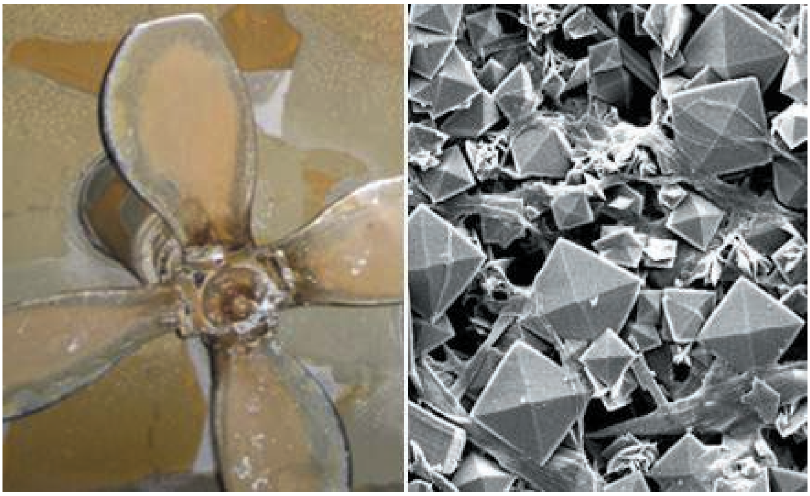
Åbo Akademi
University

Oxalic acid and calcium oxalate in production of wood-containing paper

Formation, analysis, and control

Matti Häärä



Laboratory of Wood and Paper Chemistry
Department of Chemical Engineering
Åbo Akademi University
Åbo 2014

Matti Häärä

Born 1967, Turku, Finland

M.Sc. Chemical Engineering, 1994
Åbo Akademi University, Finland

Worked in pulp and paper chemical industry, 1994-2009

Started Ph.D. work at the Laboratory of Wood and Paper Chemistry in 2010

Oxalic acid and calcium oxalate in production of wood-containing paper

Formation, analysis, and control

Matti Häärä

Academic Dissertation

Laboratory of Wood and Paper Chemistry
Process Chemistry Centre
Department of Chemical Engineering
Åbo Akademi University

Åbo, Finland 2014

Supervisors:

Professor Stefan Willför
Laboratory of Wood and Paper Chemistry
Process Chemistry Centre
Åbo Akademi University
Åbo, Finland

Docent Anna Sundberg
Laboratory of Wood and Paper Chemistry
Process Chemistry Centre
Åbo Akademi University
Åbo, Finland

Reviewer and Opponent:

Professor Bruce Sitholé
Forestry and Forest Products Research Centre
University of KwaZulu-Natal/
CSIR Natural Resources and the Environment
Durban, South Africa

Reviewer:

Professor Per Engstrand
Department of Chemical Engineering
Mid Sweden University
Sundsvall, Sweden

ISBN 978-952-12-3076-9
Painosalama Oy – Turku, Finland 2014

To Maija, Akseli, Eevertti, and Aapo

"If you want to go where the rainbows end
you´ll have to say goodbye
All our dreams come true baby up ahead
and it´s out where your memories lie"

Tom Waits & Kathleen Brennan:
Yesterday is here

PREFACE

This thesis is a summary of the following original publications, referred to in the text by their corresponding Roman numerals. Some additional data is also presented.

- I. Häärä, M., Sundberg, A., Willför, S. (2011): Calcium oxalate – a source of "hickey" problems – A literature review on oxalate formation, analysis and scale control, Nord. Pulp Pap. Res. J. 26(3), 263-282.
- II. Häärä, M., Konn, J., Sundberg, A., Willför, S. (2013): Sample pretreatment for oxalate analysis and the effect of peroxide bleaching parameters on oxalate formation, Nord. Pulp Pap. Res. J. 28(1), 42-50.
- III. Häärä, M., Pranovich A., Sundberg, A., Willför, S. (2014): Formation of oxalic acid in alkaline peroxide treatment of different wood components, Holzforschung 68(4), 393-400.
- IV. Häärä, M., Vähäsalo, L., Lundin, T., Fang, W., Sundberg, A., Willför, S. (2014): Calcium oxalate precipitation in the presence of magnesium, wood resin and galactoglucomannans, submitted 24 April, 2013 to J-FOR.
- V. Häärä, M., Konn, J., Vähäsalo, L., Lybeck, J., Sundberg, A., Willför, S. (2014): Flow cytometry as a tool to assess inhibitor performance for calcium oxalate scale control, submitted 7 February, 2014 to Nord. Pulp. Pap. Res. J. and revised 22 May, 2014.

This work was carried out during the years 2010-2014 at the Laboratory of Wood and Paper Chemistry in association with the Process Chemistry Centre (PCC) at Åbo Akademi University in Turku/Åbo, Finland. The work was done under the supervision of Professor Stefan Willför and Docent Anna Sundberg. Financing of the work was provided by Kemira Oyj, Sappi Fine Paper Europe, Process Chemistry Centre and The International Doctoral Programme in Bioproducts Technology (PaPSaT).

Contribution of the author

The author of the thesis was responsible for writing the first drafts, and was the main author of all five papers I-V. In paper II, the author planned the experimental design together with the co-authors and did part of the experimental work in collaboration with Kemira Oyj and Sappi Fine Paper Europe. The author was responsible for the experimental design, and did the experimental work in paper III. In paper IV, the author was responsible for the experimental design, and did the experimental work together with the co-authors. The author planned the experimental design together with the co-authors, and did the experimental work in paper V. The crystal and hydrate form analysis by XRD and SEM, as well as oxalate analysis by IC, were conducted in collaboration with specialists.

SUPPORTING PUBLICATIONS

Häärä, M., Vähäsalo, L., Sundberg. A., Willför, S. (2011): Formation of oxalic acid in alkaline peroxide treatment of different wood substances, In book of abstracts for Renewable Wood and Plant Resources: Chemistry, Technology, Pharmacology, Medicine, June 21-24th, 2011, St. Petersburg, Russia.

Häärä, M., Vähäsalo, L., Lundin, T., Fang, W., Sundberg. A., Willför, S. (2012): Effects of wet-end chemistry parameters on the precipitation of calcium oxalate, In book of abstracts for the 8th International Paper and Coating Chemistry Symposium, June 10-14th, 2012, Stockholm, Sweden.

Örså, F., Holmbom, B., Häärä, M. (1996): Effects of grinder shower water temperature on the release of spruce wood components into water, Pap. Puu/Pap. Tim. 78(10), 605-609.

TABLE OF CONTENTS

SOME IMPORTANT TERMS AND ABBREVIATIONS

Ara	Arabinose
BCTMP	Bleached chemi-thermomechanical pulp
CE	Capillary electrophoresis
Cellob.	Cellobiose
COD	Calcium oxalate dihydrate
COM	Calcium oxalate monohydrate
COT	Calcium oxalate trihydrate
DCS	Dissolved and colloidal substances
EMAL	Enzymatic mild acidolysis lignin
FCM	Flow cytometry
FL3	Fluorescence with 615-645 nm wavelength
FSC	Forward scattering
Gal	Galactose
GalA	Galacturonic acid
GC	Gas chromatography
GGM	Galactoglucomannan
Glc	Glucose
GlcA	Glucuronic acid
GW	Groundwood
HAc	Acetic acid
HMR	Hydroxymatairesinol
HPLC	High-performance liquid chromatography
HWE	Hot-water extraction
IC	Ion chromatography
Man	Mannose
MWL	Milled wood lignin
NTU	Nephelometric turbidity unit
PT	Process temperature
RT	Room temperature
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TMP	Thermomechanical pulp
Unbl.	Unbleached
XRD	X-ray diffraction
Xyl	Xylose

ABSTRACT

Oxalic acid that is present in wood, and formed as an oxidation product in alkaline peroxide bleaching of mechanical pulps, can together with calcium form a sparingly soluble calcium oxalate salt. Calcium oxalate scaling is one of the most difficult deposition problems occurring in pulping and papermaking, causing severe disturbances both in production and with paper quality. As the mills strive for even more closed water systems, the scale forming ions will accumulate in the process waters and the risk for precipitation is increased. Minimizing the calcium and oxalate ion concentrations by various means to decrease scaling tendency can be done to some extent, but usually both mechanical and chemical cleaning, consuming both time and resources, are needed to remove the deposits. Furthermore, chemical anti-scaling agents are often used. In this work, factors affecting both oxalic acid formation and calcium oxalate precipitation have been investigated, with a special focus on means to prevent scale build-up in production of wood-containing paper.

The effect of sample pretreatment and storage methods on oxalate analysis by ion chromatography (IC) were investigated. Laboratory peroxide-bleaching experiments were carried out in order to assess the effects of some bleaching parameters on oxalic acid formation. Also isolated wood components and model substances were submitted to alkaline peroxide treatment to clarify their role in oxalic acid formation during alkaline peroxide bleaching of mechanical pulp from spruce. The effect of some central dissolved and colloidal substances (DCS), relevant in mechanical pulps from Norway spruce, on calcium oxalate precipitation and crystallization was also studied. The applicability of flow cytometric (FCM) analysis in these experiments was evaluated. FCM was also used as a part of the analytical scheme when assessing the performance of some selected anti-scaling agents for calcium oxalate scale control.

IC was proven to be an accurate and convenient method for oxalate analysis of pulp and filtrate samples. For analysis of total oxalate in pulp samples, acidification with hydrochloric acid to pH~1 during heating and mixing ensured complete dissolution of oxalate precipitates.

Using magnesium hydroxide ($Mg(OH)_2$) instead of sodium hydroxide (NaOH) as the alkali source in peroxide bleaching had a positive effect on oxalate formation, as the substitution decreased the amount of total oxalate formed at the same brightness level, and increased oxalate solubility. Increased pulp consistency in bleaching resulted in higher brightness and decreased oxalate formation per ton of dry pulp, although the oxalate concentration calculated based on pulp volume increased.

Of the spruce wood components, lignin was found to be the major source of oxalic acid in alkaline peroxide treatment. However, the total amount of oxalic acid formed from hemicelluloses, pectins, and possibly also lignans, can also be regarded as significant, especially as their amounts among the DCS are substantial. In alkaline peroxide bleaching experiments, an increased concentration of DCS was also found to increase the oxalic acid formation. Large amounts of native oxalates were detected in spruce bark, and additional oxalic acid was formed from bark components in alkaline peroxide bleaching. Hence, effective debarking operations in the pulp mill are essential for calcium oxalate scale control.

Magnesium ions were found to decrease calcium oxalate precipitation. A strong interaction was observed between colloidal wood resin, galactoglucomannans (GGMs), and the precipitating calcium oxalate crystals. Wood resin decreased the calcium oxalate precipitation, but rendered the particles more hydrophobic by co-precipitation. In addition to the known ability of dissolved GGMs to stabilize colloidal wood resin, they also had an inhibiting effect on calcium oxalate crystal growth.

A combination of FCM and on-line turbidity monitoring as analytical tools was successfully used for studying the effects of different substances on calcium oxalate precipitation, and also for screening of different anti-scaling agents, both in a clean model system and with mechanical pulp filtrates. Based on the results, an effective additive was formulated, and this was tested in a mill-scale trial. A monitoring method based on oxalate titration was established for this purpose.

The results from this work show that oxalic acid formation and calcium oxalate precipitation can be influenced by process technical, and wet-end chemistry related means. In central roles are wood debarking, conditions in alkaline peroxide bleaching, management of DCS, and utilization of targeted anti-scaling agent chemistry.

KEYWORDS

Mechanical pulp, Peroxide bleaching, Oxalic acid, Oxalate analysis, Calcium oxalate, Precipitation, Scaling, Anti-scaling agent, Turbidity, Flow cytometry, Monitoring, Wood resin, Dissolved and colloidal substances

SVENSK SAMMANFATTNING

Ett av de svåraste problemen inom massa- och pappersindustrin är bildning av hårda, stenliknande avlagringar av kalciumoxalat. Vedråmaterialet innehåller alltid små mängder oxalat, men i barken kan halten vara flera gånger högre. I blekta mekaniska massor är den största källan för oxalat dock peroxidblekningen, där oxalsyra bildas i oxidationsreaktioner främst från lignin och hemicellulosor. När oxaljoner reagerar med löst kalcium i processvatten, bildas ett svårlösligt kalciumoxalatsalt. Avlagringar som bildas på processytor, kan förorsaka allvarliga störningar både i produktionen och med papperets kvalitet. Utöver mekaniska massaprocesser är utfällning av kalciumoxalat också ett känt problem till exempel vid blekning av sulfatmassa, vid framställning av sulfitmassa, i avdunstningssanläggningar i sockerbruk, samt i bryggerier. Kalciumoxalat är också huvudkomponenten i njurstenar hos människor, vilket är orsaken till den stora mängden forskningsresultat som finns tillgänglig om dess kristallisering.

Utfällning av kalciumoxalat kan förebyggas genom att minska kalcium- och oxalathalterna i processvattnen, men möjligheterna till detta är begränsade. Speciellt utmanande är att massa- och pappersbruken hela tiden försöker minska förbrukningen av färskvatten, varvid substanser anrikas i processvattnen, vilket också ökar risken för saltavlagringar. Kemisk och/eller mekanisk tvätt är ofta det enda alternativet att avlägsna dessa avlagringar. Båda dessa metoder kräver mycket tid och resurser, samt resulterar i minskad produktion. Utöver dessa metoder används ofta additiver avsedda för kontroll av saltavlagringar och dessa additiver doseras vanligen kontinuerligt. I detta arbete har faktorer som påverkar bildning av oxalsyra samt utfällning av kalciumoxalat studerats. Fokus har speciellt varit på olika sätt att förebygga saltavlagringar vid tillverkning av trähaltigt papper.

Effekten av olika förbehandlings- och lagringssätt av fabriksprov innan oxalatanalys med jonkromatografi (IC) undersöktes. Peroxidblekningsförsök gjordes i laboratorieskala för att studera hur några viktiga blekningsparametrar påverkar bildningen av oxalsyra. Isolerade vedkomponenter samt modellsubstanser behandlades också med peroxid vid alkaliska förhållanden, för att klargöra deras bidrag till mängden av oxalsyra som bildas vid alkalisk peroxidblekning av mekaniska massor av gran. Effekten av viktiga lösta och kolloidala (LK) substanser som finns i mekaniska massor av gran på utfällning och kristallisering av kalciumoxalat studerades också. Samtidigt utvärderades användningen av flödescytometri (FCM) för att mäta utfällning och kristallbildning. FCM användes också som en av de analytiska metoderna för evaluering av utvalda additiver som kan användas för att kontrollera/förhindra kalciumoxalatavlagringar.

Alla oxalatanalyser av massa- och filtratprov gjordes med jonkromatografi, som bekräftades vara en noggrann och behändig metod. För att bestämma mängden löst oxalat i processen måste filtrering av provet göras direkt efter provtagningen för att undvika utfällning före analys. Surgörning med saltsyra till pH~1 under omrörning och uppvärmning säkerställde fullständig upplösning av utfälld oxalat, vilket är nödvändigt för att kunna analysera den totala mängden oxalat i massaprov.

När magnesiumhydroxid ($Mg(OH)_2$) användes som alkalikälla vid peroxidblekning i stället för natriumhydroxid var totalmängden bildad oxalsyra mindre vid samma ljushetsökning. Samtidigt ökades oxalatets löslighet. Större ljushetsökning nåddes med blekning vid ökad konsistens, medan mängden oxalsyra som bildades per ton torrtänkt massa minskade. Dock ökade koncentrationen av oxalat beräknad per massavolym.

Av de testade granvedsubstanserna visades lignin vara den största källan för oxalsyra i alkalisk peroxidbehandling. Den totala mängden oxalsyra som bildades sammanlagt från hemicellulosor, pektiner och möjligtvis också från lignaner kan dock anses som betydlig, särskilt när man tänker på deras höga koncentration bland LK-substanserna. Det bekräftades också vid peroxidblekningsförsök att med ökad halt av LK-substanser i massan bildas det mera oxalsyra under blekningen. Obehandlad granbark innehöll höga mängder av oxalater och från barken bildades det ytterligare oxalsyra vid alkalisk peroxidblekning. Effektiv avbarkning i massabruk är därmed viktig, inte bara för ljusheten utan också som en del av kontrollen av kalciumoxalat-avlagringar.

Tillsats av magnesiumjoner visades minska utfällningen av kalciumoxalat. En stark växelverkan observerades mellan kolloidalt vedharts, galaktoglukomannaner (GGM), och de utfällda kalciumoxalatkristallerna. Hartset minskade utfällningen av kalciumoxalat, men de bildade partiklarna blev mer hydrofoba. Utöver den kända förmågan hos GGM att stabilisera kolloidalt vedharts visade de sig ha en inhiberande inverkan på kristalltillväxten hos kalciumoxalat.

En kombination av FCM och on-line turbiditetsmätning användes framgångsrikt för att studera effekten av olika substanser på utfällning och kristallisering av kalciumoxalat. Dessa metoder gav också värdefull information vid utvärdering av olika additiver för kontroll av saltavlagringar, både i modellsystem och i filtrat av mekanisk massa. Resultat från dessa försök möjliggjorde att ett effektivt tillsatsmedel kunde formuleras för test i fabriksskala. En uppföljningsmetod baserat på oxalattitrering utvecklades för detta ändamål.

Resultaten i denna avhandling visar att det är möjligt att påverka bildningen av oxalsyra samt utfällning av kalciumoxalat genom processtekniska och våtändskemiska metoder. Avbarkning av ved, förhållanden i alkalisk peroxidblekning, hantering och kontroll av LK-substanser, samt utnyttjande av skräddarsydd kemi för kontroll av saltavlagringar, har centrala roller i detta.

SUOMENKIELINEN YHTEENVETO

Kivimäisten ja erittäin hankalasti poistettavien kalsiumoksalaattisaostumien muodostuminen on esiintyessään eräs vaikeimmista ongelmista massa- ja paperiteollisuudessa. Puuraaka-aine sisältää aina jonkin verran oksalaattia, mutta kuoressa sen määrä voi olla moninkertainen. Puhuttaessa valkaistuista massoista, suurin oksalaatin lähde on kuitenkin yleensä hapettavat valkaisuvaiheet, joissa oksaalihappoa muodostuu lähinnä ligniinin ja hemiselluloosien hapetusreaktioissa. Mekaanisessa massanvalmistuksessa tämä vaihe on alkaalinen peroksidivalkaisu. Kun oksalaatti-ionit reagoivat prosessivesissä olevan kalsiumin kanssa, syntyy erittäin niukkaliukoinen kalsiumoksalaatti-suola. Prosessipinnoille muodostuvat kerrostumat voivat aiheuttaa monimuotoisia häiriöitä sekä tuotannossa että paperin laadussa. Mekaanisten massaprosessien lisäksi kalsiumoksalaatin saostuminen on tunnettu ongelma myös esimerkiksi kemiallisen massan valkaisussa, sulfiittimassan valmistuksessa, sokeritehtaiden haihduttamoilla sekä olutpanimoissa. Kalsiumoksalaatti on myös ihmisillä esiintyvien munuaiskivien pääkomponentti, mikä on syy siihen että sen kristallisoitumisesta löytyy suuri määrä tutkimustietoa.

Kalsiumoksalaatin saostumista voidaan ehkäistä pyrkimällä pienentämään kalsiumin ja oksalaatin pitoisuuksia vesikierroissa, mutta mahdollisuudet tähän ovat rajalliset. Tätä vaikeuttaa erityisesti se että tehdaiden tavoitteena on sulkea vesikiertoja entisestään, jolloin saostumia aiheuttavat aineet rikastuvat prosessivesissä, ja myös kivettymien muodostumisriski kasvaa. Monesti ainoaksi keinoksi jää saostumien poistaminen sekä kemiallisten että mekaanisten pesujen avulla, jotka molemmat vaativat paljon aikaa ja resursseja, jolloin tuotanto kärsii. Näiden lisäksi käytössä on myös usein kemiallisia kivettymäntorjunta-aineita, ns. antiskalantteja, joita annostellaan jatkuvatoimisesti. Tässä työssä on tutkittu oksaalihapon muodostumiseen ja kalsiumoksalaatin saostumiseen vaikuttavia tekijöitä. Tutkimuksen erityisinä kiinnostuksen kohteina ovat olleet keinot, joilla voitaisiin ehkäistä saostumien muodostumista puupitoisten painopaperien valmistuksessa.

Työssä tutkittiin näytteen esikäsittely- ja säilytysmenetelmien vaikutusta ionikromatografilla (IC) tehtyyn oksalaattianalyysiin. Eräiden peroksidivalkaisun parametrien vaikutusta oksaalihapon muodostumiseen arvioitiin laboratorio-valkaisukokeiden avulla. Myös eristettyjä kuusipuun ainesosia sekä malliaineita käsiteltiin peroksidivalkaisuolosuhteissa, jotta saataisiin kuva niiden osuudesta oksaalihapon muodostumiseen kuusesta valmistetun mekaanisen massan alkaalisessa peroksidivalkaisussa. Eräiden mekaanisessa massanvalmistuksessa esiintyvien keskeisten liuenneiden ja kolloidaalisten (LK) aineiden vaikutusta kalsiumoksalaatin saostumiseen ja kristallisoitumiseen tutkittiin. Samalla testattiin virtaussytometrin (FCM) sopivuutta näihin tutkimuksiin. Virtaussytometriä käytettiin myös osana eri analyyttisten menetelmien kokonaisuutta, jolla arvioitiin tiettyjen antiskalanttien toimintaa kalsiumoksalaattisaostumien torjunnassa.

Ionikromatografia osoittautui tarkaksi ja käteväksi menetelmäksi massa- ja suodosnäytteiden oksalaattianalyyseihin. Jotta liuenneen oksalaatin määrä prosessin tietyssä vaiheessa voitaisiin määrittää luotettavasti, tulee näyte suodattaa välittömästi näytteenoton jälkeen. Näin vältetään oksalaatin saostuminen ennen analyysiä. Analysoitaessa oksalaatin kokonaismäärää massanäytteessä, hapotus suolahapolla pH~1:een sekoitetussa ja lämmitetyssä näytteessä varmisti kaiken saostuneen oksalaatin saattamisen liukoiseen muotoon.

Natriumhydroksidin (NaOH) korvaaminen magnesiumhydroksidilla ($Mg(OH)_2$) peroksidivalkaisun alkalilähteenä vähensi oksaalihapon muodostumista samalla vaaleustasolla. Samalla myös oksalaatin liukoisuus kasvoi. Valkaisusakeuden nosto paransi saavutettua vaaleustasoa ja vähensi oksalaatin muodostumista laskettuna kuivaa massatonnia kohti, vaikkakin oksalaattipitoisuus laskettuna massan tilavuutta kohti nousi.

Kuusen eri ainesosista ligniini osoittautui suurimmaksi oksaalihapon lähteeksi alkaalisessa peroksidikäsittelyssä, kun eri komponenttien osuus kuusipuussa huomioidaan. Hemiselluloosista, pektiineistä ja mahdollisesti myös lignaaneista syntyneen oksaalihapon yhteismäärä voidaan kuitenkin katsoa merkittäväksi, varsinkin kun huomioidaan näiden komponenttien suuri määrä LK-aineissa. Myös peroksidivalkaisukokeissa havaittiin oksaalihapon muodostumisen lisääntyvän kun LK-aineiden määrä valkaistavassa massassa kasvoi. Kuusen kuoren havaittiin sisältävän suuria määriä oksalaattia jo ennen käsittelyä, ja lisää oksaalihappoa vapautui kuoren ainesosien hapetusreaktioissa alkaalisessa peroksidivalkaisussa. Voidaankin todeta että tehokas kuorinta massatehtaalla on merkittävässä roolissa, ei ainoastaan massan vaaleuden suhteen, vaan myös kalsiumoksalaattisaostumien ehkäisyssä.

Magnesium-ionien lisäys vähensi kalsiumoksalaatin saostumista. Kolloidaalisen pihkan, galaktoglukomannanien ja saostuvien kalsiumoksalaattikristallien välillä havaittiin vahvaa vuorovaikutusta. Pihka vähensi kalsiumoksalaatin saostumista, mutta teki muodostuvista partikkeleista hydrofobisempia. Hyvin tunnetun, pihkaa stabiloivan vaikutuksen lisäksi galaktoglukomannaaneilla osoitettiin olevan selvä kalsiumoksalaatin kristallikasvua ehkäisevä vaikutus.

Virtaussytometrin ja on-line sameusmittauksen käyttö analyyttisinä menetelminä osoittautui erinomaiseksi yhdistelmäksi tutkittaessa eri aineiden vaikutusta kalsiumoksalaatin saostumiseen. Nämä menetelmät antoivat myös arvokasta tietoa arvioitaessa eri antiskalanttien toimintaa sekä puhtaassa mallisysteemissä että mekaanisen massan suodoksissa. Tulosten perusteella pystyttiin kehittämään tehokas tuote, joka myös testattiin tehdasmittakaavaisessa koeajossa. Tätä varten kehitettiin myös oksalaattititraukseen perustuva seurantamenetelmä.

Tässä väitöskirjassa saadut tulokset osoittavat että oksaalihapon muodostumiseen ja kalsiumoksalaatin saostumiseen voidaan vaikuttaa sekä prosessiteknisten että märänpään kemiaan liittyvien keinojen avulla. Keskeisissä asemissa ovat puun kuorinta, olosuhteet alkaalisessa peroksidivalkaisussa, LK-aineiden hallinta sekä räätälöidyn kemian hyödyntäminen kalsiumoksalaattisaostumien torjunnassa.

1. INTRODUCTION

Mechanical pulps are mainly used for production of so-called wood-containing printing papers, including newsprint, supercalendered (SC), and light-weight coated (LWC) magazine papers. Two main technologies are used in mechanical pulping, i.e. groundwood processes and disc refiner processes. The basic principle with both is to apply mechanical energy to the wood so that the lignin in the middle lamella, mainly responsible for binding the fibers together, is softened by the friction forces, and the fibers are more easily separated. Lignin is not removed from the fibers, and thereby the yield is high, but the brightness of the pulp is low. In most cases, bleaching has to be carried out in order to get adequate pulp brightness for the end use. Bleaching with hydrogen peroxide at alkaline conditions is the most common method to increase the brightness of mechanical pulps. Dissolved and colloidal organic substances (DCS) are released from wood to process waters in mechanical pulping. The amount and especially the composition of these substances are strongly affected by the reactions taking place in alkaline peroxide bleaching.

Problems with different kinds of deposits that disturb both production and quality are common in pulping and papermaking and are also encountered in the production and use of mechanical pulps. Pitch problems, caused by hydrophobic wood resin components, are probably the most widely known. Another type of problem is formation and deposition of insoluble salts, also known as scaling. The most common, and also the most problematic scale types in mechanical pulping and bleaching are calcium oxalate and barium sulfate. In addition, calcium sulfate occurs in high temperature areas like at TMP refiner plates. Scaling problems have become more common as mills are minimizing their fresh water usage. This results in accumulation of ions in the process circulations, and an increased risk for precipitation and scale build-up.

Calcium oxalate is formed when calcium, derived from wood, water, or calcium containing fillers and pigments, forms an insoluble salt with oxalate ions. Oxalate enters the process with the wood raw material, especially with bark, but usually the major source is oxalic acid that is formed as a by-product in reactions taking place in oxidative bleaching stages, like in alkaline peroxide bleaching. Calcium oxalate precipitation has been a topic of extensive research, not least because it is also known as the main component in human kidney stones, a painful urological disease, which also has become more and more common due to the changed diet and lifestyle habits in today´s world. The future biorefineries with oxidative biomass processing are also potential candidates to experience calcium oxalate scale problems. The more stringent environmental regulations concerning effluent loads are likely to increase the scaling problems further, and therefore new solutions in order to cope with these issues are needed.

1.1 Hypothesis and objectives of the work

The hypothesis of this thesis work has been the following: “By optimizing the conditions in mechanical pulping/bleaching and in papermaking, and by applying sophisticated chemistries and monitoring tools, it is possible to control oxalic acid formation and calcium oxalate crystal growth in a way that the scaling problems are eliminated or at least tolerable”. Based on this hypothesis, the first aim was to identify suitable analytical tools, both for oxalate analysis, and for investigation of the effects of different parameters and substances on calcium oxalate precipitation. In the latter case, the main interest was in the precipitation rate and properties of the formed crystals. Secondly, the aim was to identify process parameters in the alkaline peroxide bleaching, or generally in wet-end chemistry, which could be modified in order to decrease oxalic acid formation and harmful calcium oxalate precipitation. One additional objective was also to find suitable chemistry and screening methods for effective calcium oxalate scale control.

2. BACKGROUND (I)

Calcium oxalate scaling is one of the most difficult deposit problems encountered in the production and usage of alkaline peroxide-bleached mechanical pulps. This sparingly soluble salt is formed when oxalate that is released from wood, or formed in bleaching, reacts with dissolved calcium. Hard, greyish to light brown deposit layers are formed on process surfaces, common places being pipelines, tank walls, pumps, refiners, dewatering elements, and screens (Sitholé 2002). Typical examples of the problem are shown in Fig. 2.1. Heat exchangers and evaporation units are also potential risk stages for scale build-up. Calcium oxalate scaling occurs also in other industrial processes, like bleaching of kraft pulp (Krasowski, Marton 1983; Elsander et al. 2000), sulfite pulping (Hultman et al. 1981), as well as in food industry including sugar plants (Doherty et al. 2004), and breweries (Johnson 1998). Calcium oxalate is also the main component found in human kidney stones (Ogawa et al. 2000).

