chemicals has significantly increased knowledge of the chemistry of pulping processes during the last two decades. Another focus in the research of pulping chemistry has been the characterization of composition of process effluents and filtrates as well as their effects and equilibrium behavior in pulping processes. This study deals with the latter aspect.

Due to these advances, the chemistry of pulping processes can be managed quite well nowadays. However, much of this practice is strictly on an empirical basis. Understanding of fundamental phenomena is the premise for continuous advance; it has been demonstrated quite recently that fundamental characterization of basic chemical interactions and process chemistry can result in significant breakthroughs in the development of pulping process technology /1/.

At the Helsinki University of Technology (HUT), Laboratory of Forest Products Chemistry, research focusing on the systematical characterization of chemical and charge properties of different pulps as well as on the metal ion interactions

was begun in the first half of the 1990's by Sjöström /2/, Laine et al. /3/ and by Vuorinen et al. /1/.

The research was carried out in close collaboration with research groups in Sweden, The Department of Inorganic Chemistry, University of Umeå, The Institute for Surface Chemistry, Stockholm and STFI, and with other research communities sharing the same interests.

The advances in fiber chemistry /1, 2, 3/ and modelling of equilibrium chemistry of pulp – water systems /4/ after the middle of 1990's made it possible to extend the modelling into new challenging areas, such as fiberline processes. It was required, however, to develop efficient and reasonably simple calculation methods accounting for the most important kinetic and equilibrium phenomena as well as for flow conditions in processes. This thesis summarizes the results of development work of such modelling methods. This work started in 1996 at HUT, where the basic equilibrium models were developed in the 'TCF' and 'SYKLI' projects. The kinetic extensions as well as the other model extensions were developed at the VTT Processes and University of Maine, USA, during 2000–2002. This work now continues in VTT and in HUT in close collaboration with other research groups in Finland and the USA. The objective of future research is to apply the new ideas and concepts in the solving of practical problems occurring in fiberline and papermaking processes. In several cases this goal has already been quite well achieved.

## **1.2 Hypothesis**

This study is based on the following hypotheses:

The ion exchange kinetics and ionic equilibria in pulp – water systems can be described quantitatively when the overall ionic composition accounting for anions, cations, ionic species and fiber charge properties are known.

The nature of cellulose fiber wall in ionic media as a negatively charged polyelectrolyte phase determines the mechanisms influencing the ion exchange kinetics and equilibria. Due to the highly complex chemical composition of fiber

suspensions, some of these mechanisms can be defined on a phenomenological basis only.

### 1.3 The objectives of the work

The objectives of this work were to develop equilibrium and kinetic models for the characterization of ion interactions with pulp fibers in water suspensions subject to varying amounts of ions and flow of water. The models developed in this work are extensions of formerly developed equilibrium model /4/, which was based on the use of the so-called Donnan equilibrium theory.

1. The first model development is a method to account for overall anionic and cationic composition of pulp suspensions, which is needed in many applied-oriented purposes where the calculation of pH is required when amounts of ionic components in the system vary. Such a system is, for example, a reactor with inputs and outputs of fibers, water and chemicals.
2. Secondly, a simple solution complexation model has been combined with the Donnan equilibrium model. This extension facilitates quantitative modelling of complexation equilibria, i.e. the selectivity and efficiency of chelation, in pulp suspensions. Due to the common use of chelants in oxygen chemical based bleaching processes, this model extension is of great practical interest.
3. A third model extension combines the Donnan equilibrium model with a model that describes ion exchange kinetics of pulp suspension. Ion exchange kinetics is important, for example, in washing processes where rapid and efficient removal of harmful components should be achieved with a minimum use of process water in a short time.
4. Finally, a general description of ionic conditions in porous pulp bed subject to a *displacement* flow of water has been developed. The displacement model includes all the other model extensions.

These models were developed and evaluated in Papers I–IV. Papers I and II describe the formulation and evaluation of the first and the second extensions,

i.e. the inclusion of anionic species and a complexation model into the Donnan equilibrium model. Paper III is focused on the experimental characterization of the behavior of metals in pulp beds subject to displacement flow. The kinetic models as well as the displacement model were formulated and tested in Paper IV.

As the result of this work, it is possible to characterize highly complex equilibrium and kinetic ionic interactions with fibers, to account for input or removal of water, cations, anions and ligands, as well as to characterize the effect of porous fiber network on the flow through the fiber bed. In the future further work is required on the characterization of industrial pulp suspensions instead of 'clean' laboratory systems. The present work, however, provides easily applicable principles for modelling of phenomena related to ionic equilibria in any unit processes of industrial fiberlines.

## 2 Theory

### 2.1 Cellulose fibers in ionic media

Cellulose fibers prepared by chemical pulping are composed of cellulose microfibrils, hemicelluloses and (residual) lignin. The regions between the microfibrils are permeable to water, ions and small macromolecules, the cellulose microfibrils have a highly crystalline structure and they are not permeable to water. Hemicelluloses and lignin on the surfaces of microfibrils are mostly amorphous polymers, which contain functional groups that dissociate in water and thus generate anionic charge.

A schematic picture of cellulose fiber systems in ionic media is shown in Fig. 1. The water volume in a fiber suspension is divided into two sub-volumes i.e. the volume of water surrounding the fibers and the volume of water confined to the highly porous, negatively charged fiber wall. Thus the cellulose fibers in the water – ionic systems have the characteristics of polyelectrolyte gel.

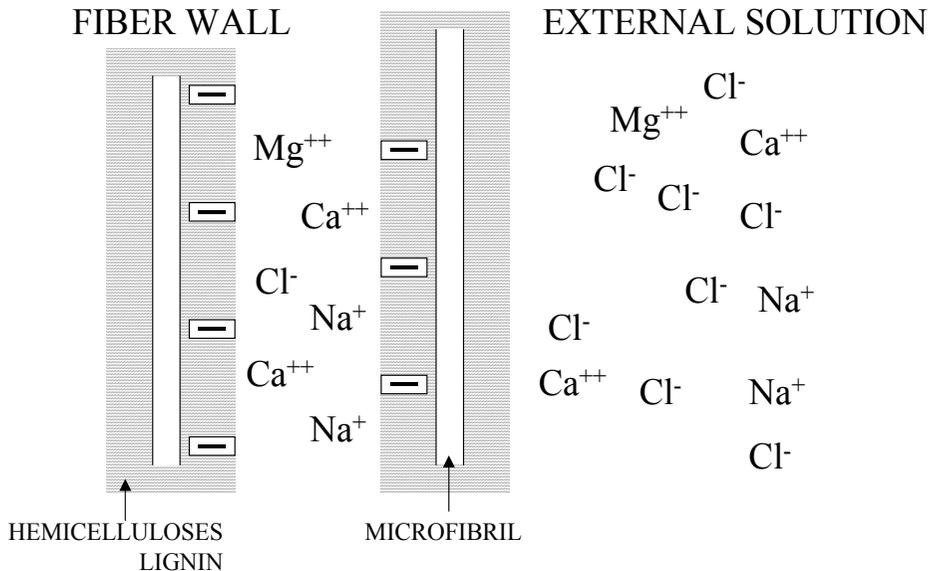


Figure 1. Cellulose fibers in ionic media, redrawn after [4].

Interactions of ions with the functional groups bound to fibers can be divided into non-specific and specific interactions. Non-specific interactions are electrostatic attraction or repulsion between ions and the charged matrix of the fiber cell wall. Specific interactions include e.g. complexation of metal cations with functional groups as well as adsorption of ions to polarized surfaces. The interactions of ions with the cellulose fibers depend largely on the charge properties of fibers. As shown in Table 1, the types and amounts of ionizable functional groups in cellulose fibers depend largely on the grade of pulp.

Table 1. Charge of different pulps.

<b>MECHANICAL /8, 9, 10/</b>	<i>total charge mmol kg<sup>-1</sup></i>	<i>ionizable groups</i>
TMP	80–110 (ubl) 150–250 (bl)	1,2,3,4
CTMP	120–180 (ubl)	1,2,3,4,5
ubl: unbleached	190–330 (bl)	
bl: bleached		
<b>CHEMICALLY DELIGNIFIED /1, 2, 3, 11, 12/</b>		
softwood kraft, unbleached, kappa 20–30	55–115	1,2,3,6
hardwood kraft, unbleached, kappa 10–20	130–190	1,2,3,6
<b>IONIZABLE GROUPS</b>	<i>pK</i>	<i>Ref</i>
<b>In hemicelluloses and pectin:</b>		
1: methylglucuronic acids, and	3.3 – 3.7	/2, 3/
2: galacturonic acids		
<b>In cellulose:</b>		
3: alcohols, hemiacetals	13 – 15	/2/
<b>In lignin:</b>		
4: guaiacyl and syringyl phenols	6.2 – 11	/2, 6/
<b>Not existing in native wood:</b>		
5: sulphonic acids (lignin, CTMP)	0 – 1	/2, 13/
6: hexenuronic acids (xylan in kraft pulp)	3.1	/14/

Native wood contains carboxylic groups in uronic, fatty and rosin acids ( $-\log K = 3.5 - 5$ ), phenolic hydroxyl groups in lignin ( $-\log K = 6 - 11$ ) and hydroxyl groups in carbohydrates ( $-\log K = 11 - 12.5$ ) /5, 6/. The chemical composition of functional groups in *mechanical*, *thermomechanical* and *chemimechanical* pulps is quite similar to native wood and thus, the charge properties of mechanical pulps depend largely on the wood raw material. Peroxide bleaching of these pulps generates new carboxyl groups and increases the total anionic charge. Dithionite used in the bleaching of chemimechanical pulps generates sulphonic acid groups that are strongly acidic. The wood raw material determines also the charge characteristics of *chemically delignified* pulps. Chemical delignification of wood in the alkaline sulphate (kraft pulping) process decreases the total charge of wood due to chemical reactions and dissolution of wood extractives, lignin and hemicelluloses. The kraft pulping process also creates carboxylic groups, i.e. hexenuronic acids that do not exist in native wood. These groups are generated from methylglucuronic acids in xylan. The xylan dissolved in kraft pulping conditions can reprecipitate on the surface of pulp fibers, which causes non-homogenous distribution of the charge in the fiber cell wall /7/.