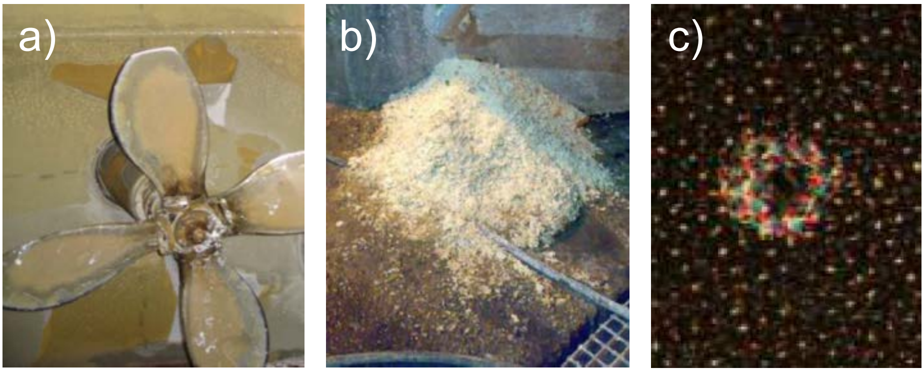


Figure 2.1 Examples of calcium oxalate scale problems: a) hard layers of scale on machine chest wall; b) crumbled scale particles from the bottom of the machine chest that could follow the pulp stream and end up in the paper; c) print defect ("hickie") caused by calcium oxalate particle.

Calcium oxalate scale can cause severe production and quality related problems in pulping and papermaking, which can have huge economic consequences. These include plugging of process equipment, reduction of heat transfer and failure of machinery and control equipment. Hard crystalline particles formed in pulp or released from scale deposits can end up in the paper web and cause holes in the sheet. Special types of print defects, so-called hickies, are formed when the crystalline particles are picked out from the paper sheet and adhere to the printing plate or blanket (Fig 2.1c).

Both mechanical and chemical methods are utilized in order to remove calcium oxalate scale deposits (Ulmgren, Rådeström 2001; Hassler 2009). Production downtime can be substantial, as extensive boil-out procedures are usually needed in chemical cleaning. Different types of anti-scaling agents are often used to control the scale build-up. However, chemical scale control has become more challenging, as the trend is towards more closed water circulations, whereby the precipitating ions will accumulate in the process waters and the scaling potential is increased. In fact, scaling risks often transpire to be the major limiting factor for water system closure.

2.1 Oxalic acid and calcium oxalate

Oxalic acid ($H_2C_2O_4 \cdot n\ H_2O$) is the simplest dicarboxylic acid, and it undergoes the following dissociation reactions in aqueous solution:

$$H_2C_2O_4 \rightleftharpoons HC_2O_4^- + H^+ \quad , pK_{a1} = 1.23 \quad (25°C)$$

$$HC_2O_4^- \rightleftharpoons C_2O_4^{2-} + H^+ \quad , pK_{a2} = 4.19 \quad (25°C)$$

From the low pK_a-values it can be understood that it is a strong acid, and it is the strongest carboxylic acid if the halogenated ones are not considered. The distribution curves for oxalic acid species as a function of pH are shown in Fig. 2.2. The divalent oxalate anion ($C_2O_4^{2-}$) starts to form at ~pH 2, and already dominates above pH 4. The pK_a-values depend on temperature and ionic strength of the solution. At elevated temperatures, the pK_a-values will be higher, which means that at the same pH, the dissociation is decreased with increased temperature (Kettler et al. 1991; Ferguson 2002).

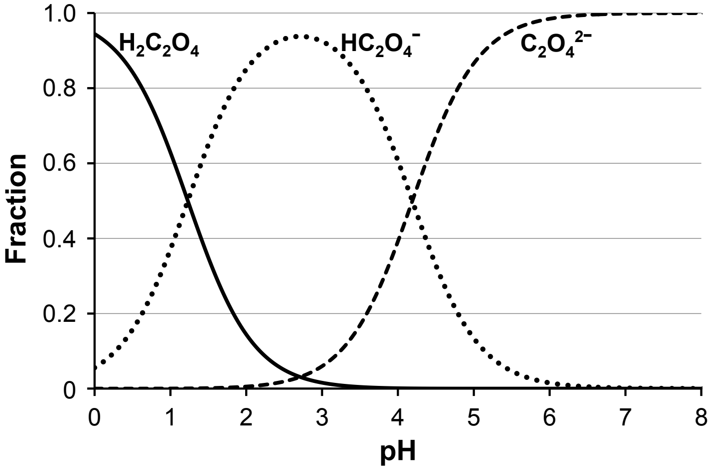


Figure 2.2 Distribution of oxalic acid/oxalate species vs. pH (drawn according to King, Kester 1990; Ferguson 2002).

Oxalic acid appears in plants and wood as water-soluble potassium, sodium, and ammonium salts, and also binds with calcium, magnesium and iron (Noonan, Savage 1999). It is formed by biosynthesis, and a number of pathways have been suggested. The most likely precursors for oxalic acid formation include compounds such as ascorbic acid, glyoxylate, glycolate, and isocitrate (Franceschi, Nakata 2005; Nakata 2012). Oxalic acid is also the major metabolite produced in the wood-decay process by wood-rotting fungi (Dutton, Evans 1996; Clausen et al. 2008; Mäkelä 2009). Oxalic acid can be found in many plants in small amounts, but there are some common oxalate-rich species that are used also as food, like spinach, rhubarb, and beetroot. The distribution of oxalate within the plant can also be uneven, and usually the leaves have a much higher content than the stem (Noonan, Savage 1999). In addition, seasonal variations occur so that an accumulation has been observed during dry conditions.

Calcium salt of oxalic acid, i.e. calcium oxalate ($CaC_2O_4 \cdot n\ H_2O$), is the most common biomineral occurring in higher plants (Horner, Wagner 1995; Franceschi, Nakata 2005). Formation of calcium oxalate crystals in plants is believed to play a key role in many important functions, including calcium regulation in plant tissue, defense against herbivores and bark-boring insects, as well as detoxification of heavy metals (Hudgins et al. 2003; Franceschi, Nakata 2005; Nakata 2012). The formation of the sparingly soluble calcium oxalate salt can be described by the following reaction equation:

$$Ca^{2+} + C_2O_4^{2-} + n\ H_2O \rightleftharpoons CaC_2O_4 \cdot n\ H_2O\ (s)$$

Calcium oxalate occurs in three different hydrate forms, and is therefore included in a group called pseudo-polymorphs (Haselhuhn et al. 2006). The thermodynamically most stable form is the monoclinic monohydrate (COM), also known as whewellite. COM is generally regarded also as the most problematic form, being the major cause of scale build-up in industrial processes, and in formation of human kidney stones, due to its highest stability and lowest solubility (Tomažič, Nancollas 1979; Babić-Ivančić et al. 1985; Ulmgren, Rådeström 2001). The two other metastable hydrate forms are the tetragonal dihydrate (COD or weddellite) and trihydrate (COT or caoxite). COD is also frequently found in nature and in precipitates together with COM, whereas the COT form is more rare. However, COT is believed to have an important role as a precursor for COM (Gardner 1975; Tomažič, Nancollas 1979). The hydrate forms differ significantly from each other in terms of solubility, aggregation tendency, and affinity to surfaces (Tomažič, Nancollas 1980). The hydrates can be identified by x-ray diffraction (XRD) and by thermogravimetric analysis (TGA) (Ulmgren, Rådeström 2001). Typical crystal structures for the three different hydrate forms are shown in the SEM-micrographs in Fig. 2.3.

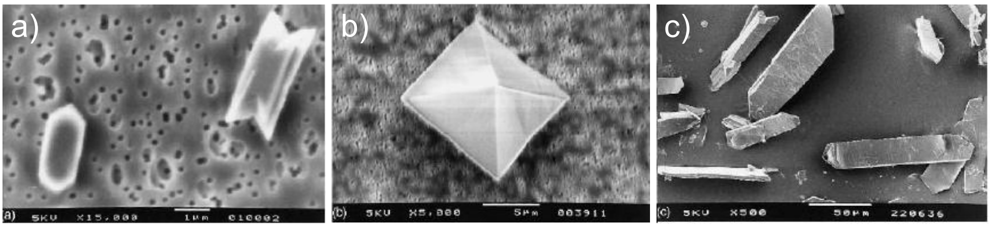


Figure 2.3 SEM-micrographs of calcium oxalate crystals formed in a pilot scale reactor: a) monohydrate (COM); b) dihydrate (COD); c) trihydrate (COT) (Houcine et al. 1997).

2.1.1. Occurrence in wood

Wood has been shown to contain 0.1-0.4 kg/ton (dry wood) of oxalic acid depending on the species (Krasowski, Marton 1983). In bark, the content is significantly higher, and oxalic acid amounts up to 15 kg/ton have been determined in bark of some hardwood species. This is mainly due to the presence of calcium oxalate crystals that have been detected in the bark of such species. Especially in hardwoods like European aspen (*Populus tremula*), the bark can contain substantial amounts of calcium oxalate (Terelius et al. 2001a; 2001b), but crystals have also shown to be present in phloem of conifers like Norway spruce (*Picea abies*) (Hudgins et al. 2003). An effective wood debarking is therefore essential in order to minimize the oxalate intake in pulp mills. Sapwood has been shown to contain larger amounts of oxalate than heartwood (Terelius et al. 2001b).

2.2 Formation of oxalic acid in oxidative pulp bleaching

When high brightness pulps are concerned, the formation of oxalic acid in oxidative bleaching stages, including chlorine dioxide, ozone, oxygen, and hydrogen peroxide, is usually the major source of oxalate in a pulp mill (Krasowski, Marton 1983; Elsander et al. 2000; Zhang et al. 2006), although there is proof that oxalate is formed also in the alkaline kraft pulping processes (Li et al. 2012). Oxidation of lignin and hemicelluloses have been pointed out as the main reactions where oxalic acid is formed. Much of the previous work on the subject has concentrated on bleaching of chemical pulps, but the alkaline peroxide bleaching of mechanical pulps has gained increasing focus more recently (Zhang et al. 2002; 2006; He et al. 2003; 2008; Yu et al. 2004a; 2005b; Sjöde et al. 2005; Yu, Ni 2005; 2006; 2007). A probable reason for this is that the calcium oxalate scaling problems have become more common in these processes because of the increased water system closure. In integrated mills, the increased usage of calcium containing fillers and pigments on the paper machine has also increased the calcium concentrations, increasing the risk for scale build-up further.

2.2.1 Alkaline peroxide bleaching of mechanical pulps

Spruce is the main raw material for production of pure mechanical pulps, i.e. thermomechanical (TMP) and groundwood (GW) pulps (Höglund 2009; Varhimo 2009). Hardwoods, like aspen, are mainly used for producing chemi-mechanical pulps, e.g. bleached chemi-thermomechanical pulp (BCTMP). Cellulose, lignin, and two hemicelluloses, i.e. the dominating *O*-acetyl-galactoglucomannan (GGM) and the minor arabinoglucuronoxylan, are the main constituents in Norway spruce (*Picea abies*) (Table 2.1). Other minor components include pectins, lipophilic and hydrophilic extractives, acetic acid, proteins, and inorganics (Alén 2000). In mechanical pulping, 1-5% of the wood is released to the process waters as dissolved and colloidal substances (DCS) (Auhorn, Melzer 1979; Holmbom, Sundberg 2003). These consist mainly of dissolved hemicelluloses, hemicellulose-lignin complexes, low-molar-mass lignin fragments, and extractives (Sjöström 1990). Concerning Norway spruce, GGM is clearly the main component among DCS (Thornton et al. 1994).

Table 2.1 Wood substances and their estimated contents in Norway spruce (*Picea abies*) based on literature (Fengel, Wegener 1989; Sjöström 1993; Alén 2000).

Wood substance	Content in spruce wood (%)
Cellulose	37-43
Lignin	25-30
Galactoglucomannans	15-20
Arabinoglucuronoxylans	5-10
Pectins	1-2
Extractives	1-2
Acetyl groups as acetic acid	1-3

The main active species that is responsible for the bleaching reactions in hydrogen peroxide bleaching is the perhydroxyl anion. This ion is formed at high pH, and therefore peroxide bleaching is carried out at alkaline conditions (pH 11-12) (Dence 1996). The perhydroxyl anion at high pH is formed according to the following reaction:

$$H_2O_2 + OH^- \rightleftharpoons OOH^- + H_2O$$

The bleaching effect in alkaline peroxide bleaching is obtained when the perhydroxyl anion attacks the colored lignin structures and changes them into non-chromophoric forms. Oxalic acid has also been shown to form in these oxidation reactions as a degradation product. The suggested reaction route is that muconic acid structures are first formed as a result of ring rupture of aromatic structures in lignin. Muconic acid is further oxidized and oxalic acid is formed as one of the end products according to reactions shown in Fig. 2.4. (Bailey, Dence 1969; Kempf, Dence 1980; Omori, Dence 1981).

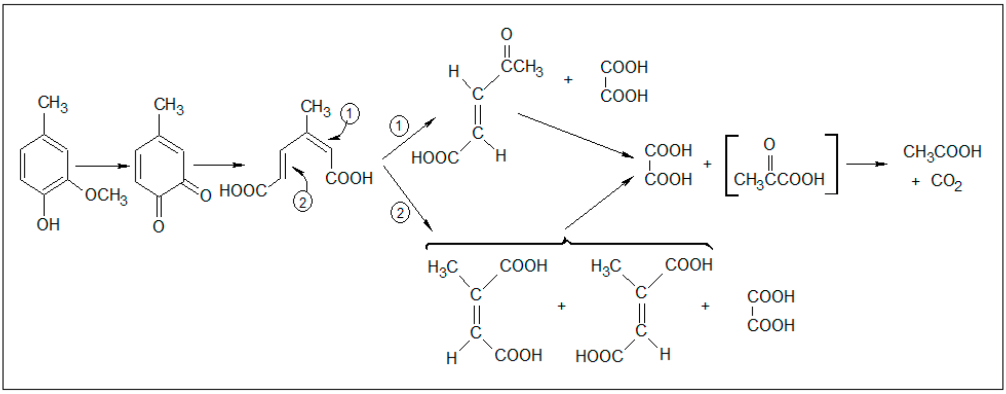


Figure 2.4 The proposed oxidative fragmentation reactions between alkaline hydrogen peroxide and creosol (adapted from Bailey, Dence 1969).

Lignin oxidation reactions have been pointed out as the main contributor to oxalic acid formation in alkaline peroxide bleaching in many studies (e.g. Krasowski, Marton 1983; Elsander et al. 2000; Yu, Ni 2005), although the role of carbohydrate degradation, and especially that of hemicelluloses, has not been excluded. More oxalic acid has been shown to be formed in peroxide bleaching of hardwood mechanical pulps compared with softwoods, which was explained by the differences in lignin structures (Fig. 2.5) (Yu, Ni 2005; He et al. 2008). This was verified by experiments with lignin model compounds, where it was found that syringyl type of structures resulted in higher oxalate formation compared with guaiacyl types, and softwood lignin is known to have much lower content of syringyl structures than hardwood lignin.

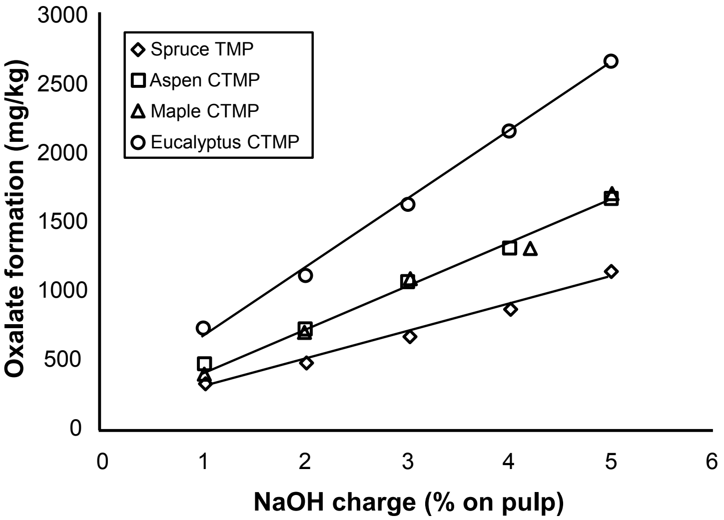


Figure 2.5 Oxalate formation in alkaline peroxide bleaching of four different mechanical pulps vs. NaOH charge (6.2% H_2O_2) (He et al. 2008).

Also xylans have been found to be a significant source of oxalate in oxidative pulp bleaching, a conclusion made from studies of ozone bleaching of kraft pulp (Nilvebrant, Reimann 1996). The precursor for oxalate is believed to be the hexenuronic acid groups that are formed from the 4-*O*-methyl-glucuronic acid groups in xylans in alkaline pulping (Buchert et al. 1995; Teleman et al. 1995; Vuorinen et al. 1997). In oxidative bleaching, the hexenuronic acids are further oxidized and oxalic acid is formed as one of the end products (Vuorinen et al. 1997). However, in alkaline peroxide bleaching of mechanical pulps this reaction path is questioned, as hexenuronic acids are not believed to be formed in mechanical pulping and bleaching conditions (Presley et al. 1997; Yu, Ni 2007). It should be noted, however, that in wood there is another source for hexenuronic acid formation apart from xylans, i.e. pectins, which do not require as severe conditions as in kraft pulping. At alkaline conditions, even at relatively low temperature, these pectins are splitted by β-elimination reaction resulting in terminal hexenuronic acid units (Kiss 1974). Contrary to earlier findings, Sjöde and co-workers (2005; 2008) concluded in their work with isolated wood substances that xylan is a more important oxalate precursor than lignin in peroxide bleaching of mechanical pulps. Lignin and galactoglucomannans were found to be minor sources. Cellulose degradation has also been shown to result in small amounts of oxalate (Krasowski, Marton 1983; Sjöde et al. 2005), whereas extractives have not been regarded as significant source (Zhang et al. 2006).

Most of the brightness increase in alkaline peroxide bleaching is gained in the initial phase of bleaching, as the concentration of perhydroxyl anions is highest at that point. Also oxalic acid is formed rapidly in this phase, and a strong correlation between brightness gain, bleaching chemical dosages, and oxalate formation has been shown (He et al. 2003; Yu et al. 2004a; He et al. 2008). Especially increased alkali (NaOH) dosage will increase oxalate formation almost linearly, as was shown in Fig. 2.5 for the four different mechanical pulps. This means that the charge of alkali should be optimized based on the peroxide dosage and brightness target in order to minimize oxalate formation (He et al. 2008). Too high alkali charges also increase the risk for decomposition of hydrogen peroxide as well as pulp darkening reactions (Dence 1996). Formation of peracetic acid in the beginning of the peroxide bleaching process has been claimed to be responsible for the high oxalate formation rate (He et al. 2003). Based on this, a sequential dosage scheme for bleaching chemicals, where peroxide was added last, was established. The formation of oxalate was shown to decrease by using this procedure.

Due to the negative side effects of using a strong alkali source like NaOH, e.g. the extensive dissolution of organic substances, there has been a growing interest in using milder alternatives as alkali source. Especially the potential of magnesium hydroxide, $Mg(OH)_2$, to replace NaOH either partially or totally, has already been verified both in laboratory experiments and in industrial applications. Increased bulk, increased opacity, and especially decreased COD load and anionic trash in the bleaching filtrate have been among the positive effects observed by usage of $Mg(OH)_2$ (Nyström et al. 1993; Kong et al. 2009; Behrooz et al. 2012; Hietanen et al. 2013). On the negative side, decreased strength properties of the final paper were reported. One of the benefits observed in $Mg(OH)_2$-based bleaching in mill-scale, has been decreased calcium oxalate scaling problems (Li et al. 2005; Harrison et al. 2008; Ni, He 2010). There is contradictory information if there is a decrease in the total amount of oxalate formed, but the studies have shown that more of the oxalate will be in soluble form (Yu et al. 2004a; Yu, Ni 2006; Yu, Ni 2007). The explanation for this is the formation of magnesium oxalates that have much higher solubility than calcium oxalate (Ulmgren, Rådeström 1999b). As $Mg(OH)_2$ is a milder alkali than NaOH, the pH-profile in $Mg(OH)_2$-based bleaching has also been found to be lower and more even, which means also a lower and more stable concentration of perhydroxyl anions during the bleaching process. This has been shown to lower the oxalate formation rate in the initial bleaching phase (Yu et al. 2004a; Kong et al. 2009).

Bleaching time and temperature, which are strongly interrelated, have not been considered as major parameters for oxalate formation in normal alkaline peroxide bleaching processes, although He and co-workers (2008) reported somewhat increased formation rate in higher temperatures. At higher temperatures, the bleaching reactions are faster, but so is also the peroxide decomposition (Lindholm 2009). Therefore, this has to be compensated by decreased bleaching time or decreased alkali dosage. However, unnecessarily high temperatures and long bleaching times should be avoided in order to minimize alkali-induced darkening reactions. Increased pulp consistency has a positive effect on brightness gain in alkaline peroxide bleaching, because higher molar concentrations of bleaching chemicals are obtained, and the contact between chemicals and fibers is improved (Presley, Hill 1996). The same effect has been shown both in NaOH- and $Mg(OH)_2$-based processes (Presley, Hill 1996; Behrooz et al. 2012). For the same reason also increased oxalate amount at increased pulp consistency in bleaching has been reported (Yu, Ni 2007). Overall, stoichiometrically favorable bleaching conditions for brightness gain have been shown to include not too high an initial pH, a low peroxide dosage and a high bleaching consistency (Moldenius 1982).

Decomposition of hydrogen peroxide at alkaline conditions results in formation of hydroxyl and superoxide radicals, especially in the presence of metal ions like manganese and iron that catalyze the reaction (Gierer, Imsgard 1977; Agnemo, Gellerstedt 1979; Dence 1996; Gellerstedt 2009). Formation of hydroxyl radicals will result in more extensive degradation of lignin and carbohydrates (Ek et al. 1989), and thereby the formation of oxalic acid may also be increased. Chelants are used to bind the metal ions in the pulp before bleaching and the peroxide is further stabilized in the process by adding for example sodium silicate and magnesium salts (Lidén, Öhman 1997; Gellerstedt 2009). Substituting $Mg(OH)_2$ for NaOH will also have a peroxide stabilizing effect and additional stabilizers are not necessarily needed in this case (Harrison et al. 2008).

Also the amount and composition of DCS is changed upon alkaline peroxide bleaching, and more lignin, xylans and especially pectic acids are released compared with unbleached pulp (Holmbom, Sundberg 2003; Pranovich et al. 2003). On the other hand, GGMs are deacetylated at the high pH and adsorbed on fiber surfaces, whereby acetic acid is released (Thornton et al. 1994). The alkaline conditions alone are responsible for a large part of the wood loss, but this can be even doubled by the oxidative effect of hydrogen peroxide, whereby more lignin, xylans and low-molar-mass degradation products are released (Pranovich et al. 2003). The extensive dissolution of pectic acids is a result of their splitting by β-elimination reactions, whereas the parallel and competing demethylation of the pectins is the major cause of increased anionic charge after alkaline peroxide bleaching (Sundberg 1999; Pranovich et al. 2003). The DCS can have a great impact on oxalic acid formation, as they are more readily available for reactions with bleaching chemicals (Fiskari 1999). In addition, the amount and composition of DCS affect the precipitation of calcium oxalate (Ulmgren, Rådeström 2001; Yu, Ni 2007). Therefore, it is of great importance how the filtrates and other process waters are circulated in the pulping process, and especially in the alkaline peroxide bleaching stage (Fiskari 1999; Ulmgren, Rådeström 2000).

2.3 Oxalate analysis

Oxalate analysis in pulp and filtrate samples containing calcium is problematic due to the low solubility of calcium oxalate. Changes in temperature, pH, or in contents of other substances in the sample can quickly change the amount of soluble oxalate. This makes the sample handling and pretreatment an essential part of oxalate analysis (Ulmgren, Rådeström 1999a; Sjöde 2007). Also a reliable sample storage method is important. For example, Muñoz et al. (2010) found that storage of urine samples for one month frozen at -20°C did not have a significant effect on the analysis result by capillary zone electrophoresis (CZE). The sample pretreatment method depends on the aim of the analysis, i.e. if the total content or only the soluble part of oxalate is to be analyzed. For soluble oxalate, usually only membrane filtration with 0.1-0.45 µm pore size is needed to remove solids and colloids, the actual pore size not being critical (Ulmgren, Rådeström 1999a). For total oxalate content, the precipitated part has to be solubilized, and this is commonly done by strong acids, for example hydrochloric acid (Hodginson 1981; Gottstein et al. 1989; Holmes, Kennedy 2000; Savage et al. 2000; Judprasong et al. 2006; Okombo, Liebman 2010). For urine samples acidification with hydrochloric acid to pH 1.6-1.8 (Hodginson 1981), and for plant material to below pH 1.5 (Holmes, Kennedy 2000), have been found to be enough to dissolve all oxalate in the samples. Hönow and Hesse (2002) stated that the challenge in acid extraction of oxalate from plant materials is the complete solubilization, and on the other hand to avoid oxalate generation from ascorbic acid or other unknown sources. However, even extraction with plain 2 M HCl was found to be suitable to accomplish this. It is also possible to use acidic cation exchange resins to solubilize precipitated oxalate (Reimann et al. 2000; SCAN-N 39:05). Sitholé et al. (2014) have recently introduced a method for pulp, filtrate, and scale samples, where methanesulphonic acid (MSA) is used to dissolve oxalate.

Several analytical methods can be used for determination of oxalate, including ion chromatography (IC) (Utzman 1993; Reimann et al. 2000; Sitholé et al. 2014), capillary electrophoresis (CE) (Sirén et al. 2000; Holmes, Kennedy 2000; Salomon, Romano 1992), high-performance liquid chromatography (HPLC) (Murray et al. 1982; Holloway et al. 1989; Schilling, Jellison 2004), and gas chromatography (GC) (Dosch 1979; Hyppänen et al. 1983; Krasowski, Marton 1983). In GC analysis, a derivatization of oxalate is required, whereas in other methods liquid samples can be analyzed directly. In addition there are methods available based on enzymatic methods and the use of biosensors (Hong et al. 2003; Milardović et al. 2008). A spectrophotometric method was developed by Chamjangali et al. (2009) and ion-selective electrodes (ISE) for oxalate have also been introduced (e.g. Rawat et al. 2010). When the different methods have been compared, none has been found superior to others for all applications (Zerwekh et al. 1983; Hesse et al. 1996; Holmes, Kennedy 2000). The choice has to be made based on the number and type of samples, resources, as well as accuracy needed. For a complex sample matrix like encountered in pulp and paper industry, IC and CE have proven to be best suited and are also most widely used today (Sjöde 2007; Sirén et al. 2000).

2.4 Calcium oxalate solubility and precipitation

Generally, it can be said that a sparingly soluble salt can precipitate from a solution when the cation and anion concentrations exceed the solubility product of the salt, and supersaturated conditions are reached. However, when evaluating for example the risk of calcium oxalate precipitation in industrial processes, many factors need to be considered, as the solubility products given in literature for pure solutions do not apply for such conditions (Ulmgren, Rådeström 1999a). Supersaturation, where the calcium oxalate solubility product is exceeded without precipitation is often encountered in oxidative pulp bleaching filtrates (Rudie, Hart 2006b), and this is the case also concerning human urine (Streit et al. 1998). One of the key parameters steering calcium oxalate solubility is the acid/base equilibria of oxalic acid/oxalate, which makes the precipitation tendency highly dependent on pH (Rudie, Hart 2006a). Oxalate has to be in the form of divalent $C_2O_4^{2-}$ ions so that calcium oxalate precipitation can occur. As it was shown in Fig. 2.2 earlier, the divalent anion starts to form above pH 2, and already dominates above pH 4. Therefore, the pH range of 4-8 is where calcium oxalate has its lowest solubility and where the risk for precipitation is the highest. Above pH 8, the carbonate ions start to form and will start to compete for the calcium ions (Ulmgren, Rådeström 1997). Also other process parameters like temperature, ionic strength and other substances present in the process waters affect the solubility (Ulmgren, Rådeström 1997; Rudie, Hart 2006a; Yu, Ni 2007).

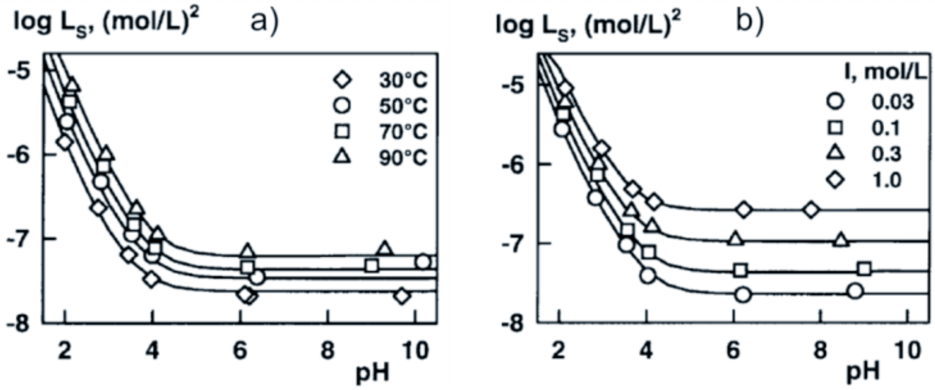


Figure 2.6 Calcium oxalate solubility as a function of pH: a) at different temperatures (ionic strength: 0.1mol/L (NaCl); Ca/Ox ratio 1 mol/mol; b) at different ionic strengths (NaCl) (70°C, Ca/Ox ratio: 1 mol/mol) (Ulmgren, Rådeström 1999a).

As already mentioned earlier, increased temperature will increase calcium oxalate solubility (Fig. 2.6a). Increased ionic strength is also known to increase the solubility (Fig. 2.6b), partly because more soluble species of oxalate will be present, and partly due to the decrease in ion mobility when the ions are more organized (Ulmgren, Rådeström 1999a; Rudie, Hart 2006a). There is also another reason why the calcium oxalate solubility in pulp bleaching filtrates has proven to be significantly higher compared to pure water systems. This is the presence of organic substances that can inhibit the crystallization process, whereby smaller and less stable particles are formed in the colloidal phase. Especially anionic substances containing carboxylic groups can act as such surfactants, and favor the formation of the metastable COD and COT forms (Ulmgren, Rådeström 1997; Ulmgren, Rådeström 2001). These forms are initially precipitated from supersaturated solutions, but will usually convert to the stable COM form with time. The solubility of the hydrates has been shown to decrease in order COT → COD → COM (Babić-Ivančić et al. 1985). Other proposed explanations for the effects of organic substances are initial formation of active, colloidal COM particles in the meta-stable phase, as well as formation of soluble complexes between calcium and substances containing carboxylic groups (Ulmgren, Rådeström 1997). These interactions together can explain why some co-precipitated organic material is most often found in the calcium oxalate scale deposits (Ulmgren, Rådeström 2001).