## 2.2 The Donnan equilibrium model

The original Donnan theory was first used in the description of the so-called sol-concentration effect of electrochemical cells /15/. Later, the theory was applied in the characterization of colloids, i.e. the molecular weight and charge of colloidal particles /16/. Donnan theory was extended to polyelectrolyte systems by Procter and Wilson /17/. The theory was used to characterize electrolyte interactions with cellulose fibers by Neale /18/ in 1929 and in 1952 by Farrar and Neale /19/.

In the original Donnan model, an immobile or impermeable charge excess is confined to one phase. To maintain electroneutrality in both phases, freely mobile ions, being able to transfer from one phase to another, are distributed unevenly due to the confinement of some charge to one phase.

The original Donnan theory assumes ideal behavior in both aqueous phases. To include non-ideal behavior, the theory was later extended e.g. by Donnan /20/, Hückel /21/ and Kameyama /22/.

In 1996, Towers and Scallan /4/ introduced a Donnan theory-based equilibrium model that describes distribution of metal cations between the solution external to fibers and the water in the fiber cell wall. Their model is a practical application of the ionic distribution model described in the original theory of Donnan. Before the introduction of the ion exchange model, Scallan had earlier related the Donnan theory to the description of swelling of pulp fibers /23/.

When applied to fiber chemistry, the Donnan theory describes the distribution of ions between the aqueous phase in fibers and the external solution according to:

$$[X_i]_f = \lambda^{z_i} [X_i]_s \quad (1)$$

Towers' and Scallan's ion exchange model /3/ cleverly combined the conditions of Donnan distribution, the mass balances of ions between the aqueous solution in fibers and the external solution surrounding the fibers, as well as the electroneutrality conditions into a single equation. Their model is expressed by:

$$(\lambda^2 - 1) \cdot [H^+]_s + z_i \cdot (\lambda^{z_i+1} - 1) \cdot \frac{\sum_i [M_i^{z_i}]_T \cdot V}{V + F (\lambda^{z_i} - 1)} - \sum_i [A_{f,i}^-]_T = 0 \quad (2)$$

For a list of symbols, see Nomenclature.

The inputs of the model of Towers and Scallan are the total amounts and valences of metals initially present in fibers, the total volume of water, the volume of water in the fiber cell wall, the mass of pulp fibers, the pH of the fiber suspension and the total charge of fibers i.e. the total amounts of fiber-bound anionic groups and their dissociation constants. From these inputs one can obtain the value of Donnan distribution coefficient as a numerical solution of Eq. (2). Using this coefficient, the concentrations of ions in the external phase can be calculated from:

$$[X_i]_s = \frac{n_{x_i}}{(V + F(\lambda^{z_i} - 1))} \quad (3)$$

Although based on the ideal behavior of aqueous phases, Towers and Scallan demonstrated that the model is able to describe ion exchange of Na<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup> and Mn<sup>++</sup> ions between pulp fibers and the external aqueous solution realistically at least under laboratory conditions /4/. Later, their model was used in many studies describing the interactions of fibers with ions in solution and other related phenomena.

Laivins and Scallan /13/ studied the effect of ionic strength on the removal of metal ions from kraft and CTMP pulps. They demonstrated that the model is able to predict the ion exchange in a wide ionic strength range and that the model can be used to describe charge and ion exchange properties of CTMP pulps with a high total charge.

Laivins and Scallan /24/ also studied the effect of the ionic form of the pulp fibers on the swelling of fibers and on the strength properties of handsheets prepared from the pulps. They qualitatively related these properties to the Donnan theory.

Lindgren /11, 25/ studied the applicability of the Donnan model in the description of the association of Al<sup>+++</sup>, Fe<sup>+++</sup> and Cu<sup>++</sup> species with pulp fibers. Lindgren demonstrated that the species of these metals also interact with fibers according to the Donnan theory, but specific interactions of these species with fibers and complexation with OH<sup>-</sup> ions must be taken into account.

Sjölander (Norberg) /26/ studied the effect of precipitation of solid metal compounds on the distribution of metal ions between the fiber phase and the external solution. Sjölander demonstrated that divalent metals Ca, Mg and Mn occur mainly as hydroxy and carbonate precipitates in oxygen-delignified kraft pulp fibers. This must be accounted for in the prediction of ionic distribution by the Donnan theory.

Athley /27/ studied the interactions of Na, Ca and Mg ions with pulp fibers, comparing the Donnan ion exchange model with a surface complexation model.

A quite similar comparison was made by Lindgren /11/. Athley demonstrated that the experimentally measured ionic distributions deviate to quite a significant degree from the theoretically predicted ones. The deviations may be caused by the assumption of ideal behavior of aqueous solution in the Donnan model.

Andersson et al. /28/ studied the washing of ionic components from the pulp. In their study the Donnan theory was qualitatively related to removal of anionic macromolecular components from pulp. It was demonstrated that the anionic macromolecules are easily removable from the pulp fibers due to their repulsive interaction with the negatively charged fiber wall.

All of the studies described above were made using the original model of Towers and Scallan. However, when considering practical or industrial applications, the Towers' and Scallan's model has several limitations. The most fundamental limitations are that the input of the ionic components is restricted to metal cations and the complexation equilibria in solution are not included in the model.

The pH is the main factor that governs the ion exchange and the complexation equilibria in fiber suspension. The electroneutrality conditions define the dependence of pH on the ionic composition of the suspension. Thus, if the overall composition of cations, simple anions and chelants in the suspension are to be accounted for in the modelling, the pH of suspension cannot be regarded as a 'known' input parameter.

In the present work, the anionic components were included in the Donnan model (Papers I and II) by using electroneutrality equations that account for the presence of different anionic species, e.g. simple anions and multivalent acids or ligands. These conditions, i.e. Eqs (4) and (5) are written for the whole suspension and for the external solution:

$$z_i \sum_i [X_i^{z_i}]_T - \sum_i [A_{i,i}^-]_T = 0 \quad (4)$$

$$z_i \sum_i [X_i^{z_i}]_s = 0 \quad (5)$$

This definition differs from Towers' and Scallan's model that used electroneutrality conditions for the external solution and fiber phase, which were combined in Eq. (2). Two electroneutrality conditions and inputs for different anionic species allow the calculation of pH of the suspension *and* the Donnan distribution coefficient  $\lambda$  as a numerical solution of Eqs (4) and (5). The concentrations of ionic species in Eqs (2) and (4) are given by:

$$[A_f^-]_T = \frac{K_{A_f} [A_f]_T}{K_{A_f} + \lambda \cdot 10^{-pH_s}} \quad (6)$$

$$[H^+]_T = \frac{10^{-pH_s} \cdot (V + F(\lambda - 1))}{V} \quad (7)$$

$$[OH^-]_T = \frac{10^{-14+pH_s} \cdot (V + F(\lambda^{-1} - 1))}{V} \quad (8)$$

$$[X_i]_T = \frac{n_{X_i}}{V} \quad (9)$$

The external concentrations in Eq. (5) are given by:

$$[H^+]_s = 10^{-pH_s} \quad (10)$$

$$[OH^-]_s = 10^{-14+pH_s} \quad (11)$$

$$[X_i]_s = \frac{n_{X_i}}{(V + F(\lambda^{z_i} - 1))} \quad (12)$$

In particular, for  $k$ -protic acids and ligands in Eqs (9) and (12) the molar amount of acid that is present as an anion formed by dissociation of  $p$  protons ( $z_i = p$ ) can be calculated from:

$$n_{A_i^{-p}} = \frac{n_{A_i} \cdot K_{A1} K_{A2} \dots K_{Ap} ([H^+]_s)^{k-p}}{([H^+]_s)^k + K_{A1} ([H^+]_s)^{k-1} + K_{A1} K_{A2} ([H^+]_s)^{k-2} + \dots + K_{A1} K_{A2} \dots K_{Ak}} \quad (13)$$

As can be seen from the electroneutrality equations the immobile fiber charge is accounted for in the overall electroneutrality condition only, i.e. in Eq. (4). The freely mobile anionic species are accounted for in both electroneutrality conditions, Eqs (4) and (5). The charge of fiber with varying ionic concentrations is calculated from the determined total charge of pulp and the dissociation constants of fiber-bound groups. The dissociation constants for ligands and many other known small-molecular-weight anionic species are available from literature /e.g. 29/.

When compared to the model of Towers and Scallan /4/ the Donnan model, as defined by eqs (1)–(13), is not fundamentally different but the formalism is more general. In earlier Donnan models, the electroneutrality conditions of the two-phase Donnan system are written separately for both phases. The way the electroneutrality condition is used in this work is consistent with the general two-phase formalism; if the whole system and the external phases are electroneutral, the fiber phase must also be electroneutral.

The inclusion of multivalent anions in the electroneutrality conditions makes it possible to account for complexation equilibria in the Donnan model. Based on the overall complex formation equilibrium:



with the stability constant:

$$K_{MY} = \frac{[MY]}{[M^+][Y^-]} \quad (15)$$

and, using the following mass balances of metals and complexes:

$$Y_T = [Y^{-\rho}] + [HY^{-(\rho-1)}] + \dots + [H_\rho Y] + \sum_i [M_i Y^{(z_i-\rho)}] = [Y'] + \sum_i [M_i Y^{(z_i-\rho)}] \quad (16)$$

$$M_T = [M'] + [MY^{(z-\rho)}] \quad (17)$$

the following equation for the concentration of uncomplexed metal ions is obtained:

$$[M'] = \frac{M_T}{1 + K_{MY} [Y']} \quad (18)$$

and, correspondingly, for the amount of uncomplexed chelant:

$$[Y'] = \frac{Y_T}{1 + \sum_i K_{M_i Y} [M'_i]} \quad (19)$$

In Eqs (15)–(19)  $[M']$  and  $[Y']$  denotes the forms of metals and chelant available for complexation, which depend on pH, see Paper II. Using Equations (15) and (19) the pH-dependent complexation of metals can be calculated. With a simple algorithm, Equations (16)–(19) can be combined with the electroneutrality Equations (4) and (5), which facilitate the calculation of the pH, the complexation equilibria and the Donnan distribution of all ionic species in the pulp suspension. An experimental validation of the Donnan model combined with the complexation equilibria is presented in Paper II.

## 2.3 Extensions of equilibrium model to include kinetics

In many applications it is necessary to account for the different kinetic phenomena related to ionic conditions in pulp suspension:

- The reaction kinetics in general depends on the thermodynamic gradient, i.e. the extent of chemical reaction, required to achieve complete equilibrium of a non-equilibrium system /30/.
- The chemical potential gradients (e.g. the concentration differences) are directly related as driving forces to the rate of physical diffusion of solute components in the fiber cell wall and between the phases. The diffusion and accessibility of ionic components in the fiber wall also depends on the internal structure of fibers, e.g. the specific surface area and the swelling of fibers /31/.
- In any aqueous (multi-component) system, the dissolution kinetics of solid metal salts and the kinetics of other specific transfer reactions between the solution and other phases must be considered as rate-limiting steps /30, 32, 33/.

The first factor generally describes all kinds of chemical systems; when a transient change in the system occurs, the system composition changes according to defined chemical laws until the system is in equilibrium. However, the overall kinetics usually depends on individual rate-determining steps or reactions, which may be difficult to define separately due to complicated reaction pathways or the occurrence of many competing reactions with similar kinetics. When applied to fiber suspensions, the initial and final equilibrium compositions are known or can be calculated by using the Donnan theory. However, internal factors, i.e. diffusion as well as the specific reactions occurring in aqueous phases determine the overall ion exchange rate.

Molecular diffusion has an important role in the mass transfer kinetics between cellulose fibers and process water. Mass transfer between two phases have been studied and modelled e.g. by Sherwood and Wei /33/ as well as by Ala-Kaila /34/ who applied mass transfer models in the description of ion exchange in cellulose fiber suspensions. Both studies applied mass transfer film theory, which accounts for diffusivity of ions through films with defined thickness and diffusion resistance as a mechanism that limits the mass transfer kinetics. By analogy to physical fiber structure, the films are confined to the aqueous immobile solution in the fiber phase /34/. Ala-Kaila defined three mass transfer films with different diffusivity resistances. The number of mass transfer films,

however, was used as a curve-fitting parameter; Ala-Kaila did not relate the number of films to any topochemical characteristics of fibers, except that the total volume of liquid in the mass transfer films was equal to the volume of solution confined in the fiber phase.

When considering molecular and ionic diffusion, the structure of the fiber cell wall has characteristics that can be accounted for as factors limiting the mass transfer rate. In water suspensions the fibers swell so that the whole internal surface area of the fibers is associated with water. Highly swollen fibers have structure freely accessible for simple ions and even for macromolecules. The swelling, however, depends on the history of pulp; never-dried pulps usually have a higher surface area than the dried and re-wetted pulps, since drying causes irreversible morphological changes in the fiber wall that reduce the specific internal surface area, modify the pore structure of fibers and reduce the accessibility and transfer of solute components between the phases. Thus, phenomenological relationships between the ionic diffusivity and the topochemical characteristics of the fibers could be defined. However, other mechanisms that do not directly depend on the structure of the fibers can be more significant as factors limiting the overall ion exchange kinetics.

Due to the highly complex compositions of pulp suspensions, the third factor, i.e. the dissolution kinetics and the other specific kinetic reactions occurring in the solution phase are difficult to account for in the modelling. Sjölander (Norberg) et al. /26/ experimentally demonstrated that many metals are present in oxygen-delignified pulp as precipitated metal hydroxides and carbonates. Various other solid forms of metals can also exist in pulps, e.g. as oxalates and sulphates. The main factor determining the solubility of different solid forms of metals is the pH. The effect of other ions in aqueous multicomponent systems on the solubility of solid metal compounds can be described theoretically when all the concentrations, solubility products and other thermodynamic properties of the components are known.

Industrial pulp suspensions, however, contain dissolved macromolecular and colloidal components that have a largely unknown effect on the precipitation of solid metal compounds. For instance Ulmgren and Rådeström /35/ have demonstrated that in practice the precipitation and the occurrence of metal concentrations in pulp suspensions and filtrates that apparently are above the

solubility limit depend on the particle size of solids, temperature, concentrations of dissolved organics (as measured by COD and TOC) as well as on the ionic strength.

These effects can be explained by well-known theoretical relations. The chemical potential of the solid, and thus the precipitation and the dissolution, depends on temperature and pressure. When the solid particles are so small (in the nm range) that surface tension effects become important their chemical potential increases, i.e. the concentration of the solute species in direct equilibrium with the solid increases. Also, deviations between theoretical and measured total solution concentrations of metal ions (free and bound in complexes) can be due to (a) all complexation reactions that they participate in have not been taken into account, e.g. binding of metal ions to “COD”, (b) effects of ionic strength have not been taken into account, i.e. the assumption of ideality does not hold, (c) the solids form only very small particles, (d) supersaturation, (e) the solubility constants used in calculations are not valid at the temperatures used in measurements, (f) slow dissolution or precipitation kinetics, i.e. the practical system has not been in equilibrium, and, (g) experimental errors.

Thus, due to the highly complex connection between the ion exchange kinetics and the ionic composition of pulp suspension, the internal factors affecting ion exchange (i.e. the diffusivity as well as solubility and other specific reaction mechanisms) in this work were replaced by simple ‘internal’ kinetics, which is phenomenological without theoretical relations to specific kinetically limited reactions and fiber properties. However, the overall ion exchange kinetics describing the transfer of ions from the fiber phase to the external phase is directly related to Donnan theory. Thus, when compared to other studies, e.g. /34/, the relations to specific mechanisms determining the ion exchange kinetics remain empirical, but the Donnan theory facilitates easier calculation of the ion exchange kinetics of complex multicomponent systems.

The present kinetic model is based on the following assumptions:

(A) The total concentration of species  $X_i$  in the fiber is the sum of a fraction that can not transfer between the phases due to the kinetic restrictions and another fraction that can transfer between the fiber and the external phase:

$$[X_i]_f = [X_i^*]_f + [X_{i,f \leftrightarrow s}]_f \quad (20)$$

(B) The non-transferable fraction (\*) is converted to the transferable fraction at a rate described by the rate constant  $k_i$



(C) The rate of transfer of species  $X_i$  between fiber and solution is described by the rate constant  $k_\lambda$ :



The concentration of  $X_{i,f \leftrightarrow s}$  is related to the Donnan equilibrium. The direction of this reaction depends on whether the concentration  $[X_i]_f$  is larger or smaller than the equilibrium concentration  $[X_i]_{f,eq}$ .

The rate equations describing the internal and overall ion exchange kinetics are:

$$-\frac{d}{dt} \frac{n_{X_{i,f}^*}}{V_f} = \frac{k_i n_{X_{i,f}^*}}{V_f} = k_i [X_i^*]_f \quad (23)$$

$$-\frac{d[X_i]_f}{dt} = k_\lambda \{ [X_i]_{f \leftrightarrow s} - [X_i]_{f,eq} \} - k_i [X_i^*]_f \quad (24)$$

Eq. (24) relates the amount of ions in the non-transferable fraction (\*) to first-order kinetics with respect to the concentration of ions  $i$  remaining in the fraction. Conceptually, it is assumed that the non-transferable fraction is present in a separate phase, which is electroneutral within the fiber phase. Eq. (24) is a mass balance equation that accounts for the transport of ions from the non-transferable fraction and the transfer of ions from the fiber phase to the external solution. This kinetics is first-order with respect to the theoretical difference between the transient and equilibrium concentrations in the fiber phase as described in Fig. 2.

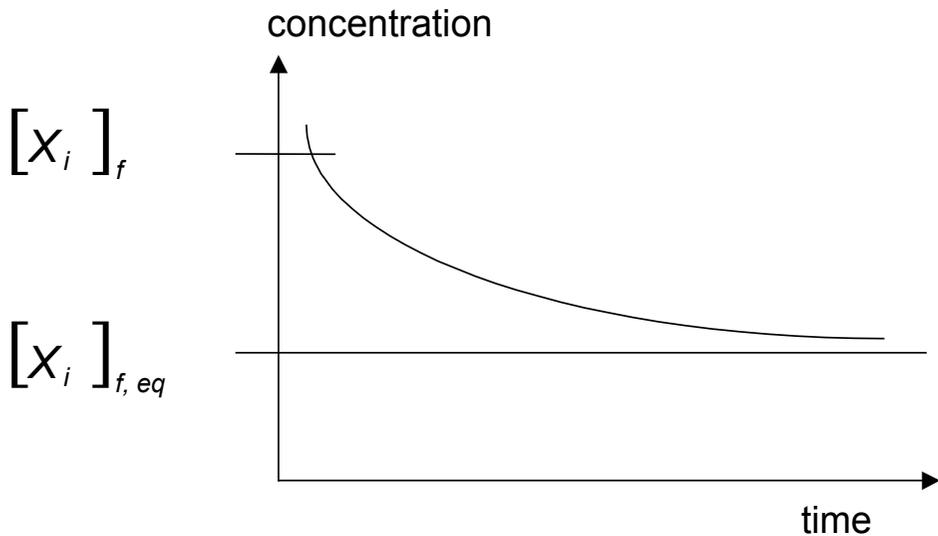


Figure 2. The relationship between transient and theoretical equilibrium concentrations in the fiber phase. The concentrations can either decrease or increase in the fiber phase depending on the overall concentration transient in the system.