Apart from the work by Ulmgren and Rådeström, also Rudie and Hart (2005, 2006a, 2006b) have studied the fundamental chemistry behind the solubility and precipitation of scale salts, including calcium oxalate, in chemical pulping and bleaching. For mechanical pulps, however, the solubility studies are very limited. In urology and kidney stone research, the studies of calcium oxalate solubility and especially the differences between the three hydrate forms has been a topic for a number of publications (e.g. Tomažič, Nancollas 1979; Škrtić et al. 1987; Bramley et al. 1997; Bretherton, Rodgers 1998; Streit et al. 1998).

2.5 Calcium oxalate scale control

The most effective way to decrease calcium oxalate scaling in a process is minimizing the concentration of free calcium, as well as the intake and formation of oxalate. However, the possibilities for this are limited, especially as the trend is towards more closed water systems (Sjöde et al. 2005). Places where both calcium and oxalate ions are accumulated should be avoided when planning the water circulations. Effective debarking should be maintained in all occasions, as bark is rich both in oxalates and calcium (Terelius et al. 2001b; Krasowski, Marton 1983). The knowledge of the effects of peroxide bleaching parameters on oxalic acid formation can also be utilized in the bleaching stage (Sjöde et al. 2005). Using $Mg(OH)_2$ instead of NaOH as alkali source, or adding $MgSO_4$ have been shown to decrease scaling problems (Terelius et al. 2001b, Harrison et al. 2008, Ni, He 2010). Addition of aluminium sulfate has also been suggested for calcium oxalate scale control in sulfite pulp mills (Hultman et al. 1981). A relatively new approach that has shown very promising results, is the usage of specific enzymes for oxalic acid degradation (Nilvebrant et al. 2002; Sjöde et al. 2008; Cassland et al. 2010; Winestrand et al. 2012). Oxalate oxidase and oxalate decarboxylase enzymes have been shown to effectively degrade oxalic acid both in mechanical and chemical pulp filtrates.

On neutral paper machines using calcium carbonate as filler/pigment, a careful pH control as well as good filler retention and recovery are in central role when controlling the concentration of dissolved calcium in the circulation waters (Thibodeau et al. 2005). The process points, where these water fractions are taken to the acid mechanical pulp mill side always involve a potential risk for scaling. In some cases, decreasing calcium concentration by ion exchange system has also proven to be effective scale control method. Technologies based on electrochemical means (e.g. Hasson et al. 2008), and utilization of magnetic treatment (e.g. Busch, Busch 1997), which can alter the reactions between scale-forming ions, are also available.

It is common that different types of anti-scaling agents are used in processes where calcium oxalate scaling occur (Keselica 1992, Sitholé 2002, Hassler 2009). These additives are usually highly selective both for the scale type as well as for the process conditions. However, most often these chemicals only decelerate the scale build-up, although used in continuous basis. Therefore, both chemical and mechanical cleaning of the deposits has to be implemented. Boil-out cleaning with acids or chelants are used, but in the case of heavy deposition, mechanical means like hydroblasting are preferred both for economical and safety reasons (Ulmgren, Rådeström 2001; Hassler 2009).

2.5.1 Anti-scaling agents

Scale control additives function in different ways depending on their chemical properties like molar mass, functional groups, and morphology. Their effect is based on four main mechanisms, i.e. chelation, threshold inhibition, crystal modification and dispersion (Keselica 1992; Ester 1994; Shevchenko, Duggirala 2010). Chelants, like EDTA and DTPA, bind calcium in a soluble complex on a stoichiometric basis, and therefore their usage for scale control is usually uneconomical (Hassler 2009; Shevchenko, Duggirala 2010). Inhibitors, crystal growth modifiers and dispersing agents work at substoichiometric level, which makes their usage more cost-effective. Characteristic for these compounds is that they have an ability to be adsorbed on crystal surfaces and stop or modify the crystallization process at different stages. The two main mechanisms for adsorption at the crystal/solution interface are electrostatic interaction, and highly selective recognition of specific crystal faces based on structural and chemical compatibility (Füredi-Milhofer, Sarig 1996; Füredi-Milhofer et al. 2002; Dutour-Sikirić, Füredi-Milhofer 2006; Farmanesh et al. 2014). Usually the commercial products used in industrial scale control applications are multi-functional formulations containing two or several active components (Keselica 1992; Shevchenko, Duggirala 2010).

Threshold inhibitors can prevent the initial stage of crystallization, i.e. nucleation, so that the degree of supersaturation in solution is significantly increased without precipitation (Shevchenko, Duggirala 2010). Inhibition of nucleation requires high specificity from the inhibitor molecule, as the molecule has to fit exactly in the crystal structure of the precipitating scale salt (Dutour-Sikirić, Füredi-Milhofer 2006). Typical components in this group include polyphosphates, organic phosphonates and low-molar-mass polycarboxylates (Glazer 1991; Hassler 2009; Shevchenko, Duggirala 2010).

The mechanism of crystal growth modifier molecules is based on their selective adsorption to specific crystal sites, whereby the morphology of the crystals is changed. Also a selective adsorption on one polymorph, like COM in this case, is possible so that the formation of the meta-stable COD and COT is favored (Füredi-Milhofer et al. 2002). These effects result in a weaker structure of the precipitates and such scale is more easily removed. The most common crystal modifier components include phosphonates and polyacrylates, but derivatives of natural substances like lignins and tannins have also been used (Flynn 1988; Glazer 1991).

Dispersing agents are usually low-molar-mass polyelectrolytes with high anionic charge density. The purpose of these additives is to stabilize crystalline particles by adsorbing to the surfaces, whereby the electrostatic repulsion forces between the particles are increased. Also a steric stabilization effect is obtained. These effects decrease particle aggregation tendency and usually also the affinity of the particles to surfaces. Dispersants for scale control are most often used as part in commercial formulations, and typical examples are different types of polycarboxylates that also can be sulfonated (Glazer 1991; Hassler 2009; Shevchenko, Duggirala 2010).

The continuing trends in pulping and papermaking, including water system closure, high brightness requirements, and neutral papermaking processes, have increased the risk for calcium oxalate scaling significantly. This has also set new requirements for chemical suppliers to come up with more effective anti-scaling agent formulations, as the performance level of the conventional ones is inadequate (Chen, Michalopoulos 1989). In addition, the use of for example phosphorus containing products have been forbidden in several mills due to stricter environmental regulation, which remarkably limits the choice of active compounds (Shevchenko, Duggirala 2010).

The effects of different synthetic additives and biopolymers on calcium oxalate crystallization have been extensively studied. Much of the work has been concentrating on the research of calcium oxalate as a component in renal stones, but studies concerning industrial processes have also been published. One can also notice similarities between these two cases, although the matrix is totally different. A comprehensive review about the effects of surface active molecules on calcium oxalate crystallization and the specific interactions has been done by Dutour-Sikirić and Füredi-Milhofer (2006). They emphasized the selectivity of the compounds to work on specific crystal planes, but also the fact that the same molecule can act both as an inhibitor and a promoter of crystallization depending on its concentration.

For polyacrylic acid derivatives it has been shown that both the type of the end groups and charge density greatly affect their adsorption tendency on crystal surfaces, and thereby their inhibiting effect (Doherty et al. 2004; Akyol, Öner 2007). The same observation was made for vinylsulfonic acid by Kırboğa and Öner (2009). A selective effect favoring COD formation instead of COM has been found for example for poly-(styrene-alt-maleic acid) (PSMA), and for poly(sodium 4-styrene-sulfonate) (PSSS) (Yu et al. 2004b; 2005c). Carboxylated biopolymer derivatives based on inulin, a polysaccharide found in root plants, have also been shown to be effective calcium oxalate crystal growth inhibitors (Akın et al. 2008).

2.6 Methods for crystallization studies and screening of additives

A common method to induce calcium oxalate crystallization in experimental work is mixing solutions of soluble salts like calcium chloride and sodium oxalate (Zauner, Jones 2000). The reaction conditions can be varied and different compounds can be added to study the effects on precipitation kinetics or on the crystal morphology of the precipitates. Experiments can be carried out both with and without so-called seed crystals, depending on the crystallization phase or application that is being studied (Achilles 1997). Supersaturation of the ions is a requirement for start of precipitation (El-Shall et al. 2004). The crystallization phenomena can thereafter be followed by several different methods and analytical tools. Some of these methods as well as different crystallization systems have been reviewed by Achilles (1997) and Kavanagh (2006). A classification of crystallization methods is shown in Fig. 2.7. No single method has been found to be superior to others for all applications. Generally, it has been acknowledged that the most difficult task is to distinguish between the different stages of crystallization, i.e. nucleation, crystal growth, aggregation and disruption (Achilles 1997; Dutour-Sikirić, Füredi-Milhofer 2006). Therefore, it is equally challenging to determine the effect of different impurities and additives in these different phases. Especially the nucleation phase is problematic, as the particles need to be already relatively large in order to be detected by the available methods (Dutour-Sikirić, Füredi-Milhofer 2006). Thus, it is recommended that more than one technique is used simultaneously in monitoring of precipitation, or for example in evaluation of inhibitor performance. As can be understood from the extent of the context, the calcium oxalate crystallization research has been strongly focused on the formation of kidney stones. However, the same methods apply also for industrial processes, as the methods used in urolithiasis research have been mainly adapted from the fields like chemical engineering and materials science (Kavanagh 2006).

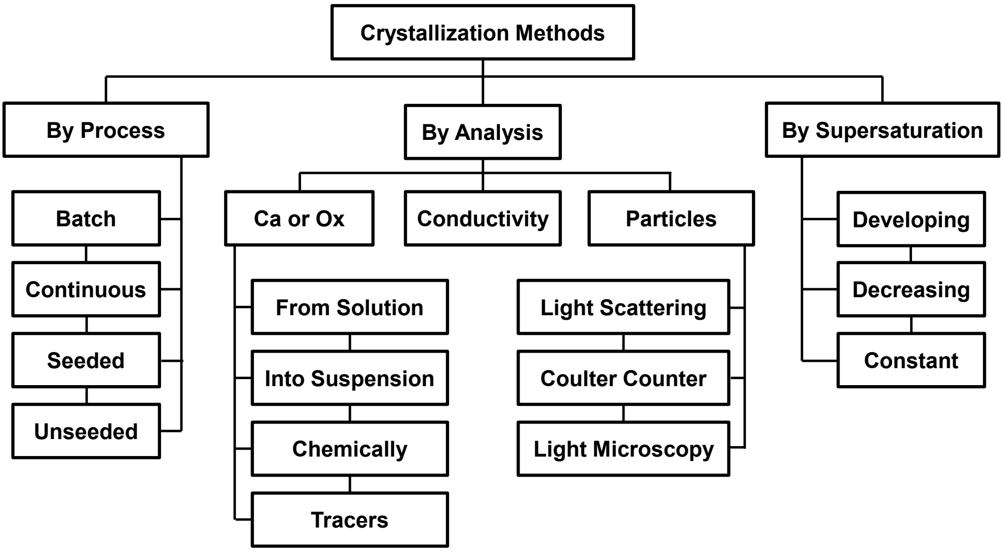


Figure 2.7 Categorization of methods for crystallization studies based on the used process, analytical tool or supersaturation control (adapted from Kavanagh 2006).

The calcium oxalate precipitation kinetics can be monitored by various direct or indirect measurements as a function of reaction time. One option is to follow the concentrations of the precipitating ions, i.e. calcium and oxalate, remaining in the liquid phase. This can be done off-line for example by ion chromatography (IC) and atom adsorption spectroscopy (AAS) (Ulmgren, Rådeström 1999a; Akın et al. 2008), or even on-line using ion selective electrodes, typically for calcium detection (Ca-ISE) (Akyol, Öner 2007; Kırboğa, Öner 2009). On the other hand, the amount of precipitate formed can be monitored for example by turbidimetric measurement or by determining the volume, weight or the number of the formed crystalline particles (Dutour-Sikirić, Füredi-Milhofer 2006). Turbidity measurement is a fairly simple method, but in many studies it has been found to be well suited for monitoring the early stages of calcium oxalate crystallization (Hennequin et al. 1993; 1997; Kavanagh et al. 2000; Doherty et al. 2004; El-Shall et al. 2004). For example, an inhibiting effect of an anti-scaling agent can be evaluated by its ability to prevent turbidity increase caused by formed crystals (Keselica 1992; Doherty et al. 2004). In the case of dispersants and crystal modifiers, however, a maintained high turbidity in unmixed crystal suspensions due to the decreased sedimentation would mean a positive effect indicating stabilizing effect (Chen, Michalopoulos 1989). A special laboratory method, based on optical fiber sensor, has been developed in order to study calcium oxalate scale build-up (Wallace et al. 2008). The benefit with this method compared with the ones described above, is claimed to be that the actual precipitation on a surface is monitored. Another similar type of method is based on quartz microbalance technology (Shevchenko, Duggirala 2010). The effect of different reaction conditions or additives on crystal morphology and hydrate forms can be determined by XRD, TGA, and SEM analysis (Babić-Ivančić et al. 1985; Škrtić et al. 1987; Yu et al. 2004b; Wang et al. 2006; Akyol, Öner 2007; Akın et al. 2008; Sayan et al. 2009).

To increase the correlation to actual conditions, real biological fluids or process waters can be used in the calcium oxalate precipitation studies. This has been common in urological research with real urine (e.g. Rodgers et al. 1995; Bretherton, Rodgers 1998; Baumann et al. 2000), or urine-like liquors (Garti et al. 1980; Randolph, Drach 1981; Brown et al. 1989; Streit et al. 1998). Also sugar solutions have been used for sugar plant evaporator scaling studies (Doherty et al. 2004; Yu et al. 2005a), as well as chemical pulp bleaching filtrates (Ulmgren, Rådeström 2000; 2001). However, any published results from studies with pure mechanical pulp filtrates have not been found.

For on-line scale formation monitoring in industrial processes, so-called scale/deposit coupons of different materials are traditionally used. These are installed in stages with high scaling potential and the build-up on surfaces is followed (Greer et al. 2003). However, this process is usually very slow and any prediction of the problem is not possible. A drawback is also that the coupon needs to be taken out from the process for analysis. Some laboratory methods have been modified to be used for on-line monitoring, and one example based on the quartz crystal microbalance technology has been patented (Shevchenko et al. 2001).

2.6.1 Flow cytometry (FCM)

Flow cytometry (FCM) is an analytical tool designed for counting and characterization of particles suspended in liquid. In this method, the sample containing the particles passes in single line a flow cell with a sheath fluid, and the stream is hydrodynamically focused (Fig. 2.8). In the flow cell, each particle is illuminated by a highly focused laser beam, and the scattered light and fluorescence of the particles is measured. The light scattering is a measure of particle size, whereas the fluorescence describes the chemical properties of the particles (Shapiro 2003). The size range of particles that can be measured is approximately 0.1-100 µm.

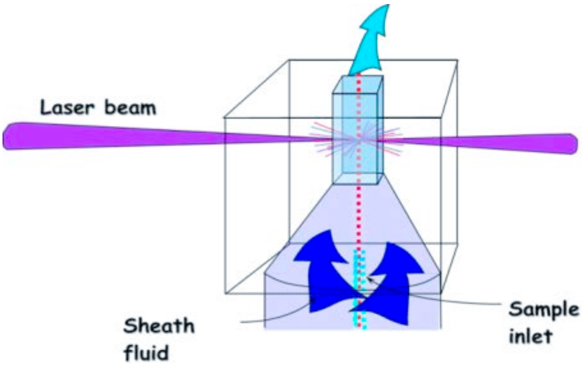


Figure 2.8 The principle of flow cytometry: particles in the sample stream (dots) are hydrodynamically focused by the sheath fluid (arrows), and illuminated in the flow cell by the laser beam (Vähäsalo 2005).

FCM has been mainly used in biomedical applications for counting and characterization of cells. One area in medical research has been in urology, where it was used to investigate calcium oxalate crystallization as a cause of renal stones (Rodgers et al. 1995). It was found to be an excellent tool for distinguishing between the different phases in crystallization process. FCM has also been adapted for use in research within pulp and paper industry (Vähäsalo et al. 2003). Particles like colloidal wood resin, white pitch, stickies, fines and microbes are examples of particles that have been analyzed (Vähäsalo et al. 2003; Kröhl et al. 2004; Vähäsalo, Holmbom 2005). It has also been possible to clarify the interactions between colloidal wood resin and filler particles by FCM (Strand et al. 2013).

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Chemicals (II-V)

NaOH (J.T. Baker, The Netherlands) and H_2O_2 (Merck, Germany) were of analytical grade. The liquid Na-silicate, with a SiO_2/Na_2O ratio of 2.55 - 2.65, was provided by a paper mill in Southern Finland (II; III). A magnesium hydroxide slurry (PaperMag 45) was supplied by SMA Mineral Magnesia AS (Norway) (II).

Oxalic acid (98%) was supplied by Sigma-Aldrich (Germany) (II), and acetic acid (HAc) was from J.T. Baker (The Netherlands) (III). The salts and the prepared stock solutions are listed in Table 3.1. All salts were of analytical grade (II; IV; V).

Table 3.1 Inorganic salts and concentration of the stock solutions (II; IV; V).

Salt	Supplier	Concentration as ion, mg/L
$Na_2C_2O_4$	VWR (Belgium)	4000 as $C_2O_4^{2-}$
$CaCl_2 \cdot 2\ H_2O$	J.T. Baker (Holland)	2000 as Ca^{2+}
$MgCl_2 \cdot 6\ H_2O$	Merck (Germany)	2000 as Mg^{2+}
$MgSO_4 \cdot 7\ H_2O$	Merck (Germany)	2000 as Mg^{2+}

The anti-scaling agents listed in Table 3.2 were provided by Kemira Oyj, with the exception of the last one (Reference) that was obtained from a paper mill in Southern Finland, where it was used in the process (V).

Table 3.2 Anti-scaling agents evaluated in the experiments (V).

Additive	*Abbreviation*
Acrylate/maleate copolymer 1	Copolymer 1
Acrylate/maleate copolymer 3	Copolymer 3
Polymaleate	Polymaleate
Polyacrylate	Polyacrylate
Sulfonated acrylate copolymer	Sulfonated copolymer 1
Sulfonated maleate copolymer	Sulfonated copolymer 3
Polyepoxy succinic acid	PESA
Polyaspartic acid	PASP
Dual component formulation 1	Blend 1
Anti-scaling agent used in the mill	Reference

3.1.2 Pulp and filtrate samples (II; III; V)

All pulp and filtrate samples were taken from the same groundwood (GW) pulp line, using Norway spruce (*Picea abies*) as raw material, in a paper mill located in Southern Finland. The peroxide bleaching in this mill is carried out at medium consistency after chelation with EDTA.

Peroxide-bleached GW pulp was sampled after the bleaching tower and acidification at a consistency of 3.7% (II).

Unbleached GW pulp with a consistency of 9.3% was sampled after the medium consistency (MC) pump (II). For bleaching and alkaline peroxide treatment experiments, the pulp was concentrated to 28.5% consistency by centrifugation (II; III).

Unbleached pulp filtrate was collected after the centrifugation of the unbleached GW pulp. The sample had a total oxalate content of 4.97 mg/L and calcium concentration of 163 mg/L. The dissolved and colloidal phase had a total organic carbon (TOC) content of 742 mg/L. The composition of the DCS in the filtrate was analyzed by GC for carbohydrates according to Sundberg et al. (1996a), and for extractives according to Örså and Holmbom (1994). The dominating organic compound in the filtrate was galactoglucomannan with a concentration of 650 mg/L. Other substances included arabinoglucuronoxylan (90 mg/L), lignans (65 mg/L) , pectic acids (40 mg/L), and low-molar-mass lignin-like substances and some lipophilic extractives (13 mg/L).

Peroxide-bleached GW pulp filtrate was the clear filtrate from the wire press after the peroxide bleaching stage. The filtrate was centrifuged for 20 min at 500 G before use in order to remove fiber and fines material (V).

3.1.3 Monosaccharides and isolated wood components (III; IV)

The following monosaccharides occurring as units in softwood hemicelluloses were used: D+mannose (Man) (Merck, Germany), D+glucose (Glc) (Merck, Germany), D+galactose (Gal) (Fluka, Sigma-Aldrich Chemie GmbH, Germany), D+xylose (Xyl) (Merck, Germany), L+arabinose (Ara) (Merck, Germany), and D+glucuronic acid (GlcA) (Calbiochem, USA). To describe pectic acids, D-galacturonic acid (GalA) (Calbiochem, USA), was also used. Analytical grade of D+cellobiose (Cellob.) (Fluka Chemie AG, Switzerland) was used to describe cellulose.

Two different samples of xylan from birch wood were used. The first one was a commercial preparate (Sigma-Aldrich Chemie GmbH, Germany). The other sample was precipitated in ethanol from a concentrated hot-water (160°C) extract (HWE) of birch saw dust, whereafter the precipitate was washed successively with ethanol, acetone, and methyl *tert*-butyl ether (MTBE) and dried in a vacuum desiccator. Galactoglucomannans (GGM) were hot-water extracted (HWE) from Norway spruce sapwood at 170°C and precipitated in ethanol (85%) according to the method described by Song et al. (2013).

The spruce milled wood lignin (MWL) sample was prepared according to Björkman (1956). The TMP lignin sample was prepared after removal of the polysaccharides by mild acid hydrolysis. Acetone-extracted TMP from spruce was treated with 0.1 M HCL in 1,4-dioxane/water, after which the pulp sample was filtered and rinsed with 1,4-dioxane/water. Thereafter the dioxane was evaporated, water was added, and the sample was left over night for sedimentation. The precipitated lignin was filtered and freeze-dried. The spruce enzymatic mild acidolysis lignin (EMAL) sample was prepared according to the method described by Rahikainen et al. (2013).

The lignan sample consisted mainly of two isomers of hydroxymatairesinol, i.e. hydroxymatairesinol 1 (HMR1) and hydroxymatairesinol 2 (HMR2), which were separated from an ethanol extract of spruce wood knots by flash chromatography. Prior to the ethanol extraction, the wood knot material was first extracted with n-hexane in order to remove the lipophilic extractives.

The samples of spruce inner and outer bark were separated by hand with a scalpel from a spruce bark sample. The samples were freeze-dried, ground in a Microfine Grinding Mill (Model MF 10, IKA Works, Germany) equipped with a 1-mm sieve, whereafter the bark powders were freeze-dried again before use.

The wood resin emulsion was prepared according to the method by Sundberg et al. (1996b) starting with extraction of thermomechanical pulp (TMP) from Norway spruce with n-hexane for 24 h, after which the extract was evaporated to remove hexane. Thereafter, the extract was re-dissolved in acetone, and the solution was injected into distilled water under agitation. The resulting emulsion was dialyzed in order to remove the acetone (IV). The sample used in the alkaline peroxide treatment experiments was prepared by sampling the acetone solution and evaporating the acetone before the experiment (III). The composition of the wood resin was analyzed by gas chromatography based on the method by Örså and Holmbom (1994). The sample consisted of 42.5% triglycerides, 25.5% resin acids, 17% steryl esters, 12% fatty acids, and 3% other substances like sterols and diglycerides. The total concentration of wood resin in the emulsion was 461.1 mg/L.

3.2 Methods

3.2.1 Sample pretreatment for oxalate analysis (II)

The peroxide-bleached groundwood pulp sample was kept in stainless steel containers placed in a water bath set to the process temperature before further processing. The different pretreatment procedures, both for soluble and total oxalate analysis, are shown in Table 3.3. Coarse filtration was carried out by vacuum filtration with MN640 filter papers to remove fibers and fines. Membrane filtration was carried out under vacuum with Whatman ME25 membranes with 0.45 µm pore size in order to remove colloids and other material that could block the ion chromatograph column. Thermostated water baths were used to keep the pulp and filtrate samples at process temperature (63°C) or at room temperature (25°C) according to the pretreatment scheme. The storage time of the samples in freezer (<-20°C) before further treatment and analysis was 16 days. Three parallel samples were treated identically in each experiment point.

When determining the soluble oxalate, the membrane filtrate was acidified with 1 M HCl to pH<2 to avoid precipitation of calcium oxalate before ion chromatographic (IC) analysis. When determining the total oxalate, 1 g of pulp sample as dry pulp was diluted to 1% consistency with de-ionized water that was tempered either to 63°C or 25°C. After this, the sample was acidified to pH<2 with 1 M HCl under magnetic stirring before membrane filtration and IC analysis.

Table 3.3 Sample pretreatment procedures and temperatures (PT= Process temperature, 63°C; RT=Room temperature, 25°C; Freezer: < -20°C).

Sample	Pulp storage	Acidification	Coarse filtration	Membrane filtration	Filtrate acidification	Filtrate storage
Soluble oxalate:						
1	PT	-	PT	PT	PT	PT
2	PT	-	PT	PT	PT	RT
3	PT	-	PT	PT	PT	Freezer
4	RT	-	RT	RT	RT	RT
5	Freezer	-	RT	RT	RT	RT
6	Freezer	-	PT	PT	PT	PT
Total oxalate:						
1	PT	PT	-	PT	-	PT
2	PT	PT	-	PT	-	RT
3	PT	PT	-	PT	-	Freezer
4	RT	RT	-	RT	-	RT
5	Freezer	RT	-	RT	-	RT
6	Freezer	PT	-	PT	-	PT

3.2.2 Oxalate recovery experiment (II)

20 g (o.d.) of the unbleached groundwood pulp was diluted in a glass beaker with de-ionized water under magnetic stirring (500 rpm), after which calcium chloride dihydrate and oxalic acid solutions were added to give a total pulp consistency of 1%, a calcium concentration of 200 mg/L, and an oxalate concentration of 50 mg/L. This pulp suspension was stirred for 20 h at room temperature (25°C). Batches of the suspension were acidified with 2 M HCl to different pH: 1.7, 1.4 and 1, both at room temperature and at 70°C under magnetic stirring (30 min). For comparison, also acidic cation exchange resins, Amberlite IR-120 (H^+), from two different suppliers (Merck, Germany and Fluka, Switzerland) were tested in acidification by adding 10 g of washed resin to 50 mL of the suspension according to the method described by Reimann et al. (2000). After the acidification, the samples were filtered on a Whatman ME25 membrane with 0.45 µm pore size and the filtrates were stored in a freezer before IC analysis. As reference, a blank sample with no acidification was prepared and filtered in the same way. Two parallel samples were included in this experiment.

3.2.3. Laboratory peroxide bleaching (II)

Unbleached groundwood pulp was concentrated up to 28.5% consistency by centrifugation and the filtrate was collected for dilution purposes. The total oxalate content both in the concentrated pulp and in the filtrate was analyzed. The samples were stored in a freezer before the bleaching experiments. The reference conditions and chemical charges in laboratory peroxide bleaching, shown in Table 3.4, were adapted from the mill from where the pulp also was sampled, as this process was particularly studied in this work. The pulp had already been chelated in the process with EDTA, so no additional chelant was added in the laboratory procedure.

Table 3.4 Conditions in laboratory peroxide bleaching.

Consistency	10%, 15%, 20%, 25%
Temperature	73°C
Time	90 min
NaOH charge	11.4 kg/t
H_2O_2 charge	20 kg/t
Na-silicate charge	16.8 kg/t
Acidification	SO_2-water to pH 4.6

The bleaching experiments were carried out in sealed polyethylene bags. Bleaching chemicals were added to pre-heated pulp and the bag was kneaded by hand between each dosage. The NaOH was added first followed by Na-silicate. Hydrogen peroxide was added last and then the plastic bag was placed in a thermostated water bath. The pulp was kneaded by hand every 30 min during the laboratory bleaching procedure. After the elapsed bleaching time (90 min), the end-pH was measured and some filtrate was pressed out from the bleached pulp with a household potato press for analysis of soluble oxalate and for the determination of residual peroxide. For soluble oxalate analysis, this press filtrate was directly further filtered with a Whatman ME25 membrane with 0.45 µm pore size and acidified to $pH < 2$ with 2 M HCl. For total oxalate analysis, 1 g of the bleached pulp (o.d.) was diluted to 1% consistency with preheated de-ionized water and acidified to pH 1 with 2 M HCl under heating and mixing (30 min, 70°C). Thereafter, this suspension was filtered on a Whatman ME25 membrane with 0.45 µm pore size. All filtrates for oxalate analysis were stored in a freezer until analysis by ion chromatography. In the bleaching experiments where handsheets were prepared, the remaining pulp sample was acidified with SO_2-water (5-6% SO_2, Merck) to pH 4.6 to stop the bleaching process. Two bleaching experiments were carried out in every sample point, except in the pulp consistency experiments, where only one test series was done.

Effect of dilution water quality

The pulp sample (28.5%) was diluted to 10% consistency with different ratios of de-ionized water/unbleached pulp filtrate: 100/0, 75/25, 50/50 and 25/75. Dilution with 100% filtrate was not possible, as some de-ionized water was needed for dilution of the bleaching chemicals and rinsing the beakers.

Effect of pulp consistency

The pulp sample (28.5%) was diluted with the collected filtrate to 10%, 15%, 20%, and 25% consistencies and the bleaching chemicals were added and mixed in the pulp in a HC laboratory mixer. The pulp was then transferred to plastic bags and the bleaching was carried out as described earlier. As the potato press was not sufficient to separate the filtrate at 20% and 25% pulp consistencies, a special pneumatic press cylinder equipped with the same wire type was used for these samples.

NaOH vs. $Mg(OH)_2$ as alkali source

Magnesium hydroxide as an alternative alkali source was evaluated by replacing sodium hydroxide so that the molar amount of hydroxide ions remained constant. Experiments were carried out both with and without Na-silicate. The charges of NaOH, $Mg(OH)_2$ and Na-silicate in these experiments are shown in Table 3.5. Other conditions and chemical dosages were the same as described previously in Table 3.4. De-ionized water was used for dilution of the pulp to 10% consistency.

Table 3.5 The charges of NaOH, $Mg(OH)_2$ and Na-silicate in the peroxide bleaching experiments.