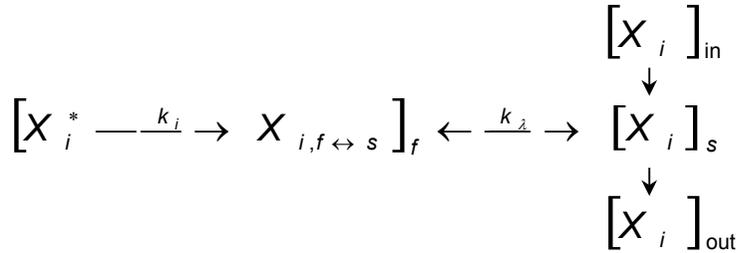
The present kinetic ion exchange model is similar to Ala-Kaila's model /34/ in the sense that the driving force for the diffusion of freely mobile ionic species is the concentration gradient between the fiber and the external phases. However, the main difference between the present model and the model of Ala-Kaila is that the multiple mass transfer films have been replaced by separate fraction(s) of non-transferable ions that can be present as separate phases in fibers. Mass transfer film models invoke diffusion as the only mechanism that limits the mass transfer kinetics. Multiple phase formalism, however, can easily be modified to account for e.g. the presence and dissolution kinetics of solid compounds that can be taken into account as separate, electroneutral phases.

## 2.4 Mobile phase model

In the two-phase Donnan equilibrium model the fiber phase consists of a solution confined to fibers and the external phase is the aqueous solution surrounding the fibers. When flow of the external solution occurs with respect to

pulp fibers, we can thus assume that the fibers contain a solution that is immobilized in the bed, while the external solution flows through the bed. It is thus easy to account for input and output of solute components with the external solution; a mass balance for such a system is shown in Fig. 3. A single control volume with input and output of water and solute components represents a continuously stirred tank reactor, CSTR.

Mass balance in a control volume:



Mass balance in a bed:

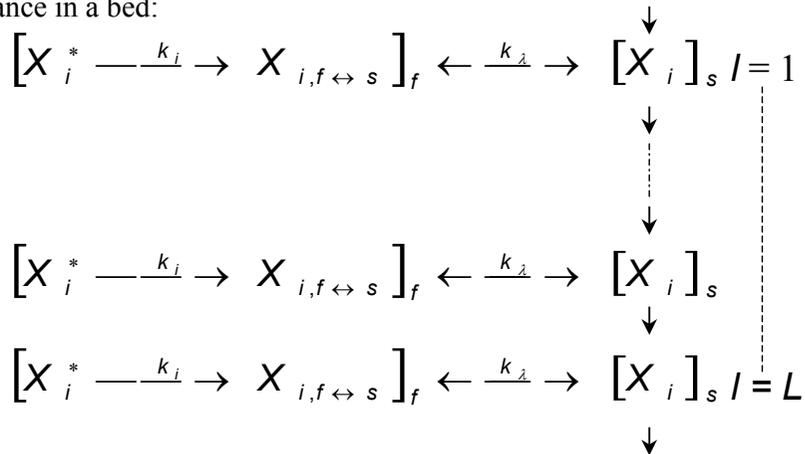


Figure 3. Extension of a kinetic ion exchange model to a mobile model and to a pulp bed model.

In many fiberline processes the fibers are not in a homogenous suspension of water but form a porous ‘cake’ or ‘bed’ through which the process water flows. In such a system, the ionic composition is not necessarily homogenous. The ionic composition of this system can be modelled by dividing the pulp bed vertically into many control volumes that describe the vertical layers of the bed. In such a model, the input of each control volume in the bed is the output from

the layer above, as shown in Fig. 3. The model consisting of many CSTRs in series describes flow that approaches ideal plug flow as the number of layers increases.

A general mass balance equation describing both systems is expressed by:

$$\frac{d[X_i]_{s,l}}{dt} = \frac{F}{V-F} \cdot k_\lambda \{ [X_i]_{f \leftrightarrow s,l} - [X_i]_{f,eq,l} \} + [X_i]_{in,l} - [X_i]_{out,l} \quad (25)$$

where the layer number  $l = L = 1$  for a system consisting of one control volume. For a series of control volumes,  $l = 1 \dots L$  with  $l = 1$  being the top layer and  $l = L$  the bottom layer.

## 2.5 Parallel Plug Flow model

The mobile phase model, i.e. Eq. (25) does not account for the flow-through properties of real pulp beds. Results from the model, however, can be used as input for the so-called parallel plug flow model which allows adjustment of flow dispersion between ideal plug flow and fully dispersed flow, i.e. the one approaching the CSTR condition. In the parallel plug flow model the exit concentration of the pulp bed is calculated as the ‘mixing cup’ average of exit concentrations of many ideal plugs with different residence times.

The exit concentration of the pulp bed is obtained from:

$$\bar{C}(T) = \frac{Q_j}{Q_d} \sum_{j=1}^J C_j(T) \quad (26)$$

where  $j = 1 \dots J$  is the number of the channel,  $C_j(T) = [X_i]_{s,L,j}(T)$ ,  $Q_j / Q_d$  is the ratio of flow rate through the channel  $j$  to total displacement flow rate through the bed, and  $T = t_d / t_r$  is the ratio of the displacement time to average residence time of the bed. The fraction  $Q_j / Q_d$  is obtained from the normalized residence time distribution,  $E(T)$ , of the bed as:

$$\frac{Q_j}{Q_d} = \int_{T_1}^{T_2} E(T) dT \quad (27)$$

and the average residence time of a single channel as:

$$T_{r_j} \cong (T_1 + T_2)/2 \quad (28)$$

The residence time distribution can be calculated on a range of residence time from the dispersed plug flow model /36/ assuming normally distributed residence time:

$$E(T) = \frac{1}{2\sqrt{\pi/Pe}} \exp\left[-\frac{(1-T)^2}{4/Pe}\right] \quad (29)$$

The Peclet number,  $Pe$ , describes the extent of flow dispersion as:

$$Pe = \frac{qH}{D} \quad (30)$$

where  $q$  is the superficial velocity of fluid,  $H$  is the bed height and  $D$  is the dispersion coefficient.

## **3 Materials and methods**

### **3.1 Pulp properties**

Oxygen delignified hardwood (birch) kraft pulp was chosen for the experiments. The hardwood kraft pulp fibers have relatively high charge (i.e. high ion exchange capacity) and high hexenuronic acid content which made it easy to modify the charge in the experiments of Paper I.

The experiments described in Papers I–IV were carried out using batch displacement cooked hardwood kraft pulp. The pulp used in the experiments of Papers I and II was the same, the analyses of fiber properties were repeated when the experiments of Paper II were carried out. The pulp used in the experiments of Paper III was obtained from the same mill, production line and similar cook. As shown in Table 2 ranges of variation of some fiber properties were determined by replicate experiments from the pulp used in the experiments of Paper III.

Between the experimental periods, the batch pulp samples were stored in a freezer. During the experiments, the pulps were stored in a refrigerator. It is well known that freezing changes the fiber properties by causing irreversible changes in the fiber structure. However, when considering the aim of the study, the changes in the fiber properties were not significant whenever there was no direct comparison between the experimental results. The charge of fibers and the metal contents of fibers were always determined anew when the pulp had been stored for a longer period. In particular, the metal analysis of fiber by AAS is subject to quite significant experimental errors, up to 20% for sodium. This depends on the homogeneity of pulps as well as on the weighing and determination of dry matter content during the metal analyses.

Table 2. Pulp properties.

	Paper I	Paper II	Papers III and IV
<b>KAPPA NUMBER</b> ml g <sup>-1</sup>	11	11	10.3–12.1
<b>VISCOSITY</b> ml g <sup>-1</sup>	980	930	890–1040
<b>FIBER SATURATION POINT</b> dm <sup>3</sup> kg <sup>-1</sup>	1.35	1.45	1.45
<b>CHARGE</b> mmol kg <sup>-1</sup>			
pK 3.1–3.6	120	128	120 (113–125)
pK 5–6	12	22	21 (18–24)
pK 8–10	9	n.d.	20 (10–30)
<b>AMOUNTS OF METALS</b> mmol kg <sup>-1</sup>			
Na + K	141	164	133 (130–170)
Mg	6.7	7.4	5.4 (5.2–5.8)
Ca	27	30	30 (26–32)
Mn	1.5	1.2	0.7 (0.7–0.9)

The metal amounts in the analysis results are quite similar with other studies e.g. those reported by Vuorinen et al; Na 123 mmol kg<sup>-1</sup>, Mg 8.1 mmol kg<sup>-1</sup>, Ca 42 mmol kg<sup>-1</sup>, Mn 1.7 mmol kg<sup>-1</sup> for oxygen delignified birch kraft pulp /37, 38/.

### 3.2 Fiber titrations and equilibrium experiments

The equilibrium experiments were carried out as titrations and batch equilibrium experiments as described in Papers I and II. Fiber charge was usually measured by potentiometric titration with commercial apparatus (Metrohm GPD 751) but also by methylene blue adsorption /39/ as well as more specific uronic acid analyses of fibers, as discussed in Paper I. All the chemicals used in the titrations and other experiments were analytical grade, except the BCA6 chelant (Paper IV) which was obtained as technical grade containing impurities from the

synthesis (monocarboxylic acids). Calculated chemical concentrations were used in the experiments and modelling.

As shown in Table 2, the determination of charge of pulp fibers is also subject to significant experimental variation. The variation depends partly on the volumetric titration method and a determination of pH by combined pH electrode. Others /3, 11, 12/ have used precision titration equipment that applies coulometric acid/base addition and the so-called “Wilhelm” bridge to connect the glass electrode and the reference electrode. Such a titration method was also available in this study, but the simpler volumetric equipment was adopted due to the more rapid titration (1 day per sample instead of 3–5 days per sample of fibers). The volumetric method was also found to be suitable for titrations with simultaneous measurement of concentrations of different ions as described in Paper I.

Another reason for experimental variation of charge is unknown chemical changes occurring in fibers. It was later found that an irreversible decrease of charge occurs during storage of pulp fibers in  $H^+$  form. In hardwood kraft fibers in Table 2 the decrease is about 10–15 mmol  $kg^{-1}$  after a storage of 1–2 days. A possible explanation for this phenomenon would be the formation of lactones /40/, although the irreversibility of charge decrease indicates the occurrence of other unknown chemical changes in fibers.

### 3.3 Determination of ion exchange kinetics

Separate experiments not reported in Papers I–IV for the determination of ion exchange kinetics of pulp suspensions were also carried out. The experimental procedure given in the following describes one such experiment.

Ion exchange kinetics was studied in a suspension of thermomechanical pulp in 1% consistency. The charge of pulp, as determined by potentiometric titration, was 162 mmol  $kg^{-1}$  with  $-\log K = 3.8$  and 68 mmol  $kg^{-1}$  with  $-\log K = 8.9$ . The metals initially present in the pulp were removed by chelation with EDTA at 1% consistency and  $pH = 6-8$ , after which the pulp was washed with 0.01 M HCl and a large amount of distilled water. The pulp in  $H^+$  form was then suspended in saturated  $Ca(OH)_2$  solution at  $pH > 9$  and 1% consistency in order to convert

the pulp to  $\text{Ca}^{++}$  form. The excess solution was removed from the pulp by centrifuging and the fibers were then suspended in a  $0.7 \text{ mmol dm}^{-3}$  solution of  $\text{CaCO}_3$  at 1% consistency in order to precipitate solid calcium carbonate into the fibers. The total amount of calcium was  $117 \text{ mmol kg}^{-1}$  o.d. fibers after the saturation treatment.

After the conversion of the pulp to  $\text{Ca}^{++}/\text{CaCO}_3$  form, the pulp was diluted to 1% consistency in distilled water. The pulp was acidified with  $\text{H}_2\text{SO}_4$  to  $\text{pH} = 4.75$ , after which samples of the suspension were taken with a syringe over a 5 hours. The suspension samples were filtered using a quantitative filter, on the assumption that most of the solid calcium carbonate remains in the pulp. Filtrate samples were acidified to  $\text{pH} = 1$  by the addition of 60 %  $\text{HNO}_3$ , after which the  $\text{Ca}^{++}$  concentration in filtrate was determined by AAS. The pH of the suspension was monitored during the experiment.

## 4 Results and discussion

### 4.1 The influence of ionic composition on the Donnan distribution

The equations formulated and tested in Papers I and II account for the anionic composition of pulp suspension and complexation equilibria in the aqueous phases. The Donnan distribution coefficient,  $\lambda$ , depends on the total amounts of all ionic species in the pulp suspension. The pH of the suspension is varied by the addition of different acids or bases, for example with  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ . The value of the Donnan distribution coefficient depends mainly on the pH-fiber charge relationship but the ionic strength and the amounts and valencies of freely mobile cations are also of importance.

Thus, the addition of chemicals and specific complexation reactions cause sharp changes in the behavior of  $\lambda$  as a function of pH. This effect is very clearly demonstrated in the calculation result presented in Fig. 4 that represents the calculated value of  $\lambda$  as a function of pH in fiber suspension in the presence of EDTA and DTPA.

The calculation results suggest that the total charge of the fibers and the ionic strength of the system determine the maximum value of  $\lambda$ . The concentrations of free cations vary due to the specific complexation with chelants in the pH range 4–7 due to the different complexation abilities of EDTA and DTPA. This has a clear effect on the calculated Donnan distribution coefficient. The fiber charge reaches its maximum at  $\text{pH} = 10$ , i.e. the fiber charge does not increase with an increasing amount of  $\text{NaOH}$ . Thus the value of the Donnan distribution coefficient decreases due to the increase of electrolyte in the fiber phase above pH 10.

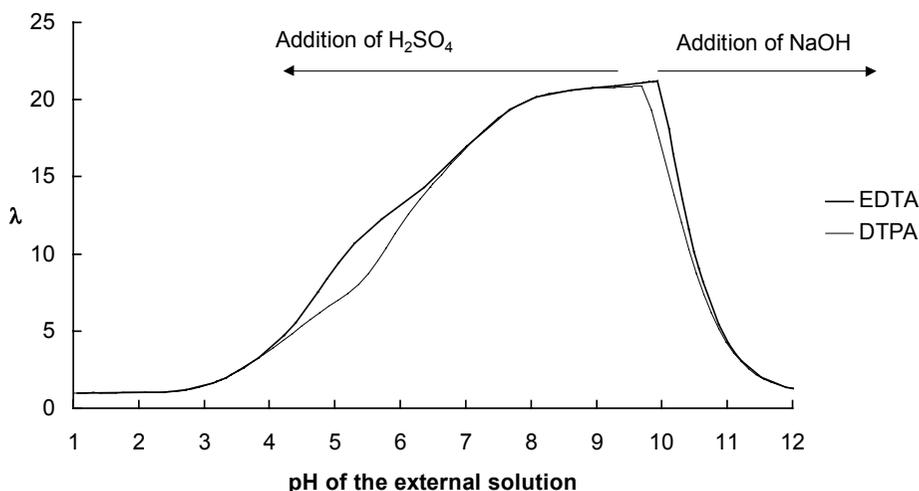


Figure 4. The calculated Donnan distribution coefficient as a value of pH in fiber suspension with EDTA and DTPA. The fiber properties and the metal amounts used in the calculation have been given in Table 2 for Paper II. The consistency of fiber suspension was 4.8% and the calculated doses of chelants were  $0.0153 \text{ mol kg}^{-1}$  o.d. fibers in both experiments. See Paper II for further details of experiments.

## 4.2 The equilibrium concentrations of metal species in fiber suspensions

The concentrations of different cations and complexes in fiber suspensions were modelled and experimentally studied in Paper II. Fig. 5 shows the comparison of experimental concentration measurements with theoretical external concentration diagrams of different metal species in pulp suspension with DTPA.

As shown by the model calculations in Fig. 5, the concentrations of all ions in the suspension decrease when pH increases to the region where fiber-bound anionic groups start to dissociate. The concentration of divalent ions in the external solution decreases due to the distribution of ions into the fiber phase in the pH range pH 2–4 for  $\text{Mn}^{++}$ , pH 2–5 for  $\text{Ca}^{++}$  and pH 1–11 for  $\text{Mg}^{++}$ . According to the Donnan model, the ions with the same valency enrich in the

fiber phase in the same molar proportions and are much more strongly enriched than the monovalent ions.

As described in Paper II, the amount of chelant was limited for the chelation of all divalent metal ions. The complex stabilities of divalent metals decrease in order of  $\text{Mn:DTPA} > \text{Ca:DTPA} > \text{Mg:DTPA}$ . The amount of chelant was sufficient for the complexation of most of the manganese and about 50 % of the calcium, while the complexation of magnesium (and sodium) was almost insignificant.

As can be seen in Fig. 5, the complexation occurs clearly at pH 3.5 for manganese and at pH 5 for calcium. According to the model calculation, most of the manganese occurs as complexes in the volume of external solution and thus the external concentration of manganese complex species should be higher than the total concentration of manganese in suspension; the model predicts that the multi-anionic ligands and metal complexes are largely excluded in the external phase. However, this effect could not be clearly detected by concentration measurements (Paper II) in the scale predicted by model. The model, however, could predict the concentration levels of calcium species and the concentrations of magnesium and sodium ions quite correctly.

In the experimental validation of the model (Paper II) it was also seen that it correctly predicts the pH ranges where the metal complex concentrations in the external phase start to increase due to complexation, i.e. the inflection points in the concentration curves of manganese and calcium.

As also shown in Fig. 5 the theoretical concentrations of all metals in the external solution start to increase above pH 10. This is directly related to result shown in Fig. 4, i.e. a decrease of the Donnan distribution coefficient due to the increase in ionic strength. However, the experiments (Paper II) were carried out in a pH range where this effect could not be observed. The experimental results concerning the distribution of Na, Ca, Mg and Mn in pulp suspensions with DTPA and EDTA are represented and discussed in more detail in Paper II.