Alkali source	**NaOH, kg/t**	**$Mg(OH)_2$, kg/t**	**Na-silicate, kg/t**
Unbleached	-	-	-
NaOH	11.4	-	-
NaOH+Na-silicate	11.4	-	16.8
$Mg(OH)_2$	-	8.31	-
$Mg(OH)_2$+Na-silicate	-	8.31	16.8

3.2.4 Alkaline peroxide treatment of model components (III)

The various substances were treated with alkaline peroxide bleaching chemicals at 2% consistency in test tubes, and the amount of oxalic acid released was determined by ion chromatography. The treatments were carried out in a water bath at 73°C for 90 minutes. The chemical dosages used were 3% sodium hydroxide, 2% sodium silicate, and 6% hydrogen peroxide, based on the amount of dry treated substance. A higher dosage of NaOH was used for HAc, GlcA and GalA in order to get an adequate starting pH over 11 at room temperature (23°C).

The weighed sample was suspended in de-ionized water and the test tube was placed in the water bath (73°C) for 5 min. Thereafter the test tube was taken out from the water bath and sodium hydroxide and sodium silicate were added, the sample was shaken, after which the start-pH was measured. The temperature during the pH measurement was round 55°C. Then hydrogen peroxide was added, the sample was shaken, and the test tube was again placed in the water bath for 90 min. Every 15 min the sample was shaken by hand. After the treatment, the sample was cooled down to room temperature (23°C) under running water, and the end-pH, as well as the residual peroxide level were determined. The sample was thereafter acidified to pH 5 with sulfurous acid (5-6% SO_2, Merck, Germany) in order to degrade the residual peroxide. Then the sample was further acidified with 2 M HCl to pH 1 in order to keep the oxalate in dissolved form and to dissolve possible precipitates. Before IC analysis, the samples were filtered with a 0.45 μm PTFE syringe filter (VWR Int., USA).

For reference, all substances were also treated similarly as described above, but without any bleaching chemicals added. This was done in order to determine whether the sample of the tested substance contained any oxalate already before the treatment, or for a possible oxalate formation in the acidification process. The amount of oxalate formed in the alkaline peroxide treatment was then calculated by subtracting this reference value from the analysis result after the treatment. Two peroxide treatment experiments, as well as reference treatments without chemicals, were carried out for every substance.

3.2.5 Calcium oxalate precipitation experiments (IV; V)

Calcium oxalate precipitation was studied by mixing calcium chloride and sodium oxalate solutions in different molar ratios of calcium and oxalate ions. Different substances were added to the test solution in order to study their effect on precipitation and crystallization (Fig. 3.1). The precipitation experiments were carried out in a 250 mL borosilicate glass vessel that was covered with black adhesive tape in order to minimize any light reflections, which could disturb the turbidity measurement. The glass vessel was placed on a hotplate equipped with a magnetic stirrer. The turbidity and temperature sensors, as well as the pH electrode, were placed in the test solution. All the tests were carried out at room temperature (23°C), with a sample volume of 200 mL and with a stirring speed of 800 rpm. A minimum of two replicates for every test series was done. The experiment conditions and concentrations of the ions and organic substances are described in the following chapters. After 10 min reaction time, a 100 µL sample of the test solution was withdrawn, diluted to 1 mL with de-ionized water, and analyzed directly by flow cytometry (FCM). In the experiments with wood resin dispersion and pulp filtrates, the diluted sample was stained with 20 µL of a hydrophobic, fluorescent dye solution (Nile red, 10 ppm in MeOH) before FCM analysis in order to determine the hydrophobicity of the particles. After 12 min (15 min in V) from starting of the experiment, a 50 mL (100 mL in V) sample of the test solution was taken and filtered on a pre-weighed Whatman ME25 membrane with a 0.45 µm pore size. The membrane with the precipitate was air-dried and finally placed in a desiccator, after which it was weighed. The calcium oxalate precipitate was collected from the membrane surface with a laboratory spatula and disintegrated with a mortar for x-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis.

Magnesium concentration (IV)

In the experiments with magnesium, a calcium ion concentration of 3 mmol/L and an oxalate ion concentration of 1 mmol/L were used. The tested magnesium ion concentrations were 0, 1, 2, 3, and 4 mmol/L. The calculated amount of calcium chloride solution was first added in de-ionized water under magnetic stirring after which magnesium chloride or magnesium sulfate solution was added. The sodium oxalate solution was then added and the turbidity monitoring was started.

Wood resin emulsion (IV)

The experiments with wood resin dispersion were carried out both at pH 5 and pH 8. The calcium ion concentration in these experiments was 2 mmol/L, and the oxalate ion concentration was 1 mmol/L. The concentrations of wood resin were 0, 2.9, 5.8, 11.5, 23, and 46 mg/L calculated as total extractives. The wood resin was added first to the de-ionized water during stirring, after which the sodium oxalate solution was added. The pH was thereafter adjusted to 5 or 8 by addition of either 0.1 M HCl or 0.1 M NaOH. The calcium chloride solution was added as the last component and the turbidity monitoring was started. The reason for this addition order is that free calcium can react with the colloidal wood resin and cause agglomeration.

Galactoglucomannans (IV)

The effect of addition of spruce galactoglucomannans (GGM) was tested with and without wood resin addition both at pH 5 and 8. Calcium ion concentration was 2 mmol/L, oxalate ion concentration was 1 mmol/L, and the two GGM concentrations tested were 100 and 200 mg/L. In the experiments with wood resin (23 mg/L), the GGM was added after resin addition to the de-ionized water. The sodium oxalate solution was added next and the pH was adjusted by addition of 0.1 M HCl or 0.1 M NaOH. The calcium chloride solution was then added and the turbidity monitoring was started.

Anti-scaling agents (V)

The tests were carried out at room temperature and pH 8, with a sample volume of 200 mL and a stirring speed of 800 rpm. The calcium ion concentration was 2 mmol/L, and the oxalate ion concentration was 1 mmol/L. An active substance concentration of 100 ppm was used for the selected chemicals. The addition order of the solutions was the following: 1. De-ionized water (dilution); 2. Calcium chloride solution; 3. Additive (diluted with de-ionized water to 1% active substance); 4. pH adjustment to pH 8 with 0.1 NaOH / 0.1 M HCl; and 5. Sodium oxalate solution. The on-line turbidity monitoring was started at the same time as the last component was added.

Peroxide-bleached groundwood pulp filtrate (V)

The experiments with addition of bleached groundwood pulp filtrate were carried out in principle in the same way as the described testing in clean system, but some modifications were necessary. Total sample volume in these experiments was 80 mL, pH was 7.5, and the concentrations of the filtrate were 0, 1, 5, 10, and 20%. The initial turbidity value that was a result of filtrate addition was recorded, and the turbidity reading was reset to zero before the monitoring was started. The addition order of the solutions was the following: 1. De-ionized water (dilution); 2. Filtrate; 3. Sodium oxalate solution 4. Additive (only Blend 1, when used); 5. pH adjustment to pH 7.5 with 0.1 NaOH / 0.1 M HCl; and 6. Calcium chloride solution. The inverse dosing order for oxalate and calcium solutions compared with the clean system experiments was used in order to avoid possible calcium-induced aggregation of colloidal wood resin present in the filtrate. The experiments were carried out at room temperature, and with concentrations of 2 mmol/L of calcium and 1 mmol/L of oxalate. In these experiments, the diluted sample for FCM was stained with 20 μL of a hydrophobic, fluorescent dye solution (Nile red, 10 ppm in MeOH) before analysis in order to determine the hydrophobicity of the particles.

3.2.6 Oxalate titration (V)

A method for evaluation of anti-scaling agent (Blend 1) performance during a full-scale trial in a paper mill was established. Samples were taken both during and outside of the trial period from the peroxide-bleached groundwood dosing chest (GW) and machine chest (MC). The two dosing points for the chemical were after the groundwood pulp storage tower before the dosing chest and in the wire pit. The samples were coarsely filtered through a 100 mesh wire bag, followed by centrifugation for 20 min at 500 G. 80 mL of the supernatant containing the dissolved and colloidal fraction was collected, cooled down to room temperature, and transferred to the glass vessel and stirring system described in chapter 3.2.5, with a stirring speed of 800 rpm. Turbidity and temperature sensors were placed in the solution, and the initial turbidity value was recorded. Thereafter the turbidity reading was reset to zero and the monitoring was started. After one minute, an addition of sodium oxalate solution equivalent to 0.1 mmol/L (8.8 mg/L) of oxalate was made. This addition was repeated after every minute up to 20 min, so that the total oxalate addition amount was 2 mmol/L (176 mg/L). After 21 min, a 100 μL sample was withdrawn, diluted to 1 mL with de-ionized water, stained with 20 μL of Nile red dye solution, and analyzed by FCM. In addition, the original centrifuged sample before any oxalate addition was stained and analyzed by FCM. The calcium and oxalate concentrations in this sample were also determined by IC after membrane filtration with a Whatman ME25 membrane with 0.45 µm pore size and acidification to pH < 2 with 2 M HCl.

The product in the trial (Blend 1) and the product previously used in the mill (Reference) were also compared off-line in the mill by the method described above. A sample was taken from the bleached groundwood storage tower before the chemical addition point, after which it was treated with 2 kg/ton of a low-molar-mass, high-charge density cationic polyamine product (fixative), used in the mill for wood pitch control. This was done in order to decrease the turbidity in the sample (>1000 NTU) to make the turbidity monitoring more reliable for calcium oxalate precipitation studies. After this, the sample was coarsely filtered with a wire bag and centrifuged. The supernatant was collected and the testing proceeded as described above, but with additions of Blend 1 (20 and 50 ppm) and Reference (50 ppm) products. The concentration of oxalate in the sample was 4.5 mg/L and that of calcium was 52.0 mg/L as analyzed by IC. The precipitates after these experiments were collected by membrane filtration with Whatman ME25 membranes with a 0.45 µm pore size, after which they were air-dried and disintegrated with a mortar for SEM analysis. The sample amount was too small for XRD analysis.

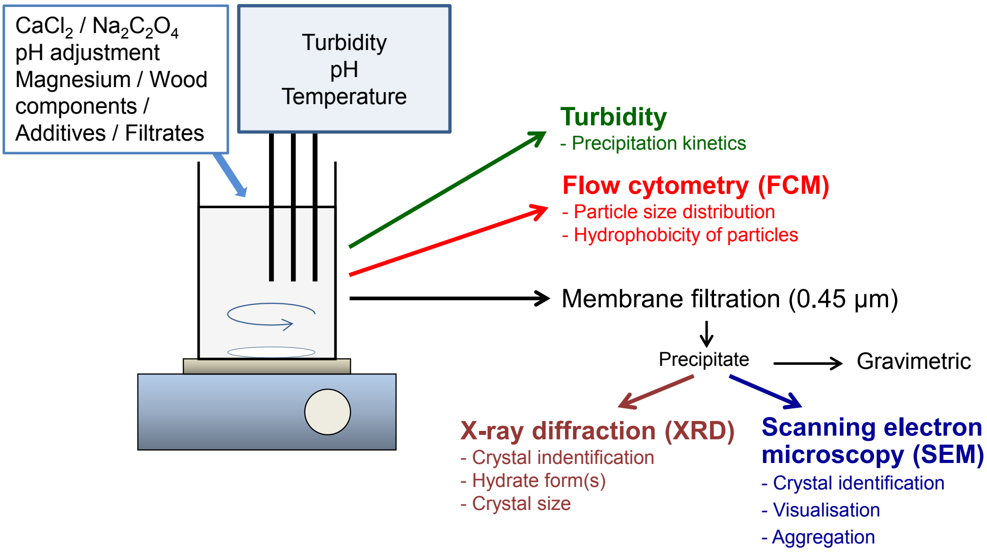


Figure 3.1 Experimental scheme in the calcium oxalate precipitation experiments.

3.3 Analysis

3.3.1 Oxalate analysis (II-V)

All oxalate analyses were carried out by ion exchange chromatography (IC) using a Dionex DX-500 ion chromatograph equipped with an auto sampler and suppressed conductivity detector. An IonPac AS19 analytical column (4 x 250 mm) and an IonPac AG19 guard column (4 x 50 mm) were used for separation. The eluent used was 12 mM KOH until 8 min running time after which it was increased to 40 mM KOH. The eluent flow was 1 mL/min. An IC chromatogram example for a standard solution is shown in Fig. 3.2.

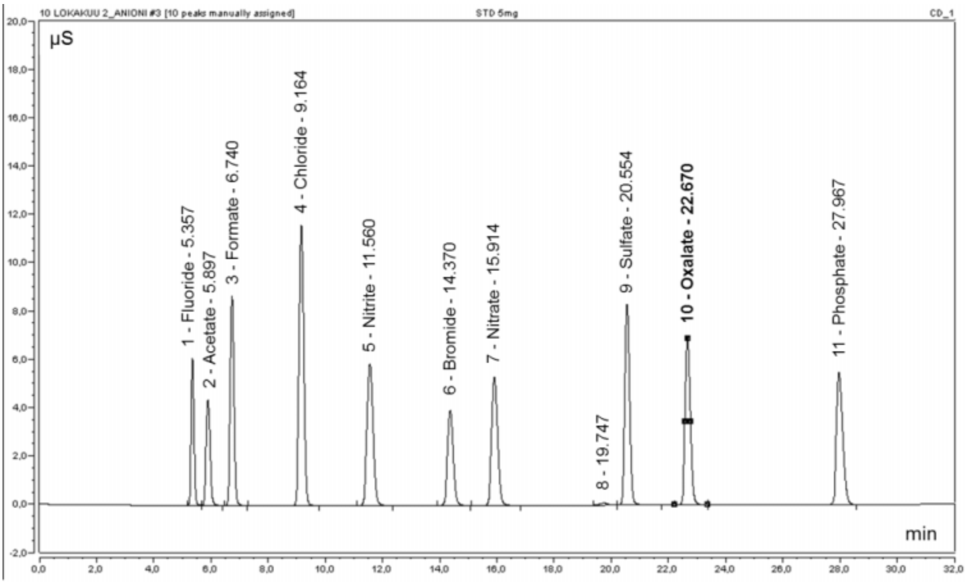


Figure 3.2 IC chromatogram for a standard solution (5 mg/L).

3.3.2 Determination of residual peroxide (II; III)

In the laboratory bleaching experiments, the residual peroxide level was determined by iodimetric titration with sodium thiosulfate (II). Merckoquant® 1.10081.0001 peroxide test strips (Merck KGaA, Germany) were used in the model compound experiments due to the small sample amount (III).

3.3.3 Total organic carbon (II)

Total organic carbon (TOC) was determined by a Shimadzu TOC-5050 Total Organic Carbon Analyzer equipped with an ASI-5000 autosampler.

3.3.4 Preparation of laboratory handsheets (II)

Handsheets of 60 g/m^2 grammage for determination of ISO-brightness were prepared with a laboratory sheet former according to the ISO 5269/1 method.

3.3.5 Brightness measurements (II)

ISO-brightness of the handsheets was measured with an Elrepho Datacolor 2000 spectrophotometer according to the ISO 2470 method.

3.3.6 pH measurement (II-V)

A SCHOTT Handylab 2 pH meter was used for the pH measurement.

3.3.7 Turbidity (IV; V)

Turbidity was measured with a Novasina Nephelometer Analite 156 turbidity meter, which was connected to a computer for automatic data collection.

3.3.8 Flow cytometry (FCM) (IV; V)

Flow cytometry measurements were performed with a Partec CyFlow SL flow cytometer with 5 optical parameters, forward scattering, side scattering, FL1 green (512-542 nm), FL2 orange (575 -605 nm), and FL3 Red (615-645 nm). Distilled water was used as sheath fluid. The Nile red (in MeOH) was used for staining of wood resin in the laboratory samples. The size of the measured particles was estimated by a size calibration performed with latex particles (Vähäsalo et al. 2003).

3.3.9 X-ray diffraction (XRD) (IV; V)

In paper IV, X-Ray diffraction (XRD) was performed using a Bruker D8 Discovery (Bruker-AXS, Germany) equipped with a monochromator (Göbel mirror), a 0.5-mm collimator and a HI-STAR 2D-detector. The oxalate samples were crushed manually in a mortar and hydraulically attached onto a SiO_2-sample holder. For phase identification a PDF-2 database (2010) was used. The crystal sizes were calculated with Topas 4.2 software (Bruker-AXS).

In paper V, XRD analysis was performed using a PANalytical X'Pert PRO MPD X-ray diffractometer equipped with an X'Celerator detector. For phase identification a PDF1 + PDF2 database (2003) was used. The crystallite sizes were calculated with a Highscore plus software (PANalytical) using the Scherrer calculator.

3.3.10 Scanning electron microscopy (SEM) (IV; V)

In paper IV, scanning electron microscopy (SEM) analyses were carried out with a Jeol JSM-6335F SEM instrument (Jeol Ltd, Tokyo. Japan). Voltages of 5 kV and 10 kV were used. In paper V, a FEI XL 30 Feg instrument was used. The size measurements were carried out using the internal measurement tool of the SEM instrument. The measured particles were randomly selected and the average of ten particles is presented as the average result.

4. RESULTS AND DISCUSSION

4.1 Sample pretreatment for oxalate analysis

This work was started around an existing calcium oxalate scaling problem in a paper mill, so the logical first step was to establish reliable and convenient analysis methods both for soluble and total oxalate. The effects of sample pretreatment and storage methods were particularly of interest, as there is often a varying time delay between sampling and actual analysis. This was needed both for determination of oxalate balances in the process, as well as for the planned laboratory experiments. In this mill, the oxalate analysis had been carried out based on a modified SCAN-N 39:05 (2005) standard method, so this was used as a starting point. An exception to this was that the total oxalate determination in pulp suspensions was done by acidification to pH<2 with hydrochloric acid instead of using a cation exchange resin as described in the informative annex A in the SCAN method. Ion chromatography (IC) was chosen as the analytical tool to be used throughout this work for oxalate analysis, as it showed very accurate and reproducible performance both in the pre-studies and in the pretreatment experiments.

4.1.1 Soluble oxalate (II)

The highest value for soluble oxalate was obtained when the peroxide-bleached groundwood pulp sample was filtered directly at the process temperature (63°C) (Fig. 4.1). Storage of this filtrate in freezer did not affect the analysis result significantly, which is in line with the findings by Muñoz et al. (2010), where urine samples were stored in a freezer before oxalate analysis by capillary electrophoresis. If the sample was allowed to cool down to room temperature (25°C) before filtration, the amount of soluble oxalate decreased remarkably. When heating the original pulp sample back to the process temperature before filtration, the recovery of soluble oxalate could be somewhat improved, but the amount was still less than half of the original. The explanation for this is the precipitation of calcium oxalate in the pulp sample over time, which is promoted by the temperature drop. This fairly rapid precipitation of the newly formed soluble oxalate has been observed also previously by Ulmgren and Rådeström (1997; 2001). It can thereby be concluded that in order to get a representative value for soluble oxalate in a specific process stage, the sample has to be filtered directly after sampling, which is also recommended in the SCAN 39:05 (2005) method description.

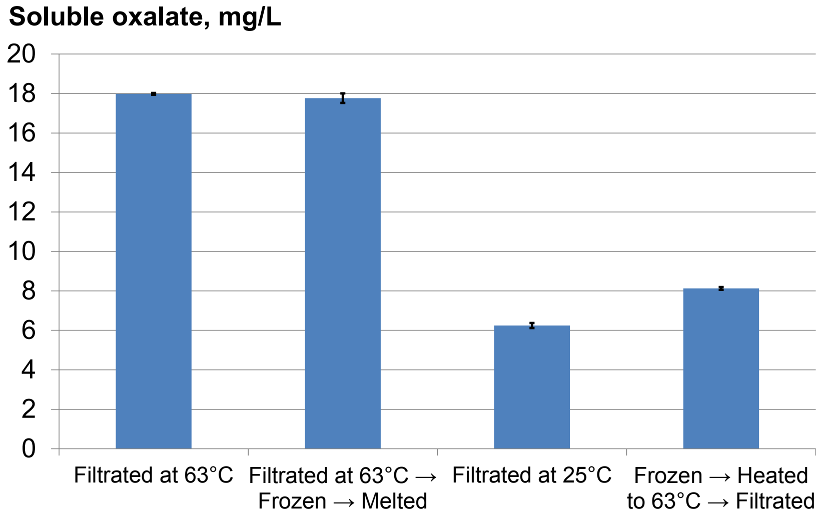


Figure 4.1 Effect of sample pretreatment procedure on soluble oxalate analysis by IC (peroxide-bleached groundwood pulp) (II).

4.1.2 Total oxalate (II)

The effect of sample pretreatment method on total oxalate analysis is shown in Fig. 4.2. It can be seen that the time delay and temperature drop between sampling, acidification, and filtration did not have a major effect on the analysis result for total oxalate. This indicates that the precipitated oxalate in the sample is still fairly easily dissolved. Heating the frozen pulp sample to the process temperature before acidification and filtration somewhat increased the analyzed oxalate value due to the increased solubility of precipitated calcium oxalate. Thereby this procedure is recommended for total oxalate analysis of pulp samples in order to maximize the recovery.

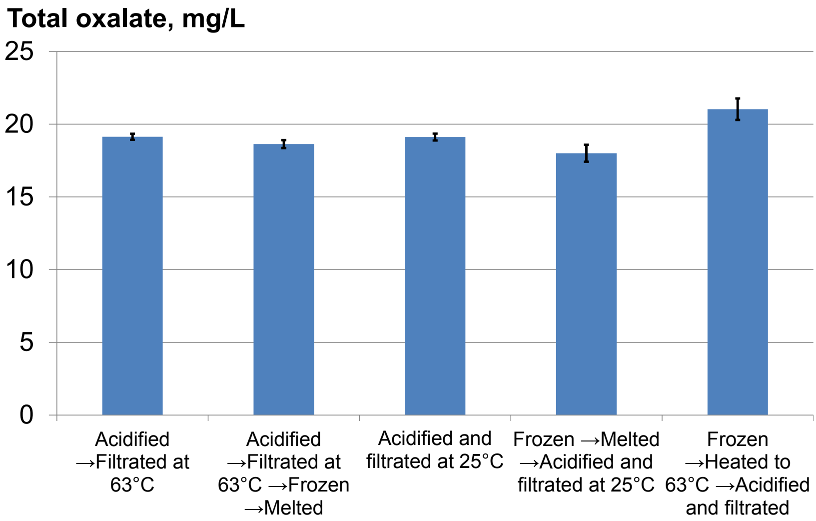


Figure 4.2 Effect of sample pretreatment procedure on total oxalate analysis by IC (peroxide-bleached groundwood pulp) (II).

As some minor variations in the total oxalate analysis results were observed when the end-pH was varied in the acidification, some oxalate recovery experiments were carried out. In these, calcium oxalate precipitation was induced in a 1% suspension of unbleached groundwood pulp, by adding known amounts of oxalic acid (50 mg/L as oxalate) and calcium chloride (200 mg/L as calcium). Calcium oxalate was allowed to precipitate over 20 h under mixing and different acidification methods were applied in order to recover the oxalate for IC analysis. Fig. 4.3 shows that only about 10% of the total oxalate was in a soluble form after the induced precipitation (Blank). Decreasing the pH in the acidification improved the oxalate recovery, and a further enhancement was obtained by heating and mixing of the sample at 70°C for 30 min. The highest total oxalate value was gained by acidification with 2 M HCl to pH 1 under heating and mixing. Good recovery was also obtained by the cation exchange resins. Drawbacks of using this type of resins are the fairly high consumption and the need to wash the resin properly before use. In addition, the analysis of metal ions like calcium in the same sample is not possible as these are bound to the resin.

These results show that if a strong precipitation of calcium oxalate has occurred in the pulp sample, also harsher acidification conditions are needed for total oxalate analysis. The acidification required for solubilization of all precipitated oxalate in the sample also depends on the hydrate form of calcium oxalate, as the more stable monohydrate is less soluble than the metastable dihydrate and trihydrate forms (Babić-Ivančić et al. 1985). Acidification of the sample with hydrochloric acid to pH 1 under heating and mixing should, however, be enough to dissolve all oxalate.

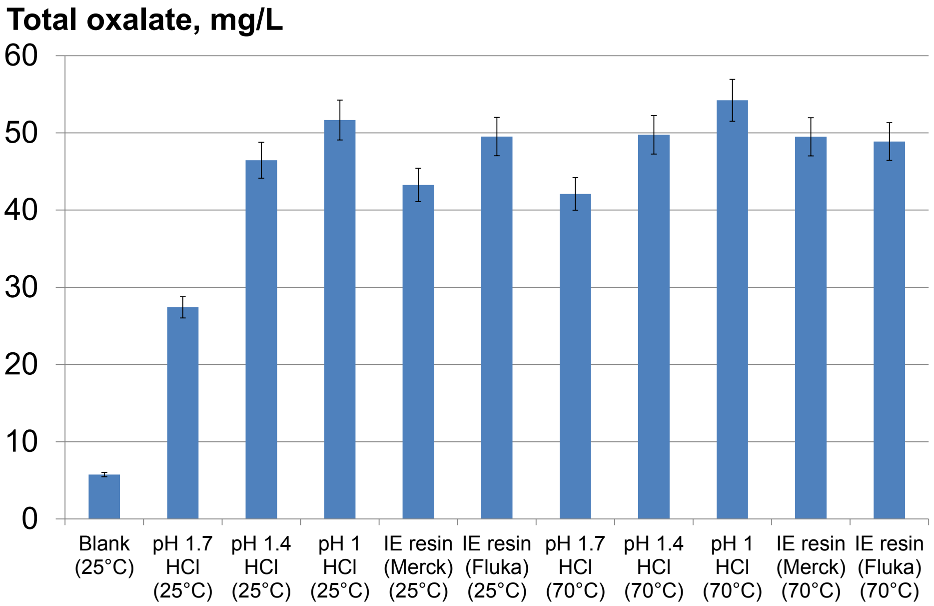


Figure 4.3 Effect of sample acidification method on oxalate recovery from unbleached groundwood pulp suspension for IC analysis (IE resin = cation exchange resin Amberlite IR-120) (II).

4.1.3 Oxalate balance case

In the mill, on which this work focused, a process modification was carried out so that a wire press was installed after the peroxide bleaching stage in order to clean the pulp going to the paper machine, and separate the water systems. Oxalate concentrations were monitored using the analytical methods described above, and the effects of the process change are shown in Fig. 4.4. It can clearly be seen that the oxalate concentrations on the pulp mill side have increased due to the stronger accumulation, also in the unbleached pulp. The wire press decreases the oxalate amount in the peroxide-bleached pulp to one third. This is reflected at the paper machine so that the oxalate concentrations in the machine chest and in the headbox have been decreased by 50% after the wire press installation. One explanation for the increased oxalate concentration in the pulp mill circulation might also be the fact that the calcium oxalate scaling was eliminated after the process change, leaving more soluble oxalate in the water phase. One obvious reason for the elimination of scale build-up was the decrease in concentration of dissolved calcium, as a result of filler and pigment system change at the paper machine.

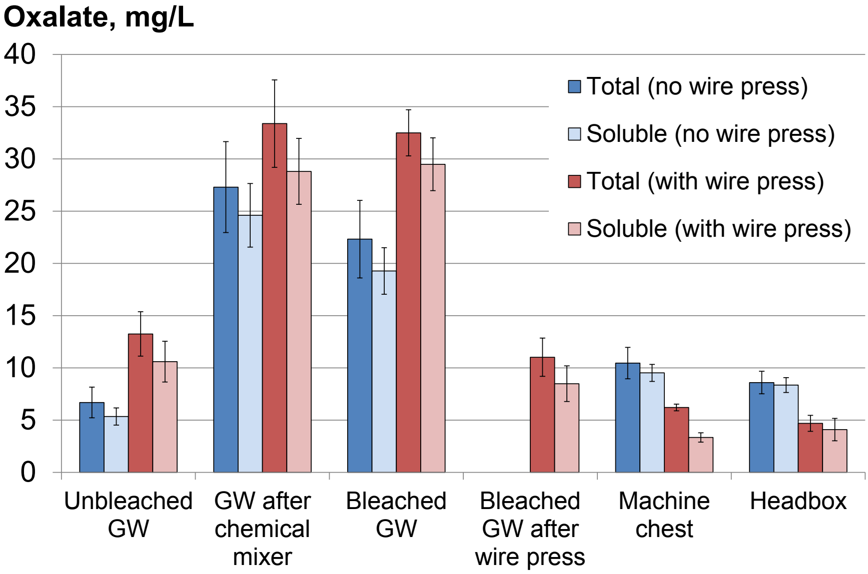


Figure 4.4 Average total and soluble oxalate concentrations in peroxide-bleached groundwood pulp line and on paper machine, before and after installation of a wire press after bleaching stage.

4.2 Oxalate formation in laboratory peroxide bleaching

Almost all new peroxide bleaching process installations include a dewatering and washing stage, e.g. a wire press, before bleaching at high consistency. However, processes using medium consistency bleaching still exist combined with a high-consistency peroxide bleaching or dithionite bleaching, depending on the brightness target (Germgård 2009). Therefore it was of interest to know how the amount of DCS, as well as the pulp consistency, affects oxalate formation in alkaline peroxide bleaching. Using $Mg(OH)_2$ as an alternative alkali source has already been commercialized for some time, and has proven to decrease calcium oxalate related scale problems. However, some contradictory information about its effect on oxalate formation still exists.

4.2.1 Effect of filtrate quality (II)

The unbleached GW pulp was peroxide-bleached at 10% consistency and different concentrations of the filtrate from the same pulp were used for dilution. The consistency of the original pulp sample was 28.5%, so some DCS were present also when 100% de-ionized water was used for additional dilution. Both the soluble and total oxalate amounts in the pulp after bleaching were analyzed. A pulp sample diluted with 100% de-ionized water that was treated in the same way, but without bleaching chemicals, was included as a reference (0% Unbleached in Fig. 4.5).

The amount of total oxalate formed as a result of alkaline peroxide bleaching was over 15 mg/L compared to the unbleached sample, when only de-ionized water was used for dilution (Fig. 4.5). This newly formed oxalate was mainly in soluble form. Increasing the unbleached pulp filtrate in the dilution water resulted in increased oxalate formation. This trend is not as clear for the soluble oxalate, most likely due to the increased calcium concentration. The relatively small amount of oxalate added with the filtrate was not responsible for this trend alone. If this amount is subtracted from the results, it is still 34% more oxalate that is formed with 75% filtrate in dilution water compared to dilution with pure de-ionized water. The most likely explanation for this difference is the high concentration of organic DCS in the filtrate, including hemicelluloses, low-molar-mass lignin-like substances, and pectic acids. These are easily available in the liquid phase to react with bleaching chemicals, and it has been shown that oxalate is formed as an oxidation product from these substances in alkaline peroxide bleaching (Sjöde et al. 2005; Yu, Ni 2005). It was also concluded by Fiskari (1999) that the composition of the DCS has a great impact on oxalate formation and not only their amount. It can be thereby of importance how the filtrate fractions are circulated in the peroxide bleaching process.

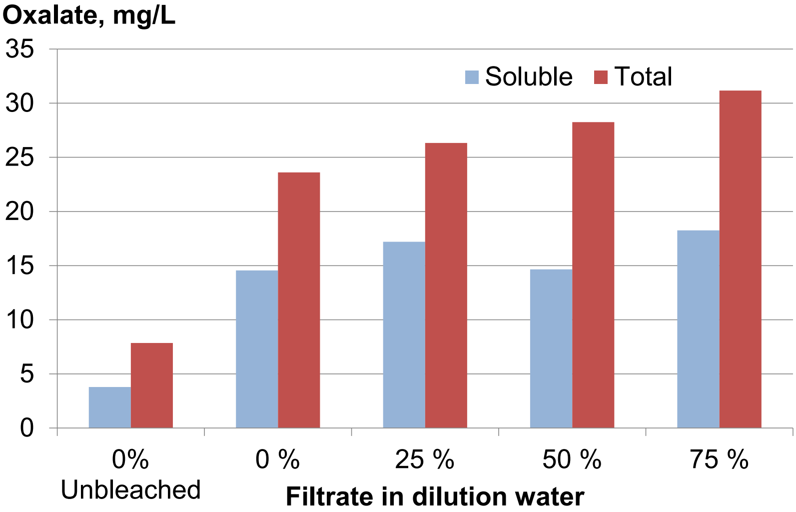


Figure 4.5 Effect of dilution water quality on oxalate formation in alkaline peroxide bleaching (II).

4.2.2 Effect of pulp consistency (II)

Data from the peroxide bleaching experiments carried out at different pulp consistencies are listed in Table 4.1. The increased brightness level with increased pulp consistency is clear, and this is also in line with previous findings, like by Behrooz et al. (2012). This is generally explained by the higher concentration of the bleaching chemicals around the fibers, and thereby better reactivity (Presley, Hill 1996; Germgård 2009). Accordingly for the same reason, also more oxalate is formed at increased pulp consistency, when the amount is given in mg/L for pulp volume (Fig. 4.6a). However, when the oxalate amount is calculated based on the dry content of the pulp, i.e. as mg/g, the trend is almost the opposite (Fig. 4.6b). So in fact less oxalate is formed from the same amount of pulp at higher pulp consistency. At the highest consistency of 25%, the soluble part of the total oxalate decreases significantly most likely due to the solubility limit.

Table 4.1 Data from peroxide bleaching experiments in different bleaching consistencies (II).

Consistency	End-pH	Res. Peroxide kg/t	Brightness ISO-%
10%	7.6	8.4	75.0
15%	7.4	7.5	75.9
20%	7.4	7.5	77.0
25%	7.5	7.5	77.5

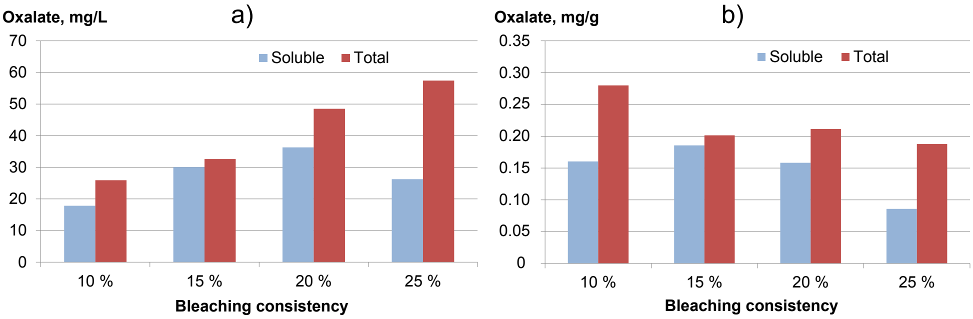


Figure 4.6 Amount of oxalate in different bleaching consistencies. a) as mg/L; b) as mg/g of dry pulp (II).

4.2.3 Mg(OH)$_2$ vs. NaOH as alkali source (II)

Oxalate formation was compared between NaOH/Na-silicate-based and Mg(OH)$_2$-based processes (Fig. 4.7). Unbleached pulp that was treated in the same way, but without bleaching chemicals, is included in the graph as a reference. The results show that about 10% less oxalate is formed when $Mg(OH)_2$ is used as alkali source, and a larger part of it is in soluble form compared with the NaOH/Na-silicate-based process. The difference in the amount can be explained by the lower alkalinity in the bleaching using $Mg(OH)_2$ alkali (more detailed bleaching data in paper II). High alkalinity caused by NaOH dosage has been shown to be the major parameter for oxalate formation in alkaline peroxide bleaching (Zhang et al. 2002; Yu, Ni 2005; Yu et al. 2005b; He et al. 2008). Magnesium ions, introduced by $Mg(OH)_2$ alkali, increase oxalate solubility by formation of magnesium oxalates, which are significantly more soluble than calcium oxalate (Ulmgren, Rådeström 1999b, Haque 2007). In addition, the more narrow pH profile observed in $Mg(OH)_2$-based process results in more even formation of oxalate during bleaching, and no sudden peak that could favor precipitation is obtained.

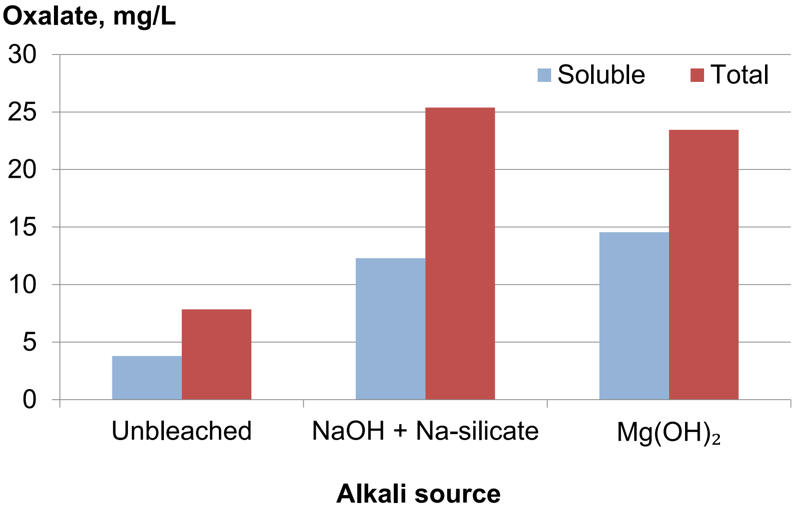


Figure 4.7 Effect of alkali source on oxalate formation in peroxide bleaching of groundwood pulp (II).

The same, or even higher brightness level was reached with $Mg(OH)_2$-based bleaching compared to NaOH/Na-silicate (II). The results also showed that $Mg(OH)_2$ worked well by itself, whereas Na-silicate was needed together with NaOH in order to reach the same level of brightness. This has also been observed in a mill-scale trial reported by Harrison et al. (2008), and is due to the stabilizing effect that magnesium ions have on peroxide against metal catalyzed decomposition (Lidén, Öhman 1997). $Mg(OH)_2$-based bleaching also generated over 30% less TOC than bleaching with NaOH/Na-silicate. This environmentally positive effect has been shown before both in laboratory and mill-scale studies

(He et al. 2004; Hietanen et al. 2013), and is explained mainly by decreased formation of acetic acid and methanol, as well as decreased lignin dissolution (He et al. 2004).

4.3 Oxalic acid formation from different wood components (III)

The oxidation reactions in alkaline peroxide bleaching are known to be the major source of oxalic acid in mechanical pulping processes. Both lignin and hemicelluloses, especially xylans, have been stated to be the main contributors to oxalic acid formation. Also an increased bark content in the pulp usually means higher oxalate content. The knowledge of oxalate sources in the alkaline peroxide bleaching stage is not only fundamental information, but can also give guidelines for planning of water circulations and the control of other organic dissolved and colloidal substances.

Monosaccharides, existing as units in cellulose, hemicelluloses, and pectins, were included in the experiments in order to clarify the possible differences between different polysaccharides, and the results are shown in Fig. 4.8. It has to be noted, however, that the monosaccharides are more easily degraded than their polymeric forms in wood components, and the results can be regarded only as directional. This applies especially for cellobiose that was used as a model compound for cellulose, as cellulose in wood is highly polymerized and crystalline, and therefore less easily degraded.

The results show that the acidic monosaccharides, i.e. galacturonic acid (GalA) and glucuronic acid (GlcA), result in the largest amount of oxalic acid formed in the alkaline peroxide treatment. GalA is the main unit in wood pectins, whereas GlcA mainly exists as a side group in arabinogalactans. In spruce xylans, the GlcA units contain a methyl group (4-*O*-MeGlcA). More oxalic acid was formed from pentoses, i.e. xylose (Xyl) and arabinose (Ara), compared to hexoses, i.e. mannose (Man), glucose (Glc), and galactose (Gal), which can be explained by the easier degradation of pentoses. These results indicate that spruce xylans, i.e. arabinoglucuronoxylans, most likely give rise to more oxalic acid than galactoglucomannans (GGMs). However, this difference is less significant when considering the content of xylans in spruce wood, which is only half of that of GGMs. The amount of oxalate formed from cellobiose was at the same level as for mannose, but due to the reasons mentioned above, this can be regarded only as a hypothetic maximum yield. Cellulose has not been found to be a major oxalate source in earlier studies (Krasowski, Marton 1983; Sjöde et al. 2005). Only a small amount of oxalic acid was formed from acetic acid. This indicates that the acetyl groups occurring naturally in hemicelluloses, and the deacetylation in alkaline conditions, does not have a major direct impact on oxalate formation during alkaline peroxide bleaching. However, a higher content of acetyl groups increases the water solubility of hemicelluloses, which means that they are more accessible for reactions with bleaching chemicals.

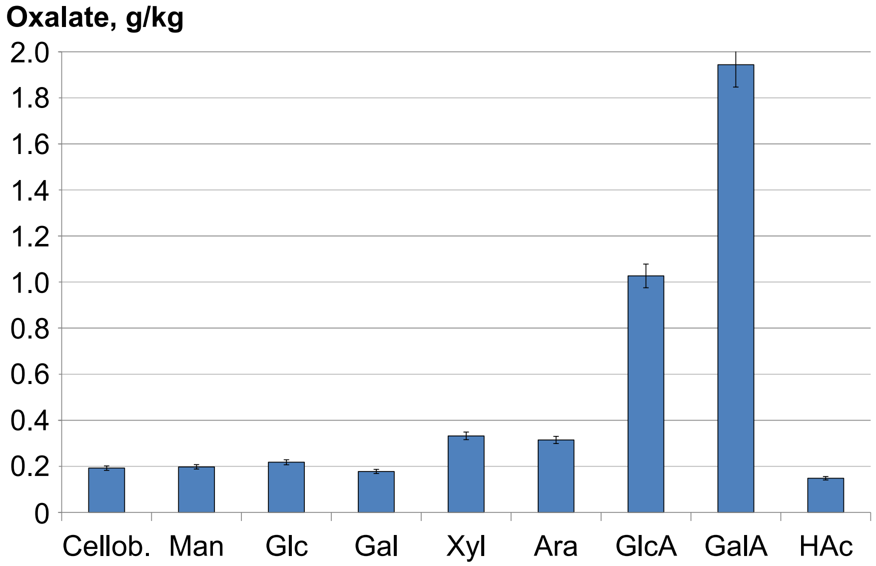


Figure 4.8 Oxalate formed in alkaline peroxide treatment of cellobiose, different monosaccharides, and acetic acid (95% confidence interval) (III).

Fig. 4.9 shows the amount of oxalic acid formed in the alkaline peroxide treatment of the isolated wood components and the oxalate content in the samples prior to the treatment (acidification only). It can be seen that the original oxalate content was substantial, especially in the commercial birch xylan preparate. One possible reason for this might be that the oxalate has been formed during the xylan isolation process, as a result of oxidation reactions during delignification. Another possible explanation is that birch bark has been included in the raw material. In an earlier study by Sjöde and co-workers (2005), large amounts of oxalate were analyzed also in another commercial birch xylan sample after alkaline peroxide treatment. However, the original oxalate content in the sample was not analyzed in that work, so the result evaluation is not totally reliable. The presence of bark or the outer region of sapwood is a possible explanation also for the fairly high oxalate content in milled wood lignin (MWL) and GGM samples. In order to verify that the acidification to pH 1 does not create any oxalic acid, the commercial birch xylan sample was also acidified to pH 2, both before and after the alkaline peroxide treatment, and the results were identical with pH 1. In addition, the effect of alkaline treatment without peroxide was studied with this sample, and this resulted in 83% less formed oxalate compared with the alkaline peroxide treatment (these results not shown).

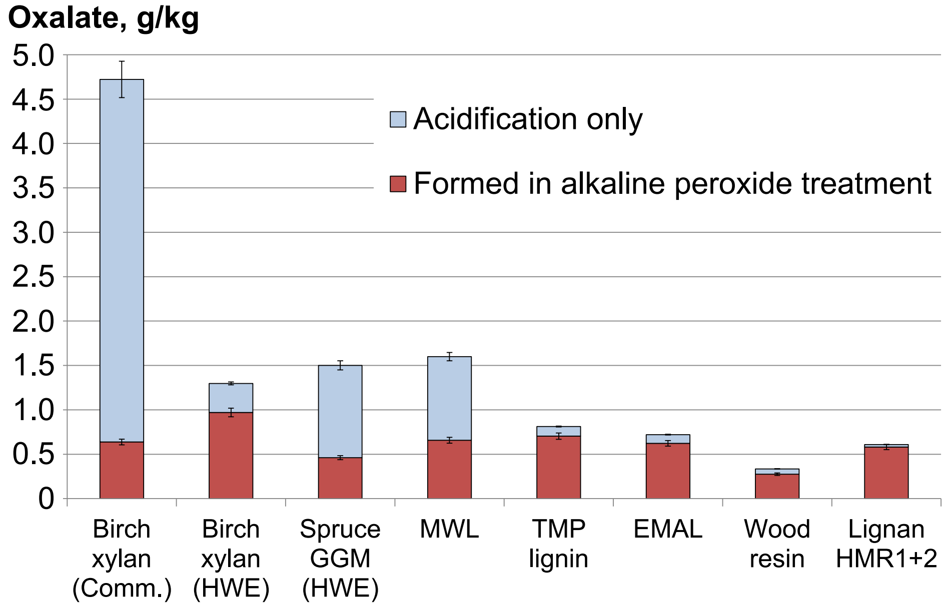


Figure 4.9 Oxalate formed from different wood-derived components in alkaline peroxide treatment, and the content in the samples prior to the treatment (acidification only) (95% confidence interval) (III).

The amount of oxalate formed in the alkaline peroxide treatment, shown in Fig. 4.9, has been obtained by subtracting the amount analyzed after acidification only, from the analyzed value after the treatment. Most oxalate was formed from hot-water extracted birch xylan sample, in which the native oxalate content was substantially lower compared to the commercial preparate. One has to remember that the isolated hemicelluloses always contain some aromatic, lignin-related impurities. All three lignin samples resulted in a similar amount of formed oxalate in alkaline peroxide treatment. Slightly smaller amount was formed from lignans, whereas the GGM and wood resin samples showed the lowest oxalate formation rate.

According to these findings, oxalic acid is mostly formed from aromatic compounds like lignin, as well as from hemicelluloses consisting of pentose and uronic acid units. As birch xylan was used instead of spruce xylan in this study, a comparison between these two substances has to be made. Spruce xylans, i.e.

arabino-4-*O*-Me-glucuronoxylans, contain on average two methyl glucuronic acid groups per 10 xylose units, which is twice as much as in birch xylans (4-*O*-Me-glucuronoxylans) (Sjöström 1993). Therefore the yield of oxalic acid from spruce xylan could be estimated higher than for birch xylan. However, it has been stated that both glucuronic acid and arabinose substituents stabilize the xylans against alkali-catalyzed degradation (Sjöström 1993), which would have an opposite effect.

The relevance of bark content in the wood raw material for oxalate intake becomes evident based on the results shown in Fig. 4.10. The original oxalate contents in outer and inner spruce bark were 13.5 g/kg and 5.5 g/kg, respectively, and relatively large amounts, compared to the isolated wood components, were further formed during the alkaline peroxide treatment. Outer bark has much higher content of lignin than inner bark, whereas the amount of cellulose, non-cellulosic polysaccharides, and hydrophilic extractives is larger in inner bark (Krogell et al. 2012). Galacturonic acid and arabinose are the dominating units in the inner bark polysaccharides. Therefore it might be that the oxalic acid formed in alkaline peroxide treatment of bark originates mainly from lignin in the case of outer bark, whereas the hemicelluloses and pectins could be the major source from inner bark. It can also be suggested that not only lignin, but also other aromatic compounds like tannins and other hydrophilic extractives are participating in oxalic acid formation.

In Fig. 4.10, a comparison has also been made between the bark samples and unbleached spruce groundwood pulp. The amount of oxalate originally in the groundwood pulp sample was small, under 0.1 g/kg. The oxalate amount formed in the alkaline peroxide treatment was smaller compared to xylan, lignin, and bark samples, but on the same level as for GGMs. The reason for the relatively low oxalate formation from groundwood pulp can be explained by the low accessibility of the key substances, i.e. lignin and hemicelluloses, in the pulp matrix compared to the isolated components. The bonding between the different substances also makes them less exposed for reactions and degradation.

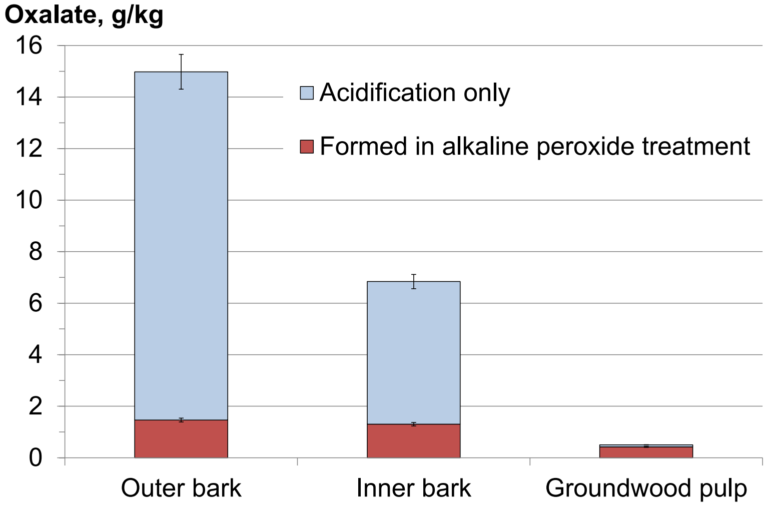


Figure 4.10 Oxalate detected in bark samples and in groundwood pulp before and after the alkaline peroxide treatment (95% confidence interval) (III).

The average contents of different components in spruce wood based on literature were shown in Table 2.1. Based on these values and the results described above, the theoretical contribution of different substances to oxalate formation during alkaline peroxide bleaching was calculated, and can be seen in Fig. 4.11. The values for bark and pulp samples include their original oxalate content, whereas for other components only the oxalate formed during the alkaline peroxide treatment has been regarded. The groundwood pulp has been calculated to represent 100% of spruce pulpwood, although a small part has been removed as dissolved and colloidal substances. Fig. 4.11 shows that lignin can be regarded as the largest single source of oxalate in alkaline peroxide bleaching of mechanical pulps from Norway spruce. Hemicelluloses, i.e. GGMs and xylans, as well as pectins, are also significant sources, especially when considering their substantial occurrence in dissolved and colloidal form. This makes them well exposed for reactions with bleaching chemicals. Also dissolved lignans can reach high concentrations in closed systems (Holmbom, Sundberg 2003), which can additionally contribute to oxalic acid formation. The contribution of spruce xylans is only an estimation, as birch xylan was used in the experiments. As discussed before, the higher content of uronic acid units in spruce xylans would lead to increased oxalate formation, whereas the higher stability and lower water solubility would decrease it. As the experiments with cellobiose showed, some oxalate can be assumed to be formed as a result of cellulose degradation in alkaline peroxide bleaching conditions. However, due to the lower reactivity of native cellulose in wood compared to isolated cellobiose, the real contribution to oxalate formation can be expected to be much lower.

From the high values presented for bark, especially for outer bark, it is clear that the debarking process before mechanical pulping is critical. Some bark will always be present in the wood after debarking, because the wood losses would otherwise be too high. The bark content values that have been used in the calculations (Fig 4.11) were 0.2% for outer bark and 0.5% for inner bark. For mechanical pulp, the acceptable bark content has been evaluated to be 0.2-0.5% (Kostinen 2000). Seasonal variations of oxalate intake can occur as frozen or dry logs are more difficult to debark. The residues from saw mills are often used as a raw material for TMP production. These are the outer parts of the wood logs, which means that they also include bark residues after debarking (Brännvall 2009). In these cases, also the oxalate content of the wood raw material can be much higher. The contribution of wood resin, lignans, and acetic acid to oxalate formation can be regarded as marginal. When the theoretical values for all the individual wood components are added up, the sum is quite close to the value calculated for the groundwood pulp, where the substances are much less available for reactions with the bleaching chemicals.

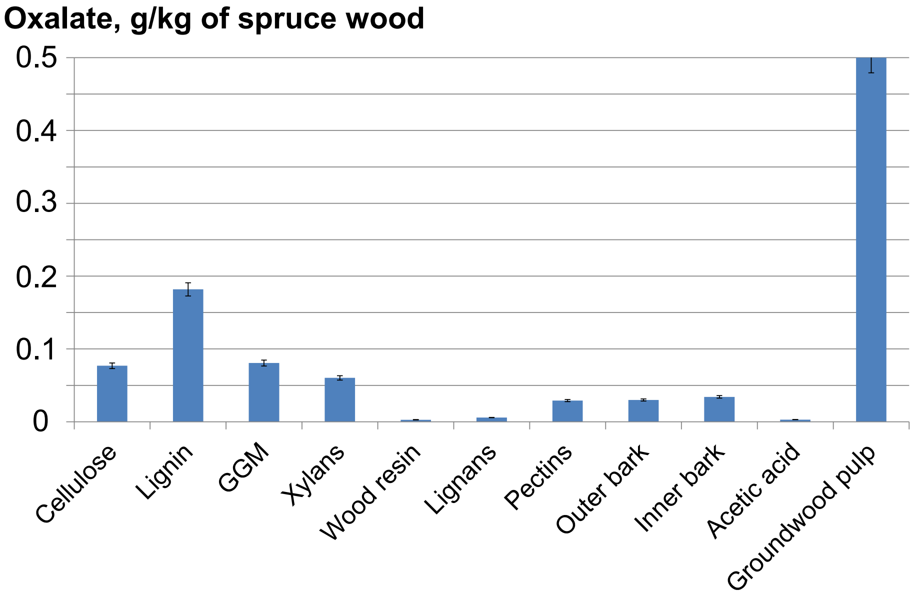


Figure 4.11 Relative contribution of different wood components on oxalate formation in alkaline peroxide treatment, based on their average content in spruce listed in Table 2.1. (The average content values used in the calculations for the individual components were the following: cellulose: 40%; lignin: 27.5%; GGM: 17.5%; xylans: 7.5%; wood resin: 1%; lignans: 1%; pectins: 1.5%; outer bark: 0.2%; inner bark: 0.5%; acetic acid: 2%; groundwood pulp: 100%) (95% confidence interval) (III).

4.4 Factors affecting calcium oxalate precipitation

On-line turbidity monitoring and flow cytometry analysis were the principal tools used for studying calcium oxalate precipitation in this work. Turbidimetric measurement has proven to be a simple and convenient method with good reproducibility, giving an indirect estimation of the crystallization kinetics (Hennequin et al. 1993; 1997; Kavanagh et al. 2000). The same conclusions can be made regarding the experiments in this work. It has to be noted, however, that any direct conclusions regarding the size, number, or shape of the formed particles cannot be drawn based on turbidity only. This also concerns the underlying crystallization mechanisms, i.e. nucleation and crystal growth (Kavanagh et al. 2000).

The turbidity monitoring curves from mixing of calcium chloride and sodium oxalate solutions in a clean de-ionized water system, at different calcium concentrations and an oxalate concentration of 1 mmol/L, are shown in Fig. 4.12. The results show that calcium oxalate precipitation takes place very quickly after addition of oxalate ions as the last component. As the calcium concentration was increased, the turbidity slope was sharper, and the end-turbidity was higher. At a calcium concentration of 2 mmol/L, the maximum turbidity value is already reached after 1 min reaction time, after which the system is stabilized and there is no sign of crystal aggregation that would decrease turbidity. Only a minor effect was observed by increasing the calcium concentration further, indicating that all the oxalate in the solution had been consumed. These experiments were carried out at room temperature and pH 5.8-6. The effect of temperature and pH on the calcium oxalate precipitation detected by turbidity monitoring was also tested. No precipitation was observed at pH 2, but already at pH 4 the maximum precipitation rate was reached (results not shown). This is because the divalent oxalate ion does not start to form until round pH 2, but already dominates after pH 4 (Fig. 2.2.) Increased temperature in the experiments decreased the precipitation rate due to the improved calcium oxalate solubility (results not shown).

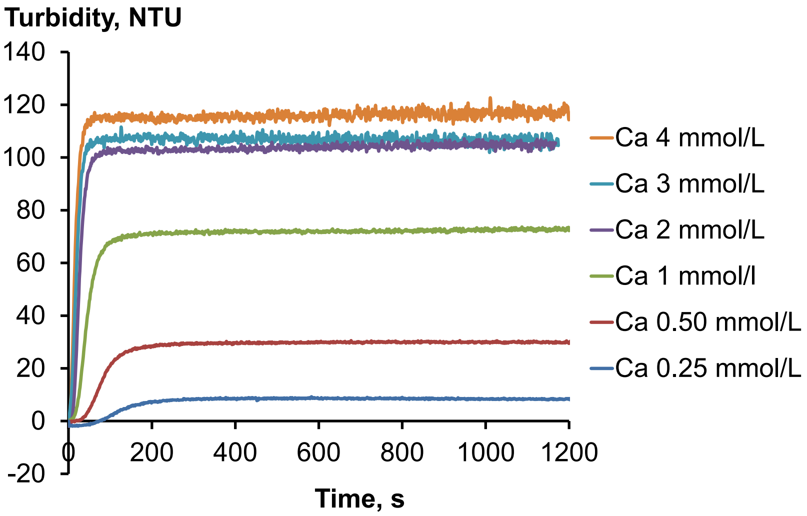


Figure 4.12 Turbidimetric monitoring of calcium oxalate precipitation at different calcium ion concentrations. (pH 5.8-6.0; 23°C; $C_2O_4^{2-}$: 1 mmol/L).

The amount of calcium oxalate precipitate formed at different calcium concentrations was determined, and the results are shown in Fig. 4.13. According to the XRD analysis of the precipitate, only calcium oxalate monohydrate (COM) was formed. The theoretical value for 1 mmol/L of COM in a solution corresponds to 146 mg/L, so the determined values up to 1 mmol/L calcium concentration are quite close to this. Only a minor increase in precipitate amount is observed by increasing calcium concentration further.

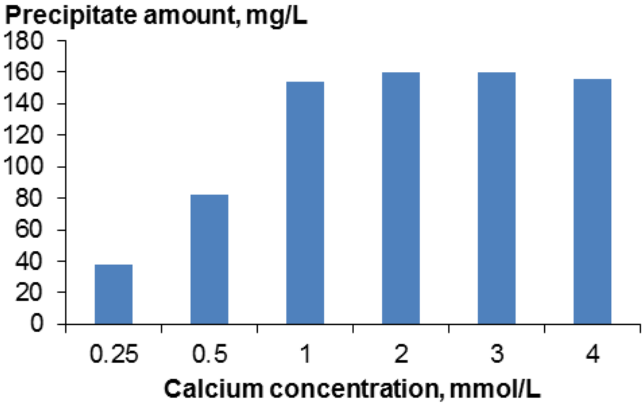


Figure 4.13 Amount of calcium oxalate precipitate at different concentrations of calcium (pH 5.8-6.0; 23°C; $C_2O_4^{2-}$: 1 mmol/L).

4.4.1 Magnesium (IV)

Addition of magnesium ions decreased the calcium oxalate precipitation rate as detected by turbidity measurements (Fig. 4.14). Only a slight effect was obtained at 1 mmol/L magnesium concentration, but an addition of 2 mmol/L already gave a significant decrease, indicating a threshold concentration. The precipitation rate was further decreased by increased magnesium concentration, but the effect started to level out. The inhibiting effect by magnesium ions can be explained by the formation of magnesium oxalates, which have much higher solubility in water compared to calcium oxalate (Ulmgren, Rådeström 1999b).