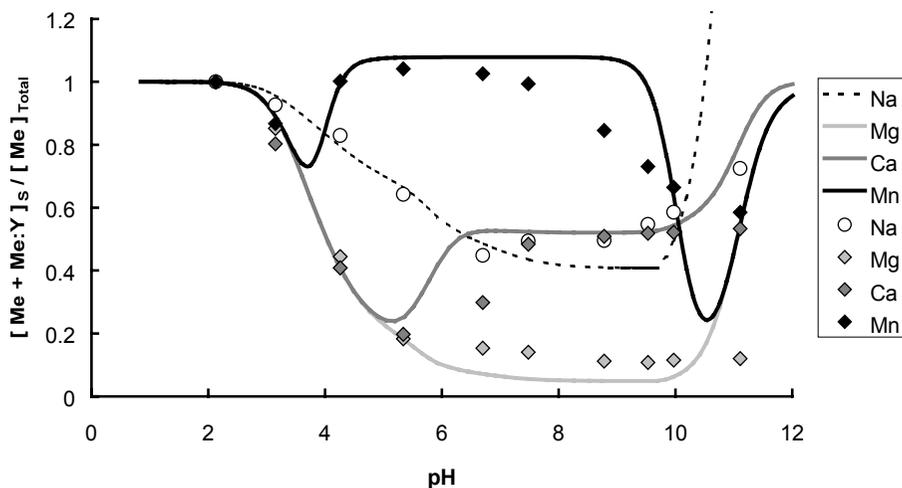


Figure 5. The experimentally determined and calculated fractions of metals in the external solution of total amount of metals present in the fiber suspension in 4.8% consistency and with calculated amount of DTPA = 0.0153 mol kg<sup>-1</sup> o.d. fibers. See Table 2 and Paper II for the pulp properties, metal amounts and further details of the experiment.

### 4.3 The kinetics of ion exchange

The kinetics of ion exchange of chemical systems is usually studied in batch reactor experiments e.g. by measuring concentration change in the external solution as a function of time. The model was validated by comparison with results of experimental studies as described above and with results of other studies /41, 42, 43/.

Fig. 6 shows experimental and modelling results of kinetic ion exchange experiment of TMP fiber suspension containing calcium carbonate. The dotted model curve represents modelling result without any rate-limiting secondary kinetics. The solid model curve represents kinetic behavior of two fractions of calcium of which the other starts to liberate from fibers at  $T = 0.45$ .

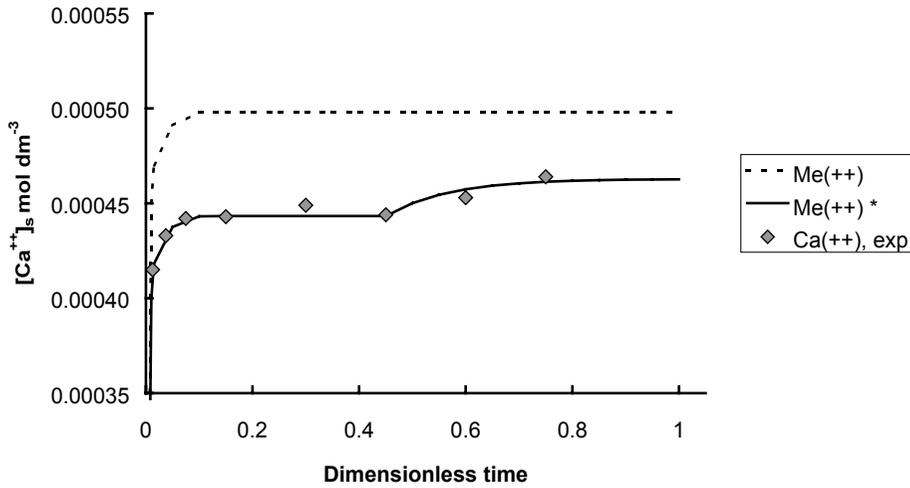


Figure 6. Ion exchange kinetics in 1% thermomechanical pulp – water suspension in presence of calcium ions and calcium carbonate. The dimensionless time  $T = 1$  is equal to 400 minutes. Kinetic rate constants normalized to dimensionless time scale are  $K_\lambda = 0.97$  and  $K_j = 0.1$ , which indicate that the ion exchange between phases occur almost instantaneously and that the rate of secondary kinetics is lower by order of magnitude. The dotted line represents a modeling result without assumption of secondary kinetics.

In the kinetic model, empirical relationships to system conditions (time, pH, ionic concentrations) can be defined. In the modelling example shown in Fig. 6 the time was chosen simply on the basis of the best curve fit. The fit of the curve to the experimental results was determined visually.

#### 4.4 Ionic interactions in pulp bed subject to displacement flow

As shown by the modelling example in Fig. 6, kinetic phenomena in fiber suspension can occur on a time scale between minutes and hours. As demonstrated in other studies /41, 42, 43/ the ion exchange of free metal cations between fibers and the external phase can occur in a time scale of seconds, but considerably slower ion exchange rates must also be taken into account for

fractions of metals. However, even the rapid kinetics must be accounted for when considering the flow of a solution in an immobile pulp bed.

In the studies presented in papers III and IV the timescale of displacement experiments, i.e. displacement of about 5 bed volumes of chemical solution through the bed, was about 3 minutes. From comparison of this time scale to other studies, e.g. to the results shown in Fig. 6, it can be concluded that the overall ion exchange kinetics is fast, i.e. the transfer of freely mobile ions between the phases, should achieve equilibrium during the time used in the experiments in this study. Hence, the internal kinetic factors determine the overall mass balance of metals removed from the bed.

The experiments described in Paper III were carried out using strong acid ( $1.5 \text{ mmol dm}^{-3} \text{ HNO}_3$ ) and  $1 \text{ mmol dm}^{-3}$  solutions of BCA6 and EDTA chelants. The predominant factor determining the overall mass balance of removed metals as well as the removal kinetics was the pH of the solution.

In the displacement with nitric acid solution without chelant, the mechanism of removal of metals from the bed can be described as follows: When acid is added to an initially alkaline bed the acid will be first neutralized by  $\text{OH}^-$  ions in free solution. Excess electrolyte, i.e. metal cations with free anions, transfers in the fiber phase. Due to the increased electrolyte concentration in fiber the phase the concentration differences of all ions between the phases reduce. When the displacement solution moves through the bed there will ideally be a neutralized 'front' of displacement solution that has increasing ionic strength with increasing distance from the top of the bed. This displacement front with increasing ionic strength also promotes the transport of free anions to the fiber phase and the charge neutralization of fiber-bound anionic groups.

The polyanionic ligands and free complexes have a higher negative valency than simple anions and thus they are excluded to a significantly larger extent from the fiber phase. The experiments with chelants described in Paper III were carried out at pH that only partially neutralized the charge of fibers. As demonstrated experimentally and by model calculations in Papers III and IV the removal of metals decreases with the higher pH of the chelant solution, which stresses the significance of reactions in the anionic fiber phase as a factor that limits the kinetics of ion exchange between the fiber and the external phases.

In the results represented in Papers III and IV, the overall removal of metals from the bed with BCA6 and EDTA chelants was significantly lower than removal with nitric acid. The low equilibrium concentrations of ligands with high ionic charge in the fiber should also have a negative effect on metal removal selectivity. Indeed, it was observed in the experiments that the removal of metal with relatively high complex stability, i.e. Mn, was reduced so that similar removals of metals with lower complex stability, i.e. Ca and Mg, was achieved. When compared to batch ion exchange experiments (Paper II and Fig. 5), the chelants are able to remove metals from fibers quantitatively and selectively when the pH is in the correct range and the reaction time is sufficient.

From the comparison of the experimental and modelling results of batch equilibrium experiments and displacement chelation, it can be concluded that the chelation takes place mostly in the external phase. Thus the internal kinetic factors in the fiber phase can limit the rate and selectivity of removal of metals.

The transfer of metal cations from the fiber phase can be seen to be caused by charge neutralization of anionic groups bound in fibers. There is a ‘competition’ between the negative charge of fibers that keeps the metal cation in fibers, and ligands in external solution that bind the cations in anionic complexes that are excluded from the fiber phase. Thus the ion exchange kinetics is of high importance when considering the flow of chemical solutions in the pulp bed or suspensions. In comparison to other displacement studies /44, 45, 46/ it can also be deduced that the chelant concentration as it determines the pH is a critical factor determining the metal removal efficiency in displacement chelation.

## 4.5 Mobile phase model

The kinetic mass balance equations can easily be extended to account for input and output of solute components in the external phase. The principle shown in Fig. 3 and the derived equation, i.e. the Eq. (25) can be used to model a single CSTR reactor as well as the flow of water approaching the plug flow in the fiber bed by combining many CSTR model units in series.

Because a single model ‘unit’, i.e.  $l = L = 1$  represents a CSTR and many units combined in series a plug flow reactor, it is possible to model different

displacement or washing efficiencies by varying the number of model units. However, as it can be quite difficult to describe the displacement efficiencies of such a unit combination, this approach is not robust. In fact, this kind of modelling attempt of washing has been carried out /47/.

The earlier washer model development /47/ consisted of many CSTR units in a two-dimensional arrangement. The ion exchange kinetics was not taken into account, i.e. it was assumed that the pulp suspension is always in equilibrium. In order to model varying washing and displacement efficiencies, the number of model units in series or in parallel had to be changed, which required extensive programming. Due to the neglect of kinetics in the model the control of overall mass balances of ionic species was only approximate /47/. However, the modelling attempt described in ref. /47/ was a preliminary proof for the applicability of the Donnan model and its extensions to modelling of washing and other fiberline processes.

A more general way to account for the varying displacement efficiency is to define a flow model that approaches an ideal plug model, which can be modelled by reasonably large number of CSTR's in series /36, 48/, the displacement efficiency can then be easily varied by using the plug flow model as an element of a Parallel Plug Flow (PPF) model. In practice, the number of CSTR model units in the plug flow model is limited to 10–50 due to the long calculation time required by multicomponent equilibrium problems; in the modelling of a series of CSTR's the calculation time increases proportionally to a number of model units squared. However, a plug flow model consisting of 10 CSTR units approaches a true plug flow sufficiently well.

Modelling examples describing the behavior of a combination of a plug flow model and parallel plug flow model are shown in Figs 7 and 8. The examples shown in Fig. 7 describe the removal of non-ionic substance ( $z_i = 0$ ) from the pulp bed by displacement at different displacement efficiencies. The examples in Fig. 7 were calculated by assuming that there are no specific or non-specific interactions between substance and pulp fibers and that the ion exchange is instantaneous at any time during the displacement.