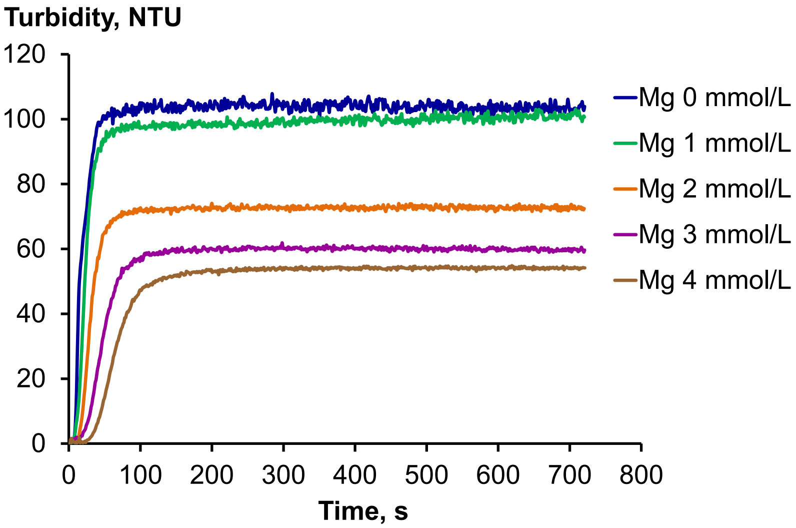


Figure 4.14 Effect of magnesium ions ($MgCl_2 \cdot 6\ H_2O$) on calcium oxalate precipitation (Ca^{2+}:3 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

The size distributions of the precipitated calcium oxalate particles at different magnesium concentrations are shown in Fig. 4.15. The curves represent smoothened histogram data of the side scattering plots from the FCM analysis. It can be seen that magnesium addition decreased the number of calcium oxalate particles formed, and the effect is clear especially in the particle size range > 2 µm. However, relatively large particles up to the size of 20 µm could still be detected at the highest magnesium concentration of 4 mmol/L. The results described above are from experiments with magnesium chloride, but similar effects were also obtained by magnesium sulfate ($MgSO_4 \cdot 7\ H_2O$). This compound, also known as Epsom salt, is commonly used as an additive in peroxide bleaching. However, considerably larger amounts are needed for calcium oxalate scale control, than is normally used for peroxide stabilization purposes (Terelius et al. 2001a; Yu, Ni 2007). This can also be understood from the results from this work, which indicate that a molar ratio between magnesium and calcium ions should be at least 2:3 in order to get a significant effect on calcium oxalate precipitation rate.

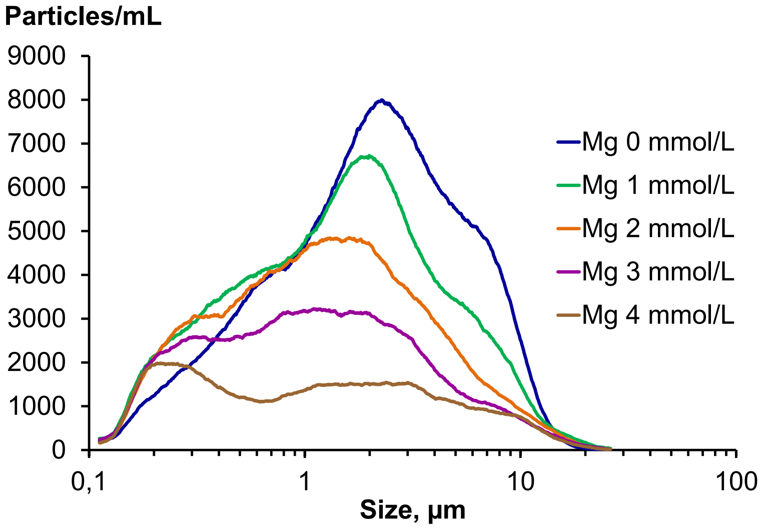


Figure 4.15 Effect of magnesium ions ($MgCl_2 \cdot 6\ H_2O$) on calcium oxalate particle size distribution determined by FCM (Ca^{2+}:3 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

The XRD analysis of the precipitates revealed that mixing of calcium chloride and sodium oxalate solutions in the used test system resulted in precipitation of COM. When magnesium ions were introduced either as magnesium chloride or magnesium sulfate, the hydrate form changed to trihydrate (COT). This is an important observation, as COT is a more soluble and less stable form than COM (Babić-Ivančić et al. 1985). A highly aggregated, film-like structure was formed on the membrane surface when the solution containing COM was filtered, whereas the COT containing precipitate formed a brittle, powder-like structure. The SEM-micrographs of the three different precipitates are shown in Fig. 4.16.

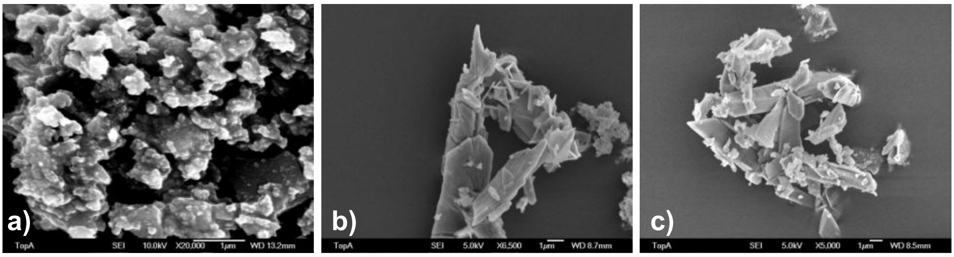


Figure 4.16 SEM-micrographs of calcium oxalate precipitates (bars indicating 1 µm): a) without magnesium: monohydrate (COM); b) with 4 mmol/L magnesium ($MgCl_2 \cdot 6\ H_2O$): trihydrate (COT); c) with 4 mmol/L magnesium ($MgSO_4 \cdot 7\ H_2O$): COT. (Ca^{2+}: 3 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

4.4.2 Colloidal wood resin (IV)

When the colloidal wood resin was added to the test solution, an increase in start-turbidity was observed so that the highest resin addition of 46 mg/L resulted in a start-turbidity of 143 NTU at pH 5, and 116 NTU at pH 8. This naturally affected the precipitation monitoring, and therefore the start-turbidity values were subtracted from the monitoring results. The resulting curves are shown in Fig. 4.17 for experiments at pH 5. The initial turbidity increase observed during the first minute after the addition of calcium chloride solution can thus be regarded solely as a result of calcium oxalate precipitation. Without wood resin addition, the turbidity was quickly stabilized to the maximum level (~ 80 NTU) after a short reaction time, as already shown earlier (Fig. 4.12). The turbidity increase in the initial stage was diminished by an increased addition of wood resin, indicating an inhibiting effect of the resin on calcium oxalate precipitation. However, after the maximum turbidity level was reached, the turbidity started to decrease gradually, the slope being sharper at higher wood resin addition. There are two possible explanations for this behavior: either the formed calcium oxalate crystals are aggregated, or the amount of colloidal wood resin in the solution is decreasing. The latter explanation is supported by the fact that the turbidity was decreased even below the initial level at the highest wood resin addition. The reasons for the decreased amount of wood resin with colloidal dimensions are calcium-induced aggregation, as well as adsorption on calcium oxalate particle surfaces. It is highly probable that both of these phenomena take place already in the initial stage of the experiment. Therefore, no direct conclusions about the effect of wood resin on calcium oxalate precipitation rate can be made only based on the turbidimetric monitoring in this case.

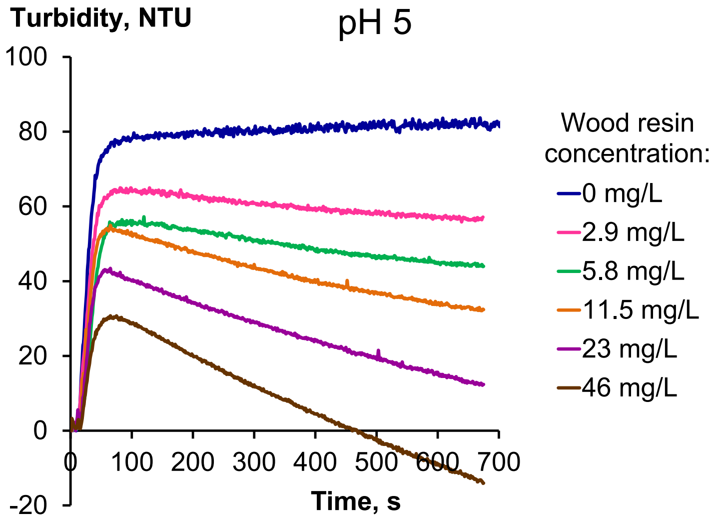


Figure 4.17 Relative effects of wood resin concentration on calcium oxalate precipitation at pH 5 and 23°C. The data indicates the relative changes in turbidity. (Ca^{2+}: 2 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

The particle size distribution curves from FCM analysis confirm that wood resin addition indeed decrease calcium oxalate precipitation (Fig. 4.18). There are two particle populations that can be distinguished, i.e. in the size ranges of 0.15-0.3 µm and 1-4 µm. The effect of wood resin can already be seen with the lowest addition of 2.9 mg/L, and especially in the larger particle size range, which mainly includes calcium oxalate particles formed as a result of continued crystal growth or aggregation. Calcium oxalate particles in the smaller sized fraction can be regarded as newly formed crystals or even nuclei. However, one has to bear in mind that any free colloidal wood resin present in the system will contribute to the amount of particles at this particle size range (Sundberg et al. 1996b), and that particles smaller than 0.1 µm are not detected by the FCM analyzer. An excess of free colloidal resin remaining in the water phase can be seen as a high peak at the highest resin addition level (46 mg/L).

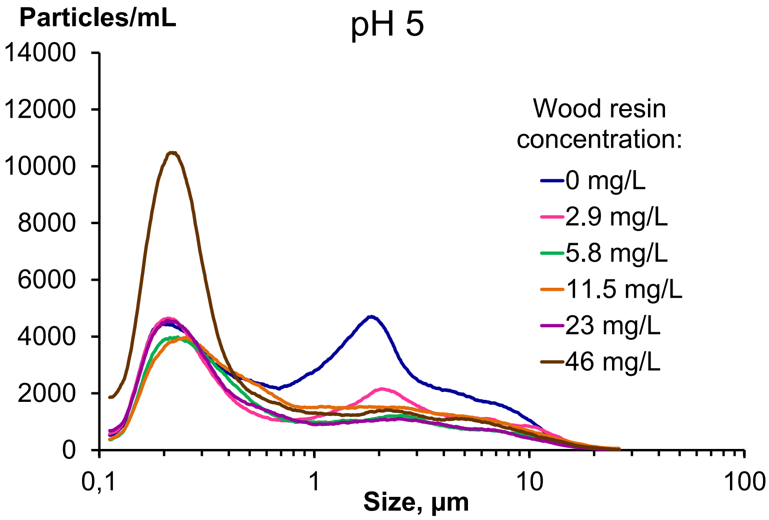


Figure 4.18 Effect of wood resin on calcium oxalate particle size distribution at pH 5 and 23°C (FCM side scattering) (Ca^{2+}: 2 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

Fig. 4.19 shows the development of particle hydrophobicity when an increasing amount of colloidal wood resin is added to the system. In these density plot diagrams, every individual particle is plotted according to its fluorescence value in the FL3 channel (= hydrophobicity) and forward scattering (FSC) (= size) value. The plot color is changed in the order of light blue → dark blue → green → yellow → red, with increasing number of particles in that area. Without added resin (upper left diagram), the same two calcium oxalate particle populations can be detected as seen in size distribution curves earlier (Fig. 4.18), and both of these fractions show very low hydrophobicity. When wood resin is added, the hydrophobicity of the particles is increased, especially in the larger sized population, which includes larger crystals and aggregates. Agglomerated wood resin particles, as well as different co-precipitates between wood resin and calcium oxalate, are most likely included in this fraction. The hydrophobicity of the smaller calcium oxalate crystals is increasing slowly with increasing wood resin addition. At the same time a third separate population representing free colloidal wood resin is appearing (Vähäsalo et al. 2003). All three different populations are marked in the lower right plot diagram (Fig. 4.19), where they can be best distinguished.

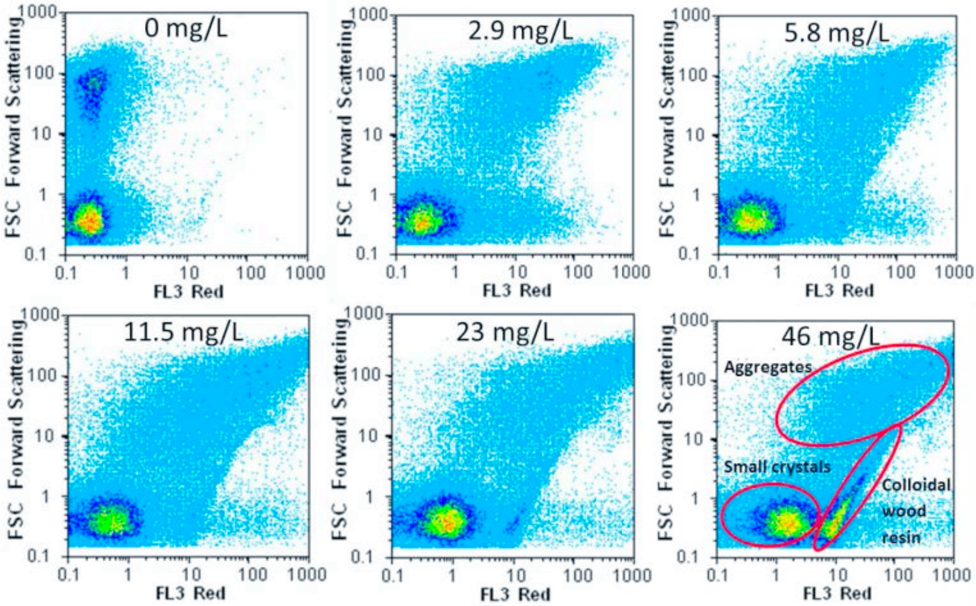


Figure 4.19 Effect of wood resin addition on hydrophobicity of particles in calcium oxalate precipitation experiments at pH 5 shown as FCM density plots in FL3 Red fluorescence channel (= hydrophobicity) and forward scattering (FSC) (=size) (Ca^{2+}: 2 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

In order to further clarify the results described by the density plots (Fig. 4.19), the hydrophobicity data is also presented as distribution curves in Fig. 4.20. These curves are based on smoothened histogram data. Two particle populations, based on their hydrophobicity, can be separated in the curves. The one on the left is representing the calcium oxalate particles, and the one on the right originates from the colloidal wood resin. It can clearly be seen that the hydrophobicity of the calcium oxalate particles is increased with increasing addition of wood resin. On the other hand, the peak for wood resin remains almost on constant level up to an addition of 23 mg/L, a phenomenon already seen in the size distribution curves (Fig. 4.18). Based on these observations it can be concluded that the colloidal wood resin interacts with calcium oxalate either by adsorption or co-precipitation, rendering the formed particles more hydrophobic.

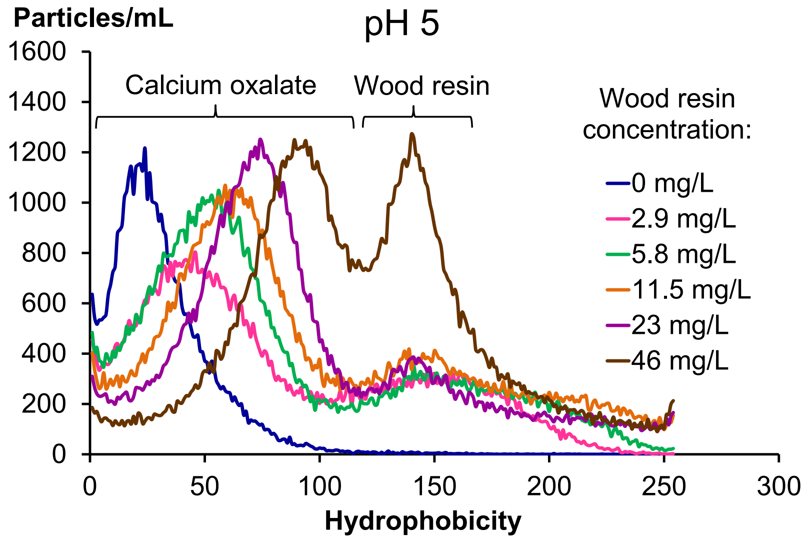


Figure 4.20 Hydrophobicity of particles with different colloidal wood resin addition levels. (Ca^{2+}: 2 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

The corresponding effects of colloidal wood resin at pH 8 have been described in more detail in paper IV. Overall, larger amount of resin was needed to get the same effect as observed at pH 5, and also more resin remained as free colloidal particles in the water phase. This was explained by the different behavior of resin at different pH, and higher stability against calcium-induced aggregation at pH 8 compared to pH 5, as observed by Sundberg et al. (2009) and Strand et al. (2011).

4.4.3 Galactoglucomannans (GGMs) (IV)

Dissolved GGMs have been shown to interact with colloidal wood resin in mechanical pulping so that the colloidal resin droplets are stabilized by sterical mechanisms (Sundberg et al. 1994; Hannuksela, Holmbom 2004). However, the effects of GGMs on calcium oxalate precipitation have not been investigated earlier. In this chapter, the results from studies with GGMs with and without colloidal wood resin are presented.

Fig. 4.21 shows the turbidity monitoring curves from the precipitation experiments with no wood resin added (left), and at a resin concentration of 23 mg/L (right). The experiments were carried out at two GGM addition levels, i.e. 100 and 200 mg/L, both at pH 5 and pH 8. The initial turbidities in the wood resin system were 69 NTU at pH 5, and 55 NTU at pH 8, and these values have been subtracted from the monitoring readings. The results show that already a 100 mg/L addition of GGMs increased the calcium oxalate precipitation rate as monitored by turbidity measurement, and a much higher end-turbidity value was reached. In the system without wood resin, no difference between pH 5 and pH 8 was observed, and also no further effect was seen by increasing the GGM addition to 200 mg/L. In the wood resin containing system, the decreasing trend in turbidity after the initial precipitation, indicating adsorption and aggregation of colloidal wood resin, is eliminated by a GGM addition of 100 mg/L at pH 5. The higher addition level of 200 mg/L is required at pH 8 to get the same effect, confirming that more GGM is needed to stabilize colloidal wood resin in the water phase.

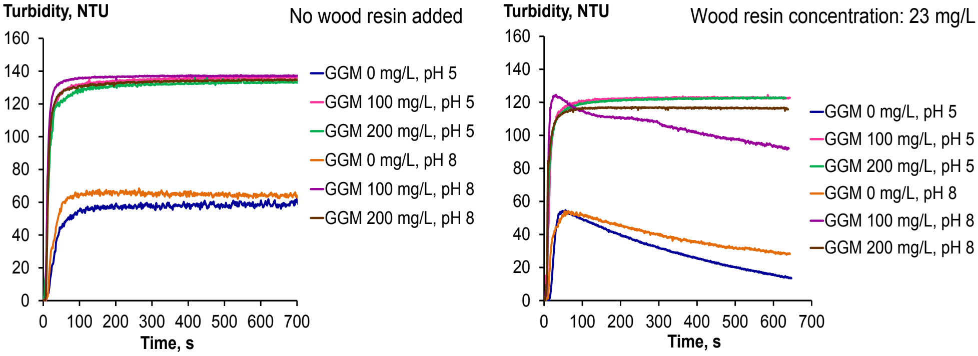


Figure 4.21 Effect of galactoglucomannans (GGMs) on calcium oxalate precipitation at pH 5 and at pH 8 without wood resin (left) and with 23 mg/L wood resin (right) (Ca^{2+}: 2 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

The results showing the effects of GGMs on calcium oxalate particle size distribution (Fig. 4.22), explain the results from the turbidimetric monitoring. The addition of GGMs clearly decreased the particle size so that more colloidal sized particles were formed, whereas particles > 3 µm are eliminated, both at pH 5 and pH 8, in the system without wood resin. In the presence of wood resin and a GGM concentration of 100 mg/L, particles > 4 µm are still formed at pH 8, but these are eliminated by an increased GGM addition. These results show that GGMs inhibit calcium oxalate crystal growth and aggregation, although the precipitation is not eliminated. It is possible that the GGMs are also adsorbed on calcium oxalate particles, as this has previously been shown to happen in case of clay and talc (Willför et al. 2000).

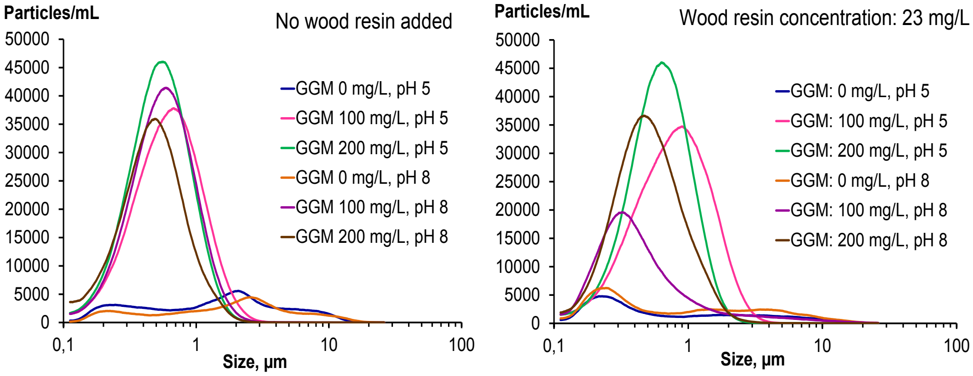


Figure 4.22 Effect of galactoglucomannans (GGMs) on calcium oxalate particle size distribution at pH 5 and at pH 8 without wood resin (left) and with 23 mg/L wood resin (right) (Ca^{2+}: 2 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

In Fig 4.23 and Fig. 4.24, the effect of GGM addition on particle hydrophobicity at 23 mg/L wood resin concentration is shown. It can be seen that the large particle fraction with high hydrophobicity, consisting of large crystals and aggregates with adsorbed wood resin, is eliminated by a GGM addition of 100 mg/L at pH 5 and 200 mg/L at pH 8. Increased addition at pH 5 is further decreasing the particle hydrophobicity.

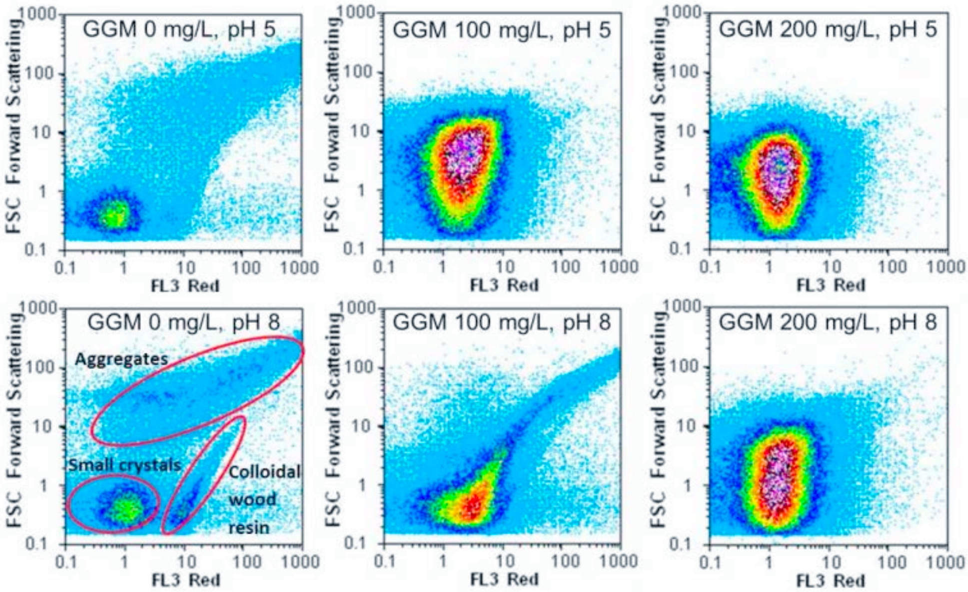


Figure 4.23 Effect of GGM addition on the hydrophobicity of particles in calcium oxalate precipitation experiments in presence of wood resin (23 mg/L) at pH 5 and 8 shown as FCM density plots in FL3 Red fluorescence channel (= hydrophobicity, FSC=size) (Ca^{2+}: 2 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

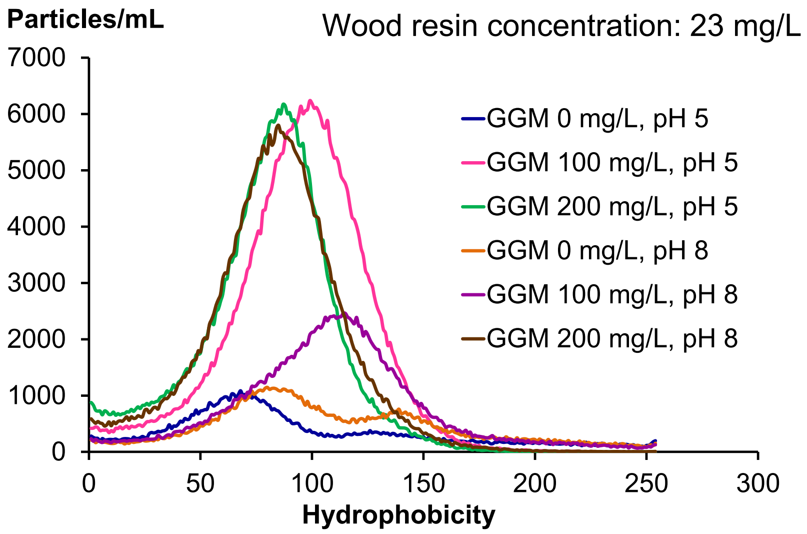


Figure 4.24 Effect of GGM on hydrophobicity of particles at pH 5 and at pH 8 with 23 mg/L wood resin (Ca^{2+}: 2 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

The XRD analysis revealed that in a pure system, where only calcium chloride and sodium oxalate solutions were mixed, the precipitates were in form of COM, and there was no difference between pH 5 and pH 8. The presence of wood resin changed the precipitate form to COT. The hydrate form was not affected by the addition of GGM, but the crystallite size decreased significantly in both cases. This is visualized in the SEM-micrographs in Fig. 4.25.

The results described above show clearly that there is a strong interaction between colloidal wood resin, GGMs and the precipitating calcium oxalate crystals. Wood resin is adsorbed on the calcium oxalate particle surfaces, making them more hydrophobic, while GGMs tend to stabilize both the resin and the small calcium oxalate crystals. It can be concluded that the balance between wood resin and dissolved GGMs in the process is an important factor not only for pitch control, but also for calcium oxalate precipitation. One possibility would be to recover the GGMs from the unbleached mechanical pulp filtrates to be used for wood resin and/or calcium oxalate scale control, as the recovery has been proved to be technically possible (Willför et al. 2003).

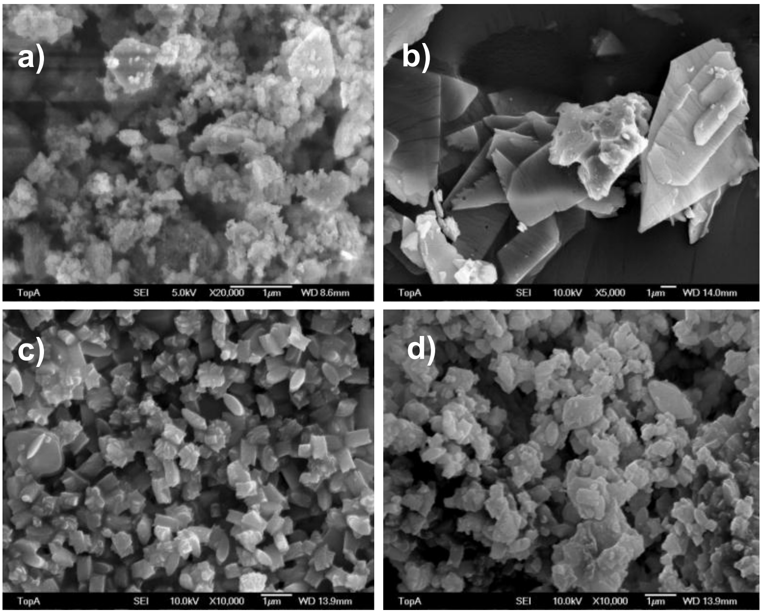


Figure 4.25 SEM-micrographs of calcium oxalate precipitates at pH 5 (bars indicating 1 μm): a) pure system with calcium and oxalate only: monohydrate (COM); b) with 23 mg/L wood resin: trihydrate (COT); c) with 200 mg/L GGM: COM; d) with 23 mg/L wood resin and 200 mg/L GGM: COT (Ca^{2+}: 2 mmol/L; $C_2O_4^{2-}$: 1 mmol/L) (IV).

4.5 Evaluation of anti-scaling agent performance

Anti-scaling agents, used for controlling inorganic deposits, work by several different mechanisms, and it is often challenging to obtain information about their way of working in different environments in normal laboratory screening. In this work, a combination of different analytical tools has been used to evaluate the effects of different types of anti-scaling agents on calcium oxalate precipitation. Flow cytometry and on-line turbidity monitoring were in key roles, while XRD and SEM were mainly utilized for crystal identification and visualization purposes. Product screening experiments were carried out first in a clean system, followed by addition of pulp filtrate, and ending up with tests and trial in a paper mill.

4.5.1 Laboratory screening in clean system (V)

Different additives were first screened in a de-ionized water system where calcium chloride and sodium oxalate solutions were mixed. In Fig. 4.26, the turbidity monitoring curves have been plotted against the Blank with no additive, and the results have been calculated to describe the inhibition rate in percentage.

100% inhibition rate means thereby that no precipitation detected by turbidimetric measurement has occurred. Significant differences in efficiency were observed between the different additives, as some had almost no inhibiting effect like Copolymer 1 (high-molar-mass) (Fig. 4.26a), whereas the best product, formulated Blend 1 (Fig 4.26b), inhibited the initial precipitation stage for almost 5 minutes. From the single component additives, PESA showed the best performance. It has to be noted that in these results the most important features for a product are the time for 100% inhibition, as well as the sharpness of the turbidity slope, a slower incline being better.

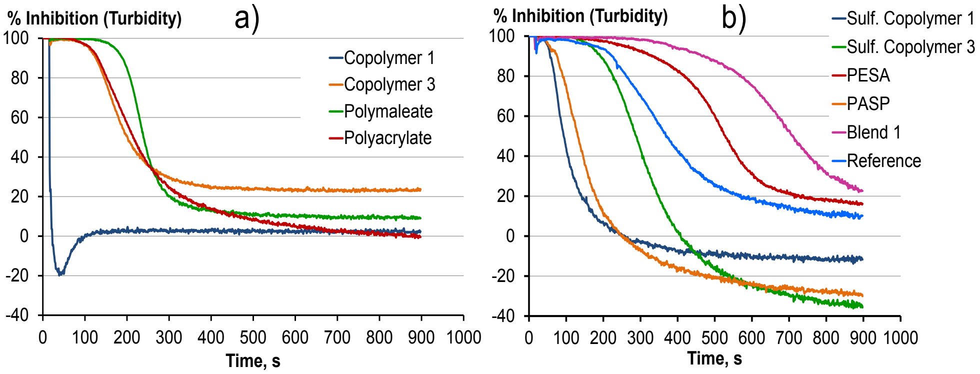


Figure 4.26 Calcium oxalate inhibition curves for different additives plotted from the turbidity monitoring curves against the Blank: a) acrylate/maleate copolymers and homopolymers; b) sulfonated copolymers, other polycarboxylates, and formulated anti-scaling products (V).

The end-turbidity is more dependent on the size of the formed particles, and therefore the negative values seen in Fig. 4.26 do not mean a negative effect. When looking at the calcium oxalate particle size distribution curves in Fig. 4.27, it can be concluded that FCM analysis and turbidity monitoring are complementary methods. For example, in the first product group (Fig. 4.27a), the polyacrylate that resulted in the highest end-turbidity had the most significant decreasing effect on the particle size. All particles formed upon addition of polyacrylate were below 1 µm, whereas in the Blank, the largest particles were over 10 µm. The strongest effect was obtained in the second product group (Fig. 4.27b) by Blend 1, as almost no calcium oxalate particles above 0.5 µm size were formed, and also the number of particles was the lowest. The ability of the product to keep the particle size small, can generally be regarded as beneficial, as this indicates inhibition of crystal growth and agglomeration.

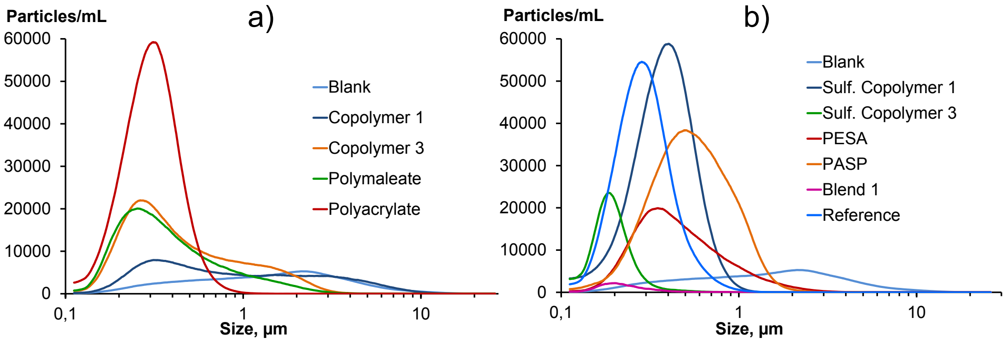


Figure 4.27 Effect of different additives on calcium oxalate particle size distribution by FCM: a) acrylate/maleate copolymers and homopolymers; b) sulfonated copolymers, other polycarboxylates, and formulated anti-scaling products (V).

XRD analysis of the precipitates revealed that all the additives, except Copolymer 1, changed the major calcium oxalate hydrate form from COM to COD (Table 4.2). In addition, some COT was co-precipitated. The hydrate form of calcium oxalate precipitate in an industrial process is an important parameter for scale build-up. COM has the highest stability and the lowest solubility of the three hydrates, and is commonly regarded as the most problematic form in industry and also in human kidney stones (Tomažič, Nancollas 1979; Babić-Ivančić et al. 1985; Ulmgren, Rådeström 2001).

Table 4.2 Calcium oxalate hydrate forms (by XRD and SEM) and the average particle/crystallite sizes determined by the different analytical tools (V).

Additive	Main hydrate	Minor hydrate(s)	FCM - Average particle size, µm	SEM - Average particle size, µm	XRD - Average crystallite size, nm
Blank	COM	-	2.04	1.50	320
Copolymer 1	COM	COD, COT	1.54	1.41	150
Copolymer 3	COD	COT	0.60	0.76	30
Polymaleate	COD	COT	0.49	0.38	20
Polyacrylate	COD	COT	0.32	0.38	20
Sulf. copolymer 1	COD	COT	0.40	0.37	110
Sulf. copolymer 3	COD	-	0.20	0.56	20
PESA	COD	COT	0.55	0.65	20
PASP	COD	COM, COT	0.60	0.79	20
Blend 1	COD	COT	0.22	0.60	30
Reference	COD	COT	0.31	0.46	20

The average particle and crystallite sizes, determined by FCM, SEM and XRD are also listed in Table 4.2. Due to the very small sample amount, the crystallite size results from XRD are only directional, and the quantification in the otherwise reliable hydrate form determination was not possible either. The average particle sizes determined by FCM and SEM showed good correlation. This proves FCM to be a reliable method, considering the fact that the crystals that were dispersed in FCM analysis, have inevitably been agglomerated during drying and disintegration of the sample for SEM analysis. SEM-micrographs of the precipitates formed in the Blank sample and in the presence of some selected additives are shown in Fig. 4.28. These show that not only the hydrate form and size of the crystals is affected by the different products, but also the particle shape and structure. Although the precipitate in the Blank was COM, only large and irregular particles could be detected instead of monoclinic crystals that are typical for this hydrate form (Fig 4.28a). This is, however, common in highly supersaturated systems as a result of rapid precipitation (Singh et al. 1988). A mixture of ball- and dumbbell shaped structures were typical in the presence of additives. A clearly different ellipse shaped COD structure was observed upon addition of sulfonated acrylate copolymer 1 (Fig. 4.28d).

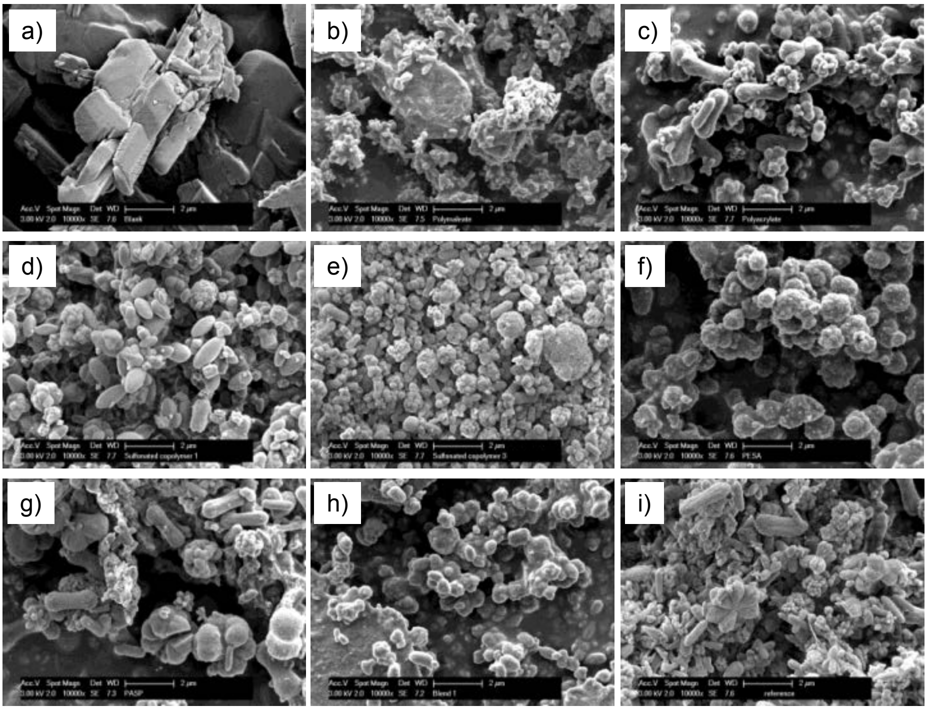


Figure 4.28 SEM-micrographs of calcium oxalate crystal structures produced in the Blank (without additives) and in presence of 100 ppm of different additives (bars indicating 2 μm): a) Blank; b) polymaleate; c) polyacrylate; d) sulfonated copolymer 1; e) sulfonated copolymer 3; f) PESA; g) PASP; h) Blend 1; i) Reference (V).

4.5.2 Effect of filtrate addition (V)

Due to the high concentration of colloidal wood resin (> 300 mg/L), the turbidity in the peroxide-bleached groundwood pulp filtrate was very high. Filtrate dilutions up to 20% (258 NTU) were used and the turbidity reading was reset to zero before starting the precipitation experiment. From the additives, only Blend 1 was tested in these experiments both in Blank (de-ionized water system) and in 10% filtrate dilution. The results from the turbidimetric monitoring in Fig. 4.29a indicate that already a 1% filtrate addition decreases the calcium oxalate precipitation rate. However, the behavior of wood resin, i.e. adsorption and changes in the particle size, also has an impact on turbidity. This makes the result interpretation more difficult. No significant changes were seen with increased filtrate concentration, where the calcium and oxalate concentrations were also somewhat higher. The inhibiting effect of Blend 1 was observed even more clearly in 10% filtrate dilution.

The particle size is gradually decreased by increased filtrate addition (Fig. 4.29b), which is partly due to the introduction of colloidal particles with a size distribution described by plain sample of 10% filtrate dilution (10% Filtrate Blank). However, as the maximum particle size is decreased from 20 µm without filtrate to 4 µm in 20% filtrate, it can be stated that the filtrate has an inhibiting effect on calcium oxalate crystal growth and aggregation. Blend 1 decreased the particle size also in the presence of 10% filtrate, resulting in a size distribution curve almost identical to the plain 10% filtrate.

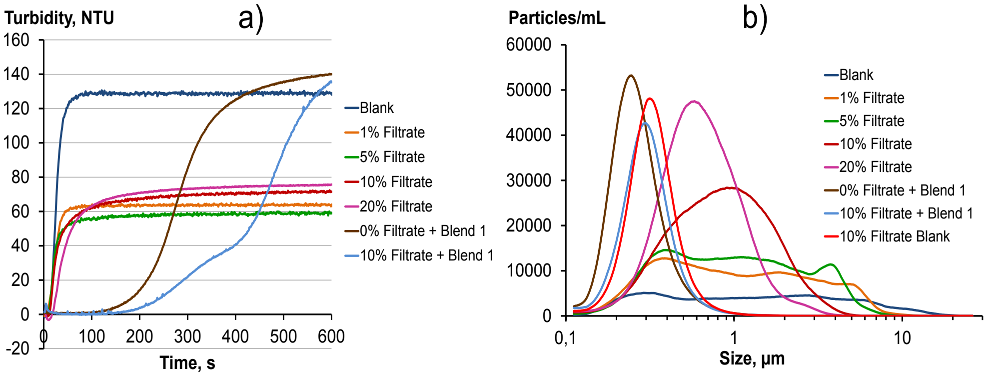


Figure 4.29 Effect of peroxide-bleached groundwood pulp filtrate on calcium oxalate precipitation: a) precipitation rate by turbidity monitoring; b) particle size distribution by FCM. (23°C, pH 7.5, added Ca^{2+}: 2 mmol/L; added $C_2O_4^{2-}$: 1 mmol/L; Blend 1: 100 ppm, when added) (V).

Increased filtrate concentration naturally increased the amount of hydrophobic particles in the test solution due to the introduction of colloidal wood resin (Fig. 4.30, row a). In the calcium oxalate precipitation experiments (Fig. 4.30, row b), three effects were observed by the filtrate addition. Firstly, the calcium oxalate particle size gradually decreased, as already seen in Fig. 4.29b. Secondly, the hydrophobicity of the formed particles increased. The third observation was that the amount of free colloidal wood resin detected in the plain filtrate dilutions decreased, which confirms that it is reacting with the calcium oxalate particles by adsorption, aggregation, or both. When Blend 1 was added without filtrate (Fig. 4.30, row c), only small crystals with low hydrophobicity were formed. When Blend 1 was added to 10% filtrate, the particle size of this fraction was somewhat decreased, and its hydrophobicity is clearly increased. In fact, this particle population overlaps with the colloidal wood resin particles that remain free in the solution, as there are not enough surfaces for adsorption. The FCM hydrophobicity data is also presented as curves based on smoothened histogram data in Fig. 4.31.

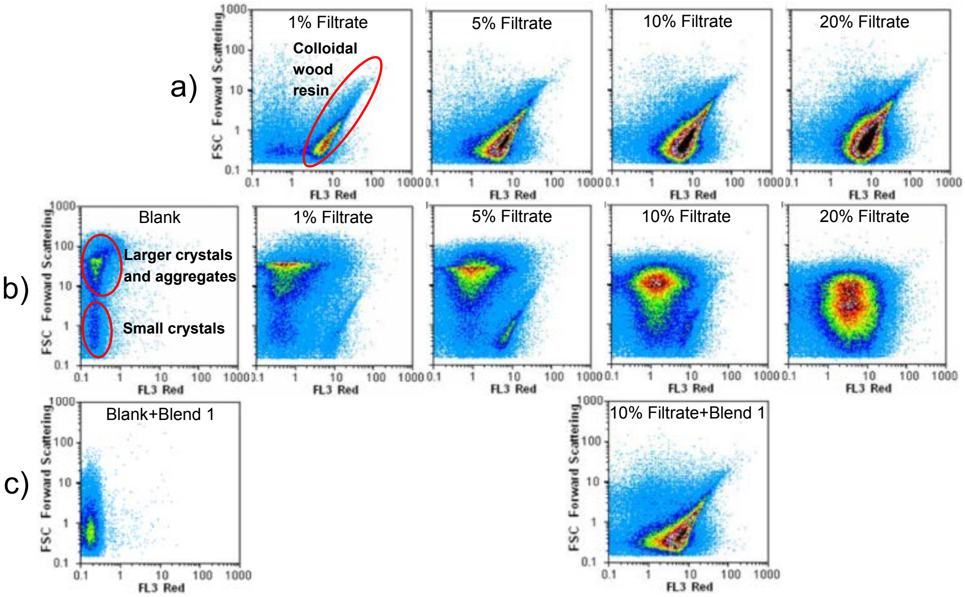


Figure 4.30 Effect of filtrate addition on hydrophobicity of particles shown as FCM density plots in FL3 Red fluorescence channel (=hydrophobicity, FSC=size): **row a)** only filtrate addition; **row b)** filtrate addition and calcium oxalate precipitates; **row c)** 100 ppm Blend 1 in blank and in 10% filtrate with calcium oxalate precipitates (V).

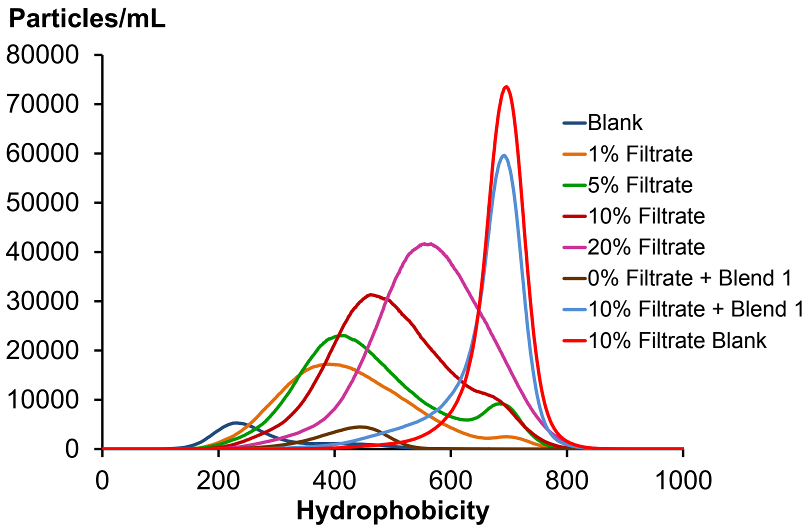


Figure 4.31 Effect of filtrate addition and Blend 1 additive on particle hydrophobicity presented as curves based on smoothened histogram data (V).

4.5.3 Mill trial monitoring (V)

Due to the implemented process changes described earlier in chapter 4.1.3, the risk for calcium oxalate precipitation and scale build-up in the mill in question had remarkably decreased. However, the oxalate titration method that was established for trial monitoring proved to be useful for off-line evaluation of the product performance, as well as for short-term process change evaluation. In this method, oxalate solution was added to the sample step-wise (0.1 mmol/L oxalate every minute). In the bleached GW pulp storage tower sample, the precipitation was initialized after 5 minutes, corresponding to an oxalate addition of 0.5 mmol/L (Fig. 4.32). Off-line addition of 20 ppm of Blend 1 increased the time to 11 minutes (1.1 mmol/L), and a dosage of 50 ppm further to 14 minutes (1.4 mmol/L). The Reference product that was used previously in the mill was clearly less effective, confirming the screening results from the clean system (Fig. 4.26).

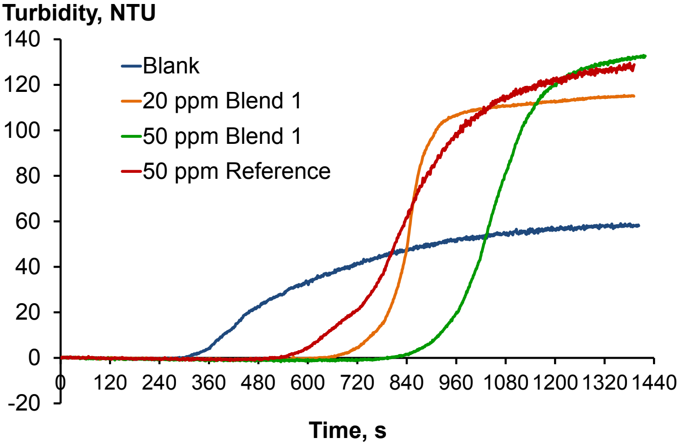


Figure 4.32 Effect of anti-scaling agents on calcium oxalate precipitation determined by turbidity monitoring during oxalate titration of bleached GW pulp storage tower sample (off-line anti-scaling agent additions) (V).

The addition of anti-scaling agents also decreased the calcium oxalate particle size determined by FCM, so that the calculated average particle size decreased from 1.54 µm in the Blank to 0.55 µm upon 50 ppm addition of Blend 1 (Fig. 4.33). There is again a good correlation between the FCM and SEM analysis, which is illustrated by the SEM-micrographs in Fig. 4.34. The Blank sample consisted mainly of different sized crystals of bipyramid shape, which are typical for COD (Fig 4.34a). According to XRD analysis, COD was also the main hydrate form in the precipitates formed in the presence of anti-scaling agents, but as the SEM-micrographs show, the crystal structure is clearly modified (Figs. 4.34b and 4.34c) Especially in case of Blend 1 the decreased particle size and aggregation can be observed (Fig 4.34b).

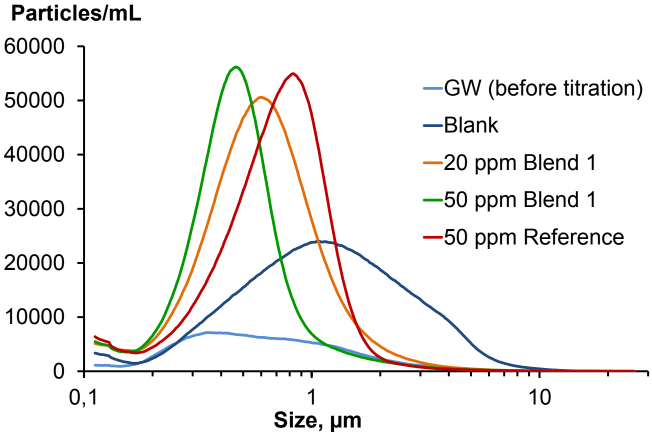


Figure 4.33 Effect of anti-scaling agents on particle size distribution analyzed by FCM after calcium oxalate precipitation in GW pulp storage tower sample (V).

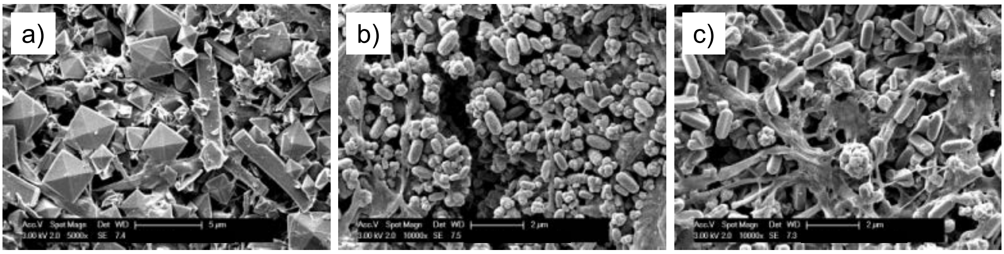


Figure 4.34 SEM-micrographs of calcium oxalate crystals precipitated in peroxide-bleached groundwood pulp filtrate by titration with sodium oxalate solution. a) Blank (bar indicating 5 µm); b) 50 ppm Blend 1 (bar indicating 2 µm); c) 50 ppm Reference (bar indicating 2 µm) (V).

The oxalate titration method was also tested for pulp samples during a full-scale trial with Blend 1. An example of the results is shown in Fig. 4.35, where samples both before and during the trial have been used. It was observed that both in groundwood and machine chest pulp samples during the trial approximately 2 minutes more, and thereby 0.2 mmol/L higher oxalate addition, was needed in order to initiate calcium oxalate precipitation detected by turbidity increase. This also confirms the product performance in the process.

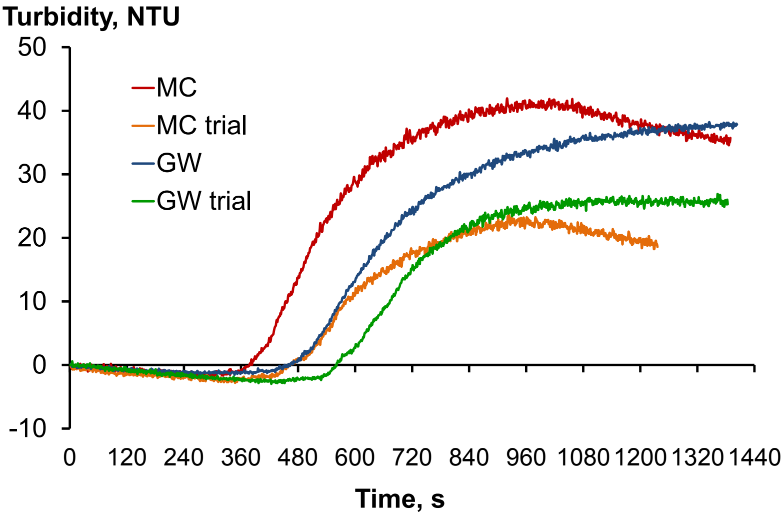


Figure 4.35 Calcium oxalate precipitation determined by turbidity monitoring during oxalate titration of machine chest (MC) and groundwood pulp dosing chest (GW) samples before and during full-scale trial with Blend 1 (V).

5. CONCLUSIONS

It is possible to decrease the risk for calcium oxalate scale build-up in mechanical pulping and bleaching processes, and in the following papermaking, by applying different process and wet-end chemistry related solutions. These means can be aimed either at decreasing the concentrations of calcium and oxalate ions, or at controlling the calcium oxalate precipitation rate and form.

In alkaline peroxide bleaching of mechanical pulps, there will most likely always be supersaturated conditions for calcium and oxalate ions, so that the calcium oxalate solubility product is exceeded. The most important factors that define the risk for calcium oxalate precipitation and scaling are the degree of supersaturation, pH, temperature, and the amount and composition of dissolved and colloidal substances (DCS) in the process waters.

For minimizing the ion concentrations, effective debarking is essential as the content of oxalate and calcium in bark is several times higher than in wood. In addition, more oxalic acid is formed as an oxidation product from bark components during alkaline peroxide bleaching. Installation of internal pulp washing equipment, like a wire press, after the alkaline peroxide bleaching process decreases the oxalate amount transferred to the paper machine. This has proven to be an effective way to separate oxalate-rich (pulping) and calcium-rich (paper machine) process water streams from each other. On the paper machine side, care should be taken in pH control and ash retention in order to minimize the dissolution of calcium-containing fillers and pigments.

It is also possible to minimize oxalic acid formation in alkaline peroxide bleaching by process modifications, without compromising the brightness gain. High consistency bleaching with magnesium hydroxide as an alternative alkali source would be a good combination both technically and environmentally. Magnesium hydroxide will both give a more even pH profile than sodium hydroxide in bleaching, as well as increase calcium oxalate solubility by formation of more soluble magnesium oxalates. The required pulp washing before high-consistency peroxide bleaching also decreases the oxidation of dissolved and colloidal organic substances that would result in increased oxalic acid formation.

It is clear that there is a strong interaction between calcium oxalate precipitation and dissolved and colloidal substances in mechanical pulping and bleaching. Colloidal wood resin decreases the precipitation rate of calcium oxalate, but increases the hydrophobicity of the formed crystals by co-precipitation. Therefore, the methods used in controlling the wood resin in a mill will also affect the calcium oxalate precipitation. Dissolved spruce galactoglucomannans (GGMs) inhibit the crystal growth of calcium oxalate, and by stabilizing colloidal wood resin they can also decrease the adsorption of the hydrophobic resin on the crystal surfaces. It can therefore be highly recommended that the GGM-rich process water before peroxide bleaching should be somehow utilized, for example by recovering the GGMs from the filtrate for use, in order to achieve the above-mentioned benefits.

Using effective and targeted anti-scaling agent chemistry can be an efficient solution for calcium oxalate scale problems. The evaluation methods used for identifying the right additives should have a good correlation to the real process. Flow cytometry was proven to give valuable information, not only about the effects and mechanisms of the additives, but also about the interaction of the calcium oxalate precipitates and dissolved and colloidal substances. This is an important aspect in process surveys as large variations in these complex systems occur. Another important issue is the availability of fast, simple, and reliable analysis methods both for soluble and total oxalate, in order to be able to determine the oxalate balance in a process.

Future research work in this area should be aimed at clarifying the affinity properties of calcium oxalate crystals towards equipment and fiber surfaces (retention), and the effect of different substances in this aspect. It would also be interesting to see some large-scale results of the effects of enzymatic degradation of oxalic acid, as this method has shown very promising results according to the literature.

The results from this work can be used as guidelines when planning new peroxide-bleached mechanical pulp lines, as well as modifying existing ones having problems with calcium oxalate scale build-up. They can also be utilized in problem solving and interpretation of existing problems, or even in the estimation of scaling potential in a particular process. The methods used in the precipitation studies and screening of anti-scaling agents in this work can also be adapted to other areas than pulping and papermaking.

6. ACKNOWLEDGEMENTS

I am deeply grateful to my supervisors Professor Stefan Willför and Docent Anna Sundberg for providing me the opportunity to work with this project, and for all the encouragement during the work. Thank you also for the warm welcome back to the Laboratory of Wood and Paper Chemistry and the academic world, I felt like coming back home. My special thanks go to Dr. Lari Vähäsalo for acting as an unofficial supervisor, and for all help and advice during the work. Especially the work with the flow cytometry would not have been possible without him.

I want to thank Sappi Fine Paper Europe for the financial support and for initiating the project. The helpful personnel in Sappi Kirkniemi mill are greatly acknowledged. I am especially grateful to Ms. Satu Karjalainen for her great interest in the project, optimism, kind words, and for making impossible things possible. I want to thank Ms. Stina Nygård (currently with Mondi Lohja Oy) for her significant role as an initiator, and Ms. Kirsi Tuominen for her valuable contribution. Ms. Päivi Herrala and Ms. Satu Vainio from the Kirkniemi laboratory are thanked for their helpfulness and skillful analysis work.

I also want to thank Kemira Oyj for the financial support and for all the practical help. Especially Dr. Jonas Konn is thanked as a co-author, and for all help and advice in research related issues and experimental work. Also Ms. Mari Zabihian, Mr. Mats Berg, Dr. Erkki Räsänen, Dr. Tom Lundin, as well as all others involved in the project at Kemira are thanked for their contribution.

I thank the whole personnel at the Laboratory of Wood and Paper Chemistry for a friendly and relaxed atmosphere, and for the help that was always available when needed. Especially I would like to thank Docent Andrey Pranovich as a co-author, but also as an endless source of wood chemistry knowledge and advice for experimental work. I also want to thank Dr. Anders Strand for the interesting discussions about wood resin droplets, Dr. Hanna Lindqvist for all the help in practical issues, and Ms. Wenwen Fang for skillful experimental work. Thanks also go to Professor (emeritus) Bjarne Holmbom, Dr. Ann-Sofie Leppänen, Mr. Leif Österholm, Mr. Jarl Hemming, Ms. Agneta Hermansson, Ms. Anita Forss, Ms. Linda Nisula, and my office mates Dr. Robin Manelius and Mr. Jens Krogell.

I would like to express my deepest gratitude to my whole family and especially my wife Maija, for understanding, and for running the household almost entirely by herself during my travelling and stays in Turku.

Last, I thank my old Peugeot that always managed to get me safely to Turku and back, no matter what the weather was like.

7. REFERENCES

Achilles, W. (1997): In vitro crystallization systems for the study of urinary stone formation, World J. Urol. 15, 244-251.

Agnemo, R., Gellerstedt, G. (1979): The reactions of lignin with alkaline hydrogen peroxide. Part II: Factors influencing the decomposition of phenolic structures, Acta Chem. Scand. B 33, 337-342.

Akın, B., Öner, M., Bayram, Y., Demadis, K.D. (2008): Effects of carboxylate-modified, "green" inulin biopolymers on the crystal growth of calcium oxalate, Cryst. Growth Des. 8(6), 1997-2005.

Akyol, E., Öner, M. (2007): Inhibition of calcium oxalate monohydrate crystal growth using polyelectrolytes, J. Cryst. Growth 307, 137-144.

Alén, R. (2000): Structure and chemical composition of wood, In: Papermaking Science and Technology, Vol. 3 Forest Products Chemistry. Ed. Stenius, P., Fapet Oy, Helsinki, Finland, 12-57.

Auhorn, W., Melzer, J. (1979): Improved efficiency of wet end additives in closed wet end systems through elimination of detrimental substances, Tappi Annual Meeting Proceedings, Tappi Press, Atlanta, USA, 49-66.