In the modelling of breakthrough curves shown in Fig. 7 mobile phase model equation, i.e. Eq. (25) with a number of CSTR units in series,  $L = 10$ , were used.

The curve denoted as “ideal plug flow” denotes output of the mobile phase model only. The output of the mobile phase model was then used as input for the PPF model (Eqs 26–30) with a number of channels,  $J = 1000$  and by varying the Peclet number in range 5–100. Actually, the PPF model reproduces a breakthrough curve that is exactly similar to the breakthrough curve from the mobile phase model (i.e. input of PPF model) when the Peclet number is very high,  $>1000$ .

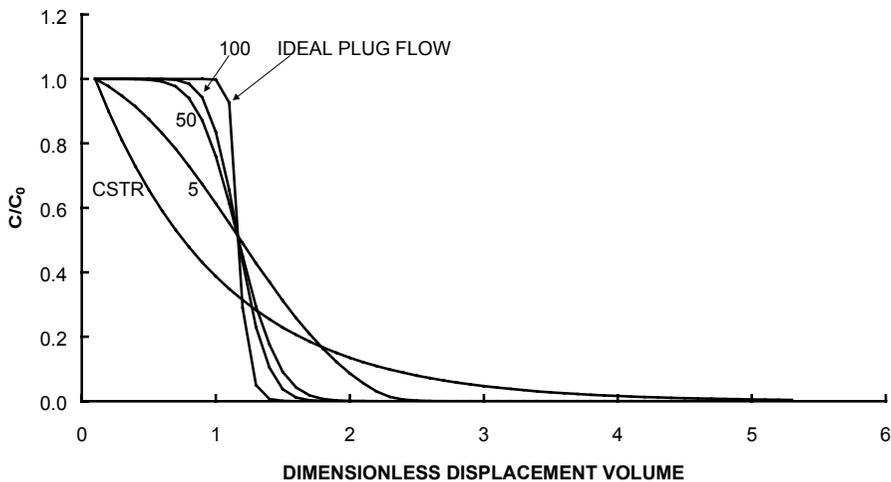


Figure 7. Theoretical removal of non-ionic substance (e.g. methanol or glucose) from a pulp bed (6% consistency) shown as a function of dimensionless displacement volume and displacement efficiency. The numbers shown denote Peclet numbers used in the modeling. The curve denoted as “Ideal Plug Flow” is the output of a mobile phase model consisting of 10 CSTR units in series.

Thus, according to the modelling results, most of the non-ionic substance is removed from the bed during the displacement of one bed volume of solution. However, mixing of substance occurs between the fiber and the external phase, and thus all of the substance is not removed immediately after displacement of one bed volume at  $V_D = 1$ . Also, the ideal plug flow BTC is slightly distorted due to mixing between the fiber and the external phases. With Peclet numbers decreasing from 100 to 5 the BTC begins smoothly decreasing and approaches the outlet concentration curve of CSTR. Thus, the PPF model can be used to adjust the displacement efficiency over a wide range just by varying the Peclet number.

Modelling of removal of calcium by BCA6 and EDTA chelants and by nitric acid from pulp beds is shown in Fig. 8. Two BTC's for displacement with BCA6 are shown in Fig. 8; the thin solid curve denoted as "IDEAL PLUG FLOW" represents the output from an almost ideal plug flow model, i.e. the exit concentration from a series of ten CSTR model units. The line denoted as "PPF MODEL" represents the modelling result when the output of an ideal plug flow model has been used as an input of a PPF model at  $Pe = 50$ . The other BTC curves represent the modelling results of displacement experiments with nitric acid (the highest concentrations) and EDTA (the lowest concentrations).

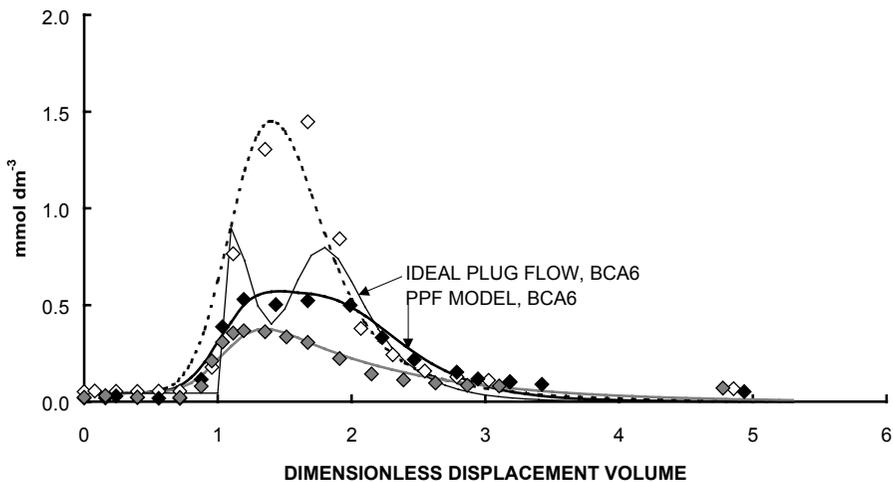


Figure 8. Theoretical and experimental breakthrough of calcium species from pulp beds (6% consistency) displaced with  $1 \text{ mmol dm}^{-3}$  solutions of EDTA (grey symbols and curve) and BCA6 (black symbols and curve) chelants as well as by  $1.5 \text{ mmol dm}^{-3}$  nitric acid (open symbols, dotted curve). The thin solid line represents the output of the mobile phase model without the PPF model (modeling of BCA6 experiment). The fiber properties and the metal amounts are those given in Table 2, Papers III–IV. Model calculations were carried out by assuming 10 CSTR units in series, 1000 channels and  $Pe = 50$  in the PPF model. For further details of the experiment and model calculation, see Papers III–IV.

As can be seen from the dotted BTC in Fig. 8, the concentration of manganese steeply increases immediately after displacement of one bed volume of chelant solution. In the PPF model, the same ideal BTC curve is normalized to different

residence times of pulp bed ‘channels’, weighed i.e. multiplied by flow fractions of each channel and integrated over a range of average residence times of the bed. The result from the PPF model is the solid model curve shown in Fig. 8. The effect of kinetics on calcium removal can be seen from the secondary maximum in the dotted BTC and as a tailing behavior of both BTC’s. The secondary concentration maximum occurs in modelling when the pH of the bed becomes acidic and the internal kinetics become significant. As can be seen by comparison of the PPF model curve with the experimental results in Fig. 8 and in the other results represented in Papers III and IV the combination of the mobile phase model with the PPF model describes quite well the removal of metals from the pulp bed.

It is not necessary to use normal distribution (Eq. 29) in the calculation of residence time distribution of the bed, although it seems to describe the RTD of real pulp beds quite well (Paper IV). As described by Ali et al. /49/ and by Ni et al. /50/ the residence time distributions of pulp beds can be measured by tracer experiments e.g. using non-ionic tracers. As demonstrated by experiments and modelling results in Paper IV and by others /44, 45, 46, 49, 50/ the same Peclet numbers can be used in the modelling of BTC’s of neutral substances and metal cations. Thus the flow topology does not have significant effect on local ionic equilibria in the bed at least when the displacement flow is good, which is usually the case in laboratory conditions ( $Pe = 30-60$ ).

## **4.6 The effect of system properties in modelling**

The basic input to all modelling examples are the fiber charge properties, the FSP or WRV of fibers, the total amounts of metals, anions and chemicals as well as the suspension and liquid volumes and mass of pulp. The determination of all of these parameters requires quite a lot of analytical work. It can also be argued that a model with many inputs is subject to inaccuracy and experimental precision when determining the model inputs. Fortunately the basic Donnan equilibrium model, as well as its extensions described in this work, is quite robust and not too sensitive to the small variations in conditions.

The total anionic charge of fibers and the composition of acid structures in fibers are quite critical parameters. The volume of water in the fibers can be assumed

to be constant although it varies with pH and can become quite a critical parameter in higher ionic strengths (as discussed in Paper I). As shown by the conceptual calculation example shown in Fig. 9 the fiber charge as a function of the external solution pH has a very significant effect when compared to the variation in swelling.

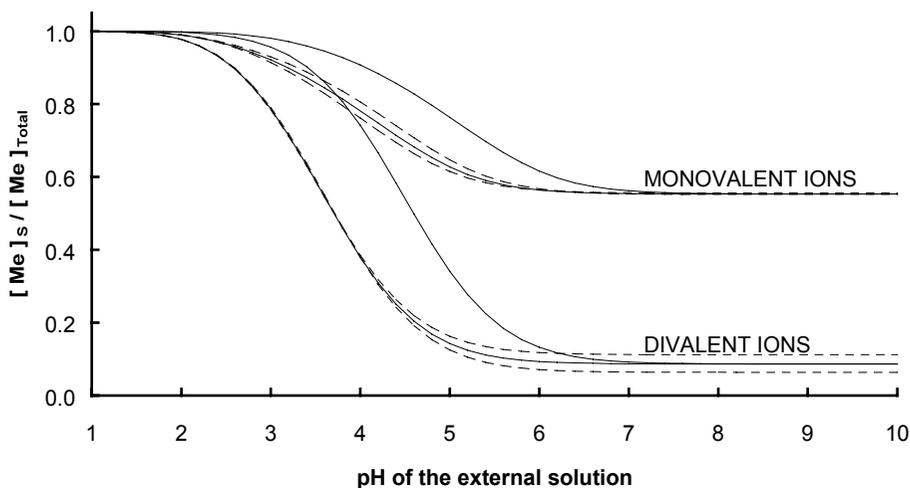


Figure 9. The theoretical concentrations of monovalent and divalent ions in external solution of 5% pulp suspension as a function of varying dissociation constant ( $-\log K$ ) of single fiber-bound group in range 3–4 (solid lines) and FSP of fibers in range 1–2  $\text{dm}^3 \text{kg}^{-1}$  (dotted lines). Solid lines were calculated using  $\text{FSP} = 1.5 \text{ dm}^3 \text{ kg}^{-1}$ . The metal amounts used in the calculation were those given in Table 2, Paper II. No chelant was assumed to be present in suspension. The concentration curves shift on the right with an increasing dissociation constant and reach a lower concentration level with increasing FSP, which can only be seen in curves of the divalent ion in this modeling example.

Thus, estimates of the fiber properties could be used in modelling when only qualitative information of the system is required. Collection of data of fiber properties from different processes and pulp grades would facilitate the rapid estimation of input parameters of models and qualitative analysis of the system. Quantitative characterization requires precise determination of fiber properties.

The ionic composition of pulp suspensions, i.e. the total amounts of metal cations and different anions, is a critical input in the Donnan model. It is an essential requirement that the total amounts of the cations dominating the cationic composition (e.g Na, K, Ca, Mg, Mn) are known. It is also essential to know the mass balances of chemicals used e.g. in the pH adjustment *or* what chemicals are used and how much. As described in Paper II, the ionic conditions in pulp suspension can be predicted quite well by calculating the theoretical metal concentration and pH curves when the additions of acids, bases or chelants are known.

The knowledge on precise anionic composition of pulp suspension becomes of very high importance when attempting to model the kinetics of ion exchange. In the present model, the kinetic part of the model is partially formulated on a phenomenological basis. However, it would be possible to define more accurate semi-empirical relationships between kinetics and system properties. The anionic composition of pulp suspensions is also very critical in the modelling of ionic conditions of real fiberline processes. As a part of this work experimental methods for the characterization of anionic composition of pulp suspensions and process filtrates were developed /47, 51/ and the models could be quite successfully calibrated to describe the pH profile and the metal balances in D-E<sub>OP</sub> bleaching.

## 5 Conclusions

This study describes development and validation of several extensions to a pulp suspension equilibrium model based on the Donnan equilibrium theory. The extensions account for the overall ionic composition of pulp suspensions, the complexation equilibria, ion exchange kinetics and flow of external phase with respect to immobile fibers. The flow model was extended to a batch displacement model.

The incorporation of the different anionic species in the Donnan model can be considered as a generalization of earlier models based on Donnan theory. However, the general formalism of the Donnan model presented in this study requires a new way of utilizing the electroneutrality conditions of the Donnan model and more precise knowledge of the overall ionic composition of pulp suspensions as input parameters. An important finding of this study is that the ion exchange kinetics of pulp suspensions plays a major role in determining the selectivity and efficiency of the chelation of pulp suspensions. The main factor determining the ion exchange kinetics is the pH through the reactions taking place within the fiber phase when the external pH is changed.

Kinetic ion exchange models developed in this work, in particular the ‘internal’ kinetic model, require further refinement. Better relations of ionic conditions of suspension to actual forms of metals in fibers and to structural characteristics of fibers need to be defined. The connection of a simple kinetic model to Donnan equilibria, however, has proven to be a quite easily manageable approach in the modelling of kinetics of complex ionic composition of pulp suspensions.

Donnan equilibrium and kinetic models were used in the modelling of displacement flow in pulp beds. The combination of multiple CSTR’s and the Parallel Plug Flow model facilitates the calculation of non-homogenous local ionic equilibria in pulp beds subject to displacement flow and to adjust the flow conditions in a displacement system between ideal plug flow and fully dispersed flow, i.e. the system approaching CSTR. Thus the model or its principle could be applied in the modelling of different fiberline processes e.g. drum and belt washers and upflow or downflow reactors.

The ionic distribution model for fiber suspension and its extensions, as generally represented by Eqs (1)–(30), facilitates quantitative modelling of equilibrium and kinetic chemical phenomena occurring in pulp suspension in systems subject to varying amounts of ions and flow of water with respect to immobile fibers in the bed. As shown in Papers I and II the Donnan equilibrium model is otherwise similar to earlier Donnan equilibrium models but it is more generally applicable for the modelling of varying ionic compositions and direct calculation of the pH of pulp suspensions. As demonstrated in Papers III and IV, realistic modelling results have been obtained by using model inputs that are measurable properties of pulp and bed and just a few adjustable parameters that describe the kinetics. The model calculations and the analysis of experimental data obtained in Papers I–IV suggest the following:

- The nature of negatively charged fiber wall is of great importance in determining the ion exchange mechanisms and kinetics of pulp suspension. Due to the negative charge of the fiber phase, anionic species like chelants are mostly excluded into the external phase. The concentration excess of anionic species in the external phase increases progressively with the negative valency of anionic species. The concentration of multivalent anionic species can be several magnitudes lower in the fiber phase than in the external solution. The complexation reactions can thus be assumed to take place mostly in the external phase. This assumption can be used to simplify the combination of complexation equations with the Donnan model (Paper II). This property of the fiber wall is an important restriction when the rate of ion exchange or metal removal must be accounted for. The Donnan model itself describes non-specific interactions of ions with fibers, but also the ion exchange kinetics seems to have non-specific characteristics (Papers III and IV).
- The pH of the suspension is the most important factor determining the ion exchange rate between the fiber and the external phases. Thus, it can be understood that the kinetics of ion transfer from the fiber phase to the external phase (or vice versa) is largely governed by the rate of change of fiber charge.
- The ion exchange kinetics can be described by dividing it into two main processes. The internal process includes sub-mechanisms that can be

dissolution of solid metal compounds and the effect of fiber structure on ion diffusion rates. The overall ion exchange of the suspension is governed by the difference between the initial concentrations and the final equilibrium state that the system is approaching.

- The metal ions occurring in the pulp fibers in highest amounts e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ , and  $\text{Mn}^{++}$  interact non-specifically with the fibers. The interactions of  $\text{Mn}^{++}$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  with chelants, however, are specific. The competition between these non-specific and specific interactions is won by fibers whenever the mass transfer kinetics of metals from the fibers is limited in the time scale of reaction. The result will be reduced chelation efficiency and selectivity. It also seems that the chelation process can be optimized and new techniques further developed by optimizing the process conditions in terms of pH, chemical concentrations and reaction time.

## 6 Ideas for future research

The equilibrium models used in this work are based on ideal Donnan theory. The models describe laboratory experiments quantitatively but they may be unsuitable for the modelling of industrial pulp suspensions. This problem can be overcome by applying nonideal solution models in the Donnan theory. Work is currently being done in the area of theoretical modelling /52/.

Concerning the chemical composition of industrial pulp suspensions, another practical aspect is the problematic characterization of acid-base properties and precipitation-dissolution equilibria of dissolved organic and colloidal matter. Work is being done in the development of practical methods for the characterization of properties of dissolved organic compounds. Potentiometric titration of filtrates seems to be a promising approach, although some technical difficulties have to be faced.

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Author(s) Räsänen, Erkki			
Title <b>Modelling ion exchange and flow in pulp suspensions</b>			
Abstract This thesis summarizes the results of four papers dealing with modelling of ion exchange between cellulosic fibers and their surrounding aqueous solution. Transition metals, in particular manganese, iron and copper, induce fiber-deteriorating radical reactions in oxygen-chemical-based bleaching, while magnesium inhibits such reactions. Thus the removal of the harmful transition metals from a pulp is required while the beneficial magnesium should be retained in a pulp. Selective control of metal contents of pulps is a key factor in the control of bleaching chemistry. Thus, ability to predict the extent of ion exchange and amounts of metals are of great practical interest. An ion exchange model to describe interaction of ionic species with kraft pulps has been developed in the present work. The model can be applied in pulp washing and chelation. The present model takes into account overall ionic composition of pulp suspensions, i.e. the cations and simple anions as well as the ligands and the complexes. The model facilitates calculation of pH, complexation and distribution of ionic species between the aqueous phase confined to fibers and the external solution. The present model also accounts for the ion exchange kinetics and flow of water through the immobile fiber network, i.e. the "pulp bed". The present model is based on the formerly developed ion exchange model, which is based on so-called Donnan equilibrium theory. The development of the new model required the inclusion of the different anionic species to model and the combination of the Donnan model with a complexation model. The ion exchange kinetics is described as a two-step phenomenon. The first rate-limiting step can be due to the dissolution of solid metal compounds in the fiber phase as well as the diffusion of ions in the fiber wall, while the second step is the transfer of the ionic species between the fiber phase and the external solution, which is governed by the concentration gradient between the phases. In the model, the transfer of ions between the phases is directly related to the Donnan theory. In the testing of the elements of the ion exchange model, it was found that the combination of the Donnan model with a complexation model quantitatively predicts the pH, the ionic distribution as well as the complexation equilibria in batch-type systems when the time to achieve full equilibrium is not limited. In the pulp beds subject to flow the ion exchange kinetics reduces the metal removal efficiency and selectivity. This can be considered to be due to the repulsion of anionic species (simple anions, ligands and complexes) from the negatively charged fiber phase. It can also be considered that the rate of change of fiber charge determines the overall ion exchange kinetics. It was found in the experiments that a low pH of displacement solution favors rapid metal removal from pulp beds. However, a low pH reduces the metal removal selectivity, i.e. harmful manganese and the beneficial magnesium is also removed from the pulp. The metal removal process in laboratory or in industrial scale could be optimized in terms of chemical concentrations, pH, reaction time and wash flow conditions. The present model facilitates realistic modelling of these conditions.			
Keywords ion exchange, paper and pulp, pulp suspensions, cellulosic fibers, aqueous solutions, models, modelling, transition metals, bleaching, chelants, metal complexes, theses, dissertations			
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