Babić-Ivančić, V., Füredi-Milhofer, H., Purgarić, B., Brničević, N., Despotović, Z. (1985): Precipitation of calcium oxalates from high ionic strength solutions. III. The influence of reactant concentrations on the properties of the precipitates, J. Cryst. Growth 71, 655-663.

Bailey, C.W., Dence, C.W. (1969): Reactions of alkaline hydrogen peroxide with softwood lignin model compounds, spruce milled-groundwood lignin and spruce groundwood, Tappi J. 52(3), 491-500.

Baumann, J.M., Affolter, B., Caprez, U., Lauper, D., Maier, F., Siegrist, H.P., Zysset, T. (2000): Nucleation and aggregation of calcium oxalate in whole urine; spectrophotometric sedimentation analysis: a new approach to study the aggregation of calcium oxalate dihydrate, Urol. Res. 28, 147-154.

Behrooz, R., Ghasemi, S., Atoii, G.A., Fatehi, P. (2012): $Mg(OH)_2$-based hydrogen peroxide bleaching of CMP pulps at high consistency, BioResources 7(1), 161-172.

Björkman, A. (1956): Studies on finely divided wood, Part I. Extraction of lignin with neutral solvents, Svensk Papperstidn.-Nordisk Cellulosa 59(13), 477-485.

Bramley, A.S., Hounslow, M.J., Ryall, R.L. (1997): Aggregation during precipitation from solution. Kinetics for calcium oxalate monohydrate, Chem. Eng. Sci. 52(5), 747-757.

Bretherton, T., Rodgers, A. (1998): Crystallization of calcium oxalate in minimally diluted urine, J. Cryst. Growth 192, 448-455.

Brown, P., Ackermann, D., Finlayson, B. (1989): Calcium oxalate dihydrate (weddellite) precipitation, J. Cryst. Growth 98, 285-292.

Brännvall E. (2009): Wood handling, In: Pulping chemistry and technology. Eds. Ek, M., Gellerstedt, G., Henriksson, G., Walter de Gruyter GmbH & Co., Berlin, Germany, 13 – 34.

Buchert, J., Teleman, A., Harjunpää, V., Tenkanen, M., Viikari, L., Vuorinen, T. (1995): Effect of cooking and bleaching on the structure of xylan in conventional pine kraft pulp, Tappi J. 78(11), 125-130.

Busch, K.W., Busch, M.A. (1997): Laboratory studies on magnetic water treatment and their relationship to a possible mechanism for scale reduction, Desalination 109, 131-148.

Cassland, P., Sjöde, A., Winestrand, S., Jönsson, L.J., Nilvebrant, N.-O. (2010): Evaluation of oxalate decarboxylase and oxalate oxidase for industrial applications, Appl. Biochem. Biotechnol. 161, 255-263.

Chamjangali, M.A., Sharif-Razavian, L., Yousefi, M., Amin, A.H. (2009): Determination of trace amounts of oxalate in vegetable and water samples using a new kinetic-catalytic reaction system, Spectrochim. Acta Part A 73, 112-116.

Chen, F., Michalopoulos, D. (1989): Method for calcium oxalate scale control, U.S. Patent 4872995.

Clausen, C.A., Kenealy, W., Lebow, P.K. (2008): Oxalate analysis methodology for decayed wood, Int. Biodet. Biodegr. 62, 372-375.

Dence, C.W. (1996): Chemistry in mechanical pulp bleaching, In: Pulp bleaching - Principles and practice, Eds. Dence, C.W., Reeve, D.W., TAPPI Press, Atlanta, GA, USA, 161-181.

Doherty, W.O.S., Fellows, C.M., Gorjian, S., Senogles, E., Cheung, W.H. (2004): Inhibition of calcium oxalate monohydrate by poly(acrylic acid)s with different end groups, J. Appl. Polym. Sci. 91, 2035-2041.

Dosch, W. (1979): Rapid and direct gas chromatographic determination of oxalic acid in urine, Urol. Res. 7, 227-234.

Dutton, M.V., Evans, C.S. (1996): Oxalate production by fungi: Its role in pathogenicity and ecology in the soil environment, Can. J. Microbiol. 42, 881-895.

Dutour-Sikirić, M. Füredi-Milhofer, H. (2006): The influence of surface active molecules on the crystallization of biominerals in solution, Adv. Coll. Interface Sci. 128-130, 135-158.

Ek, M., Gierer, J., Jansbro, K., Reitberger, T. (1989): Study on the selectivity of bleaching with oxygen-containing species, Holzforschung 43, 391-396.

Elsander, A., Ek, M., Gellerstedt, G. (2000): Oxalic acid formation during ECF and TCF bleaching of kraft pulp, Tappi J. 83(2), 73-77.

El-Shall, H., Jeon, J., Abdel-Aal, E.A., Khan, S., Gower, L., Rabinovich, Y. (2004): A study of primary nucleation of calcium oxalate monohydrate: I – Effect of supersaturation, Cryst. Res. Technol. 39(3), 214-221.

Ester, D.R. (1994): Reduction of bleach plant deposits yields better pulp, less downtime, Pulp Pap. 95(9), 135-137.

Farmanesh, S., Ramamoorthy, S., Chung, J., Asplin, J.R., Karande, P., Rimer, J.T. (2014): Specificity of growth inhibitors and their cooperative effects in calcium oxalate monohydrate crystallization, J. Am. Chem. Soc. 136, 367-376.

Fengel, D., Wegener, G. (1989): Chemical composition and analysis of wood, In: Wood - Chemistry, Ultrastructure, Reactions. Walter de Gruyter, Berlin, Germany, 26-59.

Ferguson, R. J. (2002): Predicting calcium oxalate scale, Paper No. 02-399, French Creek Software, Inc., Kimberton, PA, USA.

Fiskari, J. (1999): Oxalic acid formation in oxygen chemical bleaching, Proceedings of 1999 TAPPI Pulping Conference, 31 Oct-4 Nov, 1999, Orlando, FL, USA, vol. 1, 7-10.

Flynn, D. (1988): Deposit control, In: The Nalco Water Handbook, Ed. Kemmer, F.N., 2nd edition, McGraw-Hill.

Franceschi, V.R., Nakata, P.A. (2005): Calcium oxalate in plants: formation and function, Annu. Rev. Plant Biol. 56, 41-71.

Füredi-Milhofer, H., Sarig, S. (1996): Interactions between polyelectrolytes and sparingly soluble salts, Prog. Cryst. Growth and Charact. 32, 45-74.

Füredi-Milhofer, H., Sikirić, M., Tunik, L., Filipović-Vinceković, N., Garti, N. (2002): Interactions of organic additives with ionic crystal hydrates: the importance of the hydrated layer, Int. J. Mod. Phys. B 16(1&2), 359-366.

Gardner, G.L. (1975): Nucleation and crystal growth of calcium oxalate trihydrate, J. Cryst. Growth 30, 158-168.

Garti, N., Tibika, F., Sarig, S., Perlberg, S. (1980): The inhibitory effect of polymeric carboxylic amino-acids and urine on calcium oxalate crystallization, Biochem. Biophis. Res. Comm. 97(3), 1154-1162.

Gellerstedt, G. (2009): Mechanical pulping chemistry, In: Pulping chemistry and technology. Eds. Ek, M., Gellerstedt, G., Henriksson, G., Walter de Gruyter GmbH & Co., Berlin, Germany, 35-56.

Germgård, U. (2009): Pulp bleaching, In: Pulping chemistry and technology. Eds. Ek, M., Gellerstedt, G., Henriksson, G., Walter de Gruyter GmbH & Co., Berlin, Germany, 271-275.

Gierer, J., Imsgard, F. (1977): The reactions of lignins with oxygen and hydrogen peroxide in alkaline media, Svensk Papperstidn. 80, 510-518.

Glazer, J.A. (1991): Overview of deposit control, Tappi J. 74(7), 72-74.

Gottstein, H.D., Zook, M.N., Kuć, J.A. (1989): Detection and quantitation of oxalic acid by capillary gas chromatography, J. Chromatogr. 481, 55-61.

Greer, C., Shevchenko, S. and Duggirala, P. (2003): New method for monitoring scale buildup helps eliminate bleaching deposit problems, Pulp Pap. 77(7), 36-39.

Hannuksela, T., Holmbom, B. (2004): Stabilization of wood resin emulsions by dissolved galactoglucomannans and glucomannans, J. Pulp Pap. Sci. 30(6), 159-164.

Haque, M.R. (2007): Minimizing fouling in spiral heat exchangers at a BCTMP mill, Pulp Pap. Can. 108(4), 35-44.

Harrison, R., Parrish, T., Gibson, A., Knapp, C., Wajer, M., Johnson, D. (2008): Refiner bleaching with magnesium hydroxide ($Mg(OH)_2$) and hydrogen peroxide, Tappi J. 7(9), 16-20.

Haselhuhn, F., Doyle, S., Kind, M. (2006): Synchrotron radiation X-ray study of the particle formation of pseudo-polymorphic calcium oxalate, J. Cryst. Growth 289, 727-733.

Hassler, T. (2009): Improving productivity and quality by controlling organic, inorganic and microbiological deposits, In: Applications of wet-end paper chemistry, 2nd edition, Eds. Thorn, I., Au, C.O., Springer, Netherlands, 7-38.

Hasson, D., Lumelsky, V., Greenberg, G., Pinhas, Y., Semiat, R. (2008): Development of the electrochemical scale removal technique for desalination applications, Desalination 230, 329-342.

He, Z., Ni, Y., Zhang, E. (2003): Comparison of oxalate formation from spruce TMP: Conventional peroxide bleaching process versus the P_M process, J. Pulp Pap. Sci. 29(12), 391-394.

He, Z.B., Wekesa, M., Ni, Y.H. (2004): Pulp properties and effluent characteristics from the $Mg(OH)_2$-based peroxide bleaching process, Tappi J. 3(12), 27-31.

He, Z., Yang, Y., Ni, Y. (2008): Comparison of oxalate formation in peroxide bleaching of softwood and hardwood mechanical pulps, J. Pulp Pap. Sci. 34(3), 153-160.

Hennequin, C., Lalanne, V., Daudon, M., Lacour, B., Drueke, T. (1993): A new approach to studying inhibitors of calcium oxalate crystal growth, Urol. Res. 21, 101-108.

Hennequin, C., Lalanne, V., Estepa, L., Drueke, T., Daudon, M., Lacour, B. (1997): Validation by image analysis of a turbidimetric method to study calcium oxalate crystallization, Clin. Nephrol. 48, 292-297.

Hesse, A., Bongartz, D., Heynck, H., Berg, W. (1996): Measurement of urinary oxalic acid: a comparison of five methods, Clin. Biochem. 29(5), 467-472.

Hietanen, T., Tamper J., Backfolk K. (2013): Environmental benefits of magnesium hydroxide-based peroxide bleaching of mechanical pulp – mill results, Tappi J. 12(6), 9-15.

Hodginson, A. (1981): Sampling errors in the determination of urine calcium and oxalate: solubility of calcium oxalate in HCl-urine mixtures, Clin. Chim. Acta 109, 239-244.

Holloway, W.D., Argall, M.E., Jealous, W.T., Lee, J.A., Bradbury, J.H. (1989): Organic acids and calcium oxalate in tropical root crops, J. Agric. Food Chem. 37, 337-341.

Holmbom, B., Sundberg A. (2003): Dissolved and colloidal substances accumulation in papermaking process waters, Wochenbl. Papierfabr. 131(21), 1305-1311.

Holmes, R.P., Kennedy, M. (2000): Estimation of the oxalate content of foods and daily oxalate intake, Kidney Int. 57, 1662-1667.

Hong, F., Nilvebrant, N.-O., Jönsson, L.J. (2003): Rapid and convenient determination of oxalic acid employing a novel oxalate biosensor based on oxalate oxidase and SIRE technology, Biosens. Bioelectron. 18, 1173-1181.

Horner, H.T., Wagner, B.L. (1995): Calcium oxalate formation in higher plants, In: Calcium oxalate in biological systems, Ed. Khan, S.R., CRC Press, Inc., Boca Raton FL, USA.

Houcine, I., Plasari, E., David, R., Villermaux, J. (1997): Influence of mixing characteristics on the quality and size of precipitated calcium oxalate in a pilot scale reactor, Trans IChemE 75, Part A, 252-256.

Hudgins, J.W., Krekling, T., Franceschi, V.R. (2003): Distribution of calcium oxalate crystals in the secondary phloem of conifers: a constitutive defense mechanism?, New Phytol. 159, 677-690.

Hultman, B., Nilsson, C., Sjöberg, S. (1981): Inhibition of calcium oxalate deposits in a sulphite mill by the addition of aluminium sulphate, Svensk Papperstidn. 84, R163-168.

Hyppänen, T., Sjöström, E., Vuorinen, T. (1983): Gas-liquid chromatographic determination of hydroxyl carboxylic acids on a fused-silica capillary column, J. Chromatogr. 261, 320-323.

Höglund, H. (2009): Mechanical pulping, In: Pulping chemistry and technology. Eds. Ek, M., Gellerstedt, G., Henriksson, G., Walter de Gruyter GmbH & Co., Berlin, Germany, 57-90.

Hönow, R., Hesse, A. (2002): Comparison of extraction methods for the determination of soluble and total oxalate in foods by HPLC-enzyme-reactor, Food Chem. 78, 511–521.

ISO 2470-1 (2009): Measurement of diffuse blue reflectance factor - Part 1: Indoor daylight conditions (ISO brightness).

ISO 5269-1 (2005): Preparation of laboratory sheets for physical testing - Part 1: Conventional sheet-former method.

Johnson, D. (1998): Removing beerstone: a look at alternative cleaning methods, Modern Brew. Age 49(March 23), 37.

Judprasong, K., Charoenkiatkul, S., Sungpuag, P., Vasanachitt, K., Nakjamanong, Y. (2006): Total and soluble oxalate contents in Thai vegetables, cereal grains and legume seeds and their changes after cooking, J. Food Compos. Anal. 19, 340-347.

Kavanagh, J.P., Jones, L., Rao, P.N. (2000): Calcium oxalate crystallization kinetics studied by oxalate-induced turbidity in fresh human urine and artificial urine, Clin. Sci. 98, 151-158.

Kavanagh, J.P. (2006): In vitro calcium oxalate crystallization methods, Urol. Res. 34, 139-145.

Kempf, A.W., Dence, C.W. (1980): The reactions of hardwood lignin models with alkaline hydrogen peroxide, In: Chemistry of Delignification with Oxygen, Ozone and Peroxides, Eds. Singh, R., Nakano, J., Gratzl, J., Uni Publishers Co., Ltd., Tokyo, Japan, 207-216.

Keselica, D.S. (1992): Chemical process aids for the deinking plant: antiscalants and flocculants, Proceedings of Tappi 1992 Pulping Conference, Book 2, Tappi Press, Atlanta, USA, 445-450.

Kettler, R. M., Palmer, D. A., Wesolowski, D. J. (1991): Dissociation quotients of oxalic acid in aqueous sodium chloride media to 175°C. J. Solution Chem. 20, 905-927.

King, D.W, Kester, D.R. (1990): A general approach for calculating polyprotic acid speciation and buffer capacity, J. Chem. Educ. 67(11), 932-933.

Kırboğa, S. and Öner, M. (2009): Inhibition of calcium oxalate crystallization by graft copolymers, Cryst. Growth Des. 9(5), 2159-2167.

Kiss, J. (1974): β-eliminative degradation of carbohydrates containing uronic acid residues, Adv. Carbohydr. Chem. Biochem. 29, 229-303.

Kong, F., Ni, Y., He, Z. (2009): A partial magnesium hydroxide substitution for sodium hydroxide in peroxide bleaching of an aspen CTMP, J. Wood Chem. Technol. 29, 136-149.

Kostinen, K. (2000): Wood handling application, In: Papermaking Science and Technology, Vol. 6A Chemical Pulping. Eds. Gullichsen, J., Fogelholm, C.-J., Fapet Oy, Helsinki, Finland, 331 – 340.

Krasowski, J.A., Marton, J. (1983): The formation of oxalic acid during bleaching of kraft pulp, J. Wood Chem. Technol. 3(4), 445-458.

Krogell, J., Holmbom, B., Pranovich, A., Hemming, J., Willför, S. (2012): Extraction and chemical characterization of Norway spruce inner and outer bark, Nord. Pulp Pap. Res. J. 27(1), 6-17.

Kröhl, T., Lorenčak, P., Gierulski, A., Eipel, H., Horn, D. (2004): A new laser-optical method for counting colloidally dispersed pitch, Nord. Pulp Pap. Res. J. 9(1), 26-30, 36.

Li, H., Chai, X.-S., DeMartini, N. (2012): Oxalate release and formation during alkaline pulping, J. Wood Chem. Technol. 32(3), 187-197.

Li, Z., Court, G., Belliveau, R., Crowell, M., Murphy, A., Gibson, A., Wajer, M., Branch, B., Ni, Y. (2005): Using magnesium hydroxide ($Mg(OH)_2$) as the alkali source in peroxide bleaching at Irving paper, Pulp Pap. Can. 106(6), 24-28.

Lidén, J., Öhman, L.O. (1997): Redox stabilization of iron and manganese in the +II oxidation state by magnesium precipitates and some anionic polymers. Implications for the use of oxygenbased bleaching chemicals, J. Pulp Pap. Sci. 23(5), 193-199.

Lindholm, C.-A. (2009): Bleaching of mechanical pulps, In: Papermaking Science and Technology, Book 5 Mechanical Pulping, Ed. Lönnberg, B., Paper Engineers' association/Paperi ja Puu Oy, Helsinki, Finland, 360-398.

Milardović, S., Kereković, I., Nodilo, M. (2008): A novel biamperometric biosensor for urinary oxalate determination using flow-injection analysis, Talanta 77, 222–228.

Muñoz, J.A., López-Mesas, M., Valiente, M. (2010): Development and validation of a simple determination of urine metabolites (oxalate, citrate, ruic acid and creatine) by capillary zone electrophoresis, Talanta 81, 392-397.

Moldenius, S. (1982): The stoichiometry of peroxide bleaching of mechanical pulps, Svensk Papperstidn. 85(15), 116-120.

Murray, Jr., J.F., Nolen, III, H.W., Gordon, G.R., Peters, J.H. (1982): The measurement of urinary oxalic acid by derivatization coupled with liquid chromatography, Anal. Biochem. 121, 301-309.

Mäkelä, M. (2009): The white-rot fungi *Phlebia radiata* and *Dichomitus squalens* in wood-based cultures: expression of laccases, lignin peroxidases, and oxalate decarboxylase, Doctoral thesis, University of Helsinki, Department of Applied Chemistry and Microbiology, Helsinki, Finland.

Nakata, P.A. (2012): Plant calcium oxalate crystal formation, function, and its impact on human health, Front. Biol. 7(3), 254-266.

Ni, Y., He, Z. (2010): Review: Using magnesium hydroxide as the alkali source for peroxide bleaching of mechanical pulps - process chemistry and industrial implementation, Nord. Pulp Pap. Res. J. 25(2), 170-177.

Nilvebrant, N.-O., Reimann, A. (1996): Xylan as a source for oxalic acid during ozone bleaching, Proceedings of the 4th European Workshop on Lignocellulosics and Pulp (EWLP 1996), Stresa, Italy, 485-491.

Nilvebrant, N.-O., Reimann, A., de Sousa, F., Cassland, P., Larsson, S., Hong, F., Jönsson, L.J. (2002): Enzymatic degradation of oxalic acid for prevention of scaling, Prog. Biotechnol. 21, 231-238.

Noonan, S.C., Savage, G.P. (1999): Oxalate content of foods and its effect on humans. Asia Pacific J. Clin. Nutr. 8(1), 64-74.

Nyström, M., Pykäläinen, J., Lehto, J. (1993): Peroxide bleaching of mechanical pulp using different types of alkali, Pap. Puu 75(6), 419-425.

Ogawa, Y, Miyazato, T., Hatano, T. (2000): Oxalate and urinary stones, World J. Surg. 24(10), 1154-1159.

Okombo, J., Liebman, M. (2010): Oxalate content of selected breads and crackers, J. Food Compos. Anal. 23, 118-121.

Omori, S., Dence, C.W. (1981): The reactions of alkaline hydrogen peroxide with lignin model dimers, Wood Sci. Technol. 15(2), 113-123.

Pranovich, A., Sundberg, K., Holmbom, B. (2003): Chemical changes in thermomechanical pulp at alkaline conditions, J. Wood Chem. Tech. 23, 89-112.

Presley, J.R., Hill, R.T. (1996): Peroxide bleaching of (chemi)mechanical pulps, In: Pulp bleaching - Principles and practice, Eds. Dence, C.W., Reeve, D.W., TAPPI Press, Atlanta, GA, USA, 457-489.

Presley, J.R., Hill, R.T., Chauvheid, E., Devenyns, J. (1997): New metals control technique improves bleaching performance, Pulp Pap. 71(10), 125-131.

Rahikainen, J.L., Martin-Sampedro, R., Heikkinen, H., Rovio, S., Marjamaa, K., Tamminen, T., Rojas, O.J., Kruus, K. (2013): Inhibitory effect of lignin during cellulose bioconversion: The effect of lignin chemistry on non-productive enzyme adsorption, Bioresource Technol. 133, 270–278.

Randolph, A.D. and Drach, G.W. (1981): Some measurements of calcium oxalate nucleation and growth rates in urine-like liquors, J. Cryst. Growth 53, 195-201.

Rawat, A., Sulekh, C., Anjana, S. (2010): Highly selective potentiometric oxalate ion sensor based on Ni(II) bis-(m-aminoacetophenone)ethylenediamine, Chin. J. Chem. 28, 1140-1146.

Reimann, A., De Sousa, F., Jansson, M.B. (2000): A method for the analysis of oxalic acid and calcium oxalate in kraft mill bleaching samples, Poster presentation, 6th European Workshop on Lignocellulosics and Pulp (EWLP 2000), 3-6 Sep, 2000, Bordeaux, France, 543-546.

Rodgers, A., Hibbert, B., Probyn, T. (1995): Determination of urinary calcium oxalate crystallization mechanisms and kinetics using flow cytometry, Urol. Int. 55, 93-100.

Rudie, A., Hart, P. (2005): Managing calcium oxalate scale in the bleach plant, Tappi Sol. June 2005, 45-46.

Rudie, A.W., Hart, P.W. (2006a): Mineral scale management, Part II. Fundamental chemistry, Tappi J. 5(7), 17-23.

Rudie, A.W., Hart, P.W. (2006b): Mineral scale management, Part III. Nonprocess elements in the paper industry, Tappi J. 5(8), 3-10.

Salomon, D.R., Romano, J. (1992): Applications of capillary ion electrophoresis in the pulp and paper industry, J. Chromatogr. 602, 219-225.

Savage, G.P., Vanhanen, L., Mason, S.M., Ross, A.B. (2000): Effect of cooking on the soluble and insoluble oxalate content of some New Zealand foods, J. Food Compos. Anal., 13, pp. 201-206.

Sayan, P., Sargut, S.T. and Kıran, B. (2009): Calcium oxalate crystallization in the presence of amino acids, proteins and carboxyllic acids, Cryst. Res. Technol. 44(8), 807-817.

SCAN-test Method SCAN-N 39:05 (2005): Dissolved and precipitated oxalate, Scandinavian Pulp, Paper and Board Testing Committee, Stockholm, Sweden.

Schilling, J.S., Jellison, J. (2004): High-performance liquid chromatographic analysis of soluble and total oxalate in Ca- and Mg-amended liquid cultures of three wood decay fungi, Holzforschung 58, 682-687.

Shapiro, H. M. (2003): Practical flow cytometry, 4th edition, John Wiley & Sons, New Jersey, USA.

Shevchenko, S., Duggirala, P.Y. (2010): Deposit management for the bleach plant, IPPTA J., 22(1), pp. 135-140.

Shevchenko, S.M., Kouznetsov, D.L. and Duggirala, P.Y. (2001): Apparatus for measuring calcium oxalate scaling, European Patent 2 058 654 A1.

Singh R.P., Gaur, S.S., Sheehan, M.E., Nancollas, G.H. (1988): Crystal growth of calcium oxalate monohydrate, J. Cryst. Growth 87, 318-324.

Sirén, H., Kokkonen, R., Hiissa, T., Särme, T., Rimpinen, O., Laitinen, R. (2000): Determination of soluble anions and cations from waters of pulp and paper mills with on-line coupled capillary electrophoresis, J. Chromatogr. A 895, 189-196.

Sitholé, B. (2002): Scale deposit problems in pulp and paper mills. Proceedings of TAPPSA African Pulp and Paper Week, 8-11-October 2002, Durban, South Africa.

Sitholé, B., Azeez, A., Ramjugernath, D. (2014): A new method for the analysis of soluble and insoluble oxalate in pulp and paper matrices, J. Wood Chem. Technol. 34(1), 55-66.

Sjöde, A., Jönsson, L.J., Nilvebrant N.-O. (2005): Oxalic acid in bleaching processes - formation and control, Proceedings of 13th International Symposium on Wood, Fibre and Pulping Chemistry, 16-19 May, 2005, Auckland, New Zealand, 2: 303-309.

Sjöde, A. (2007): Oxalic acid – a source for incrusts; consequences and analyses. 4th Pulp and Paper Chemical Analysis seminar "Modern analytical techniques for the future mills", 10-11 Sep 2007, Stockholm, Sweden.

Sjöde, A. (2008): Chemical characterization in the biorefinery of lignocellulose. Formation and management of oxalic acid and analysis of feedstocks for bioethanol production, Ph.D. thesis, Karlstad University, Faculty of Technology and Science, Sweden.

Sjöde, A., Winestrand, S., Nilvebrant, N.-O., Jönsson, L.J. (2008): Enzyme-based control of oxalic acid in the pulp and paper industry, Enzyme Microbial Tech. 43, 78-83.

Sjöström, J. (1990): Fractionation and characterization of organic substances dissolved in water during groundwood pulping of spruce, Nord. Pulp Pap. Res. J. 5, 9-15.

Sjöström, E. (1993): Wood Chemistry - Fundamentals and Applications. 2nd edn., Academic Press Inc., San Diego, CA, USA, 49-108, 208.

Škrtić, D., Füredi-Milhofer, H., Marković, M. (1987): Precipitation of calcium oxalates from high ionic strength solutions. V. The influence of precipitation conditions and some additives on the nucleating phase, J. Cryst. Growth 80, 113-120.

Song, T., Pranovich, A., Holmbom, B. (2013): Separation of polymeric galactoglucomannans from hot-water extract of spruce wood, Bioresource Technol. 130, 198 – 203.

Strand, A., Sundberg, A., Vähäsalo, L., Holmbom, B. (2011): Aggregation and destabilisation of colloidal wood pitch by calcium ions in TMP suspensions, Nord. Pulp Pap. Res. J. 26(4), 429-437.

Strand, A., Lindqvist, H., Vähäsalo, L., Blomquist, M., Sundberg A. (2013): Analysis of interactions between colloidal wood pitch and various mineral particles by flow cytometry, BioResources 8(3), 3884-3900.

Streit, J., Tran-Ho, L.-C., Königsberger, E. (1998): Solubility of the three calcium oxalate hydrates in sodium chloride solutions and urine-like liquors, Monatshefte Chem. 129, 1225-1236.

Sundberg, A. (1999): Wood resin and polysaccharides in mechanical pulps. Chemical analysis, interactions and effects in papermaking, Doctoral thesis, Åbo Akademi University, Faculty of Chemical Engineering, Turku, Finland.

Sundberg, A., Sundberg, K., Lillandt, C., Holmbom, B. (1996a): Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography, Nord. Pulp Pap. Res. J. 11(4), 216-219, 226.

Sundberg, A., Strand, A., Vähäsalo, L., Holmbom, B. (2009): Phase distribution of resin and fatty acids in colloidal wood pitch emulsions at different pH-levels, J. Disp. Sci. Technol. 30(6), 912-919.

Sundberg, K., Thornton, J., Pettersson, C., Holmbom, B., Ekman, R., (1994): Calcium-induced aggregation of dissolved and colloidal substances in mechanical pulp suspensions, J. Pulp Pap. Sci. 20(11), 317-322.

Sundberg, K., Pettersson, C., Eckerman, C., Holmbom, B. (1996b): Preparation and properties of a model dispersion of colloidal wood resin from Norway spruce, J. Pulp Pap. Sci. 22(7), 226-230.

Teleman, A., Harjunpää, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg, T., Vuorinen, T. (1995): Characterisation of 4-deoxy-β-L-*threo*-hex-4-enopyranosyl-uronic acid attached to xylan in pine kraft pulp and pulping liquor by 1H and 13C NMR spectroscopy, Carbohydr. Res. 272, 55-71.

Terelius, H., Nilsson, M., Blomberg, T. (2001a): Kalciumoxalat i mekanisk massa, Svensk Papperstidn. 104(4), 47-48.

Terelius, H., Nilsson, M. and Blomberg, T. (2001b): Calcium oxalate in mechanical pulp, Proceedings in International Mechanical Pulping Conference (IMPC 2001), June 4-8, 2001, Helsinki, Finland, 125-132.

Thibodeau, J.-B., Chabot, B., Daneault, C. (2005): Calcium ion removal by a synthetic zeolite in the manufacture of mechanical grade papers, Pulp Pap. Can. 106(3), 42-45.

Thornton, J., Ekman, R., Holmbom, B., Örså, F. (1994): Polysaccharides dissolved from Norway spruce in thermomechanical pulping and peroxide bleaching, J. Wood Chem. Technol. 14, 159-175.

Tomažič, B., Nancollas, G.H. (1979): The kinetics of dissolution of calcium oxalate hydrates, J. Cryst. Growth 46, 355-361.

Tomažič, B., Nancollas, G.H. (1980): Crystal growth of calcium oxalate hydrates: a comparative kinetics study, J. Colloid Interface Sci. 75(1), 149-160.

Ulmgren, P., Rådeström, R. (1997): Calcium oxalate in bleach plant filtrates, Proceedings of 1997 TAPPI Minimum Effluent Mills Symposium, TAPPI Press, Atlanta, Georgia, USA, 51-62.

Ulmgren, P. Rådeström, R. (1999a): An equilibrium model of the solubility of calcium oxalate in sodium chloride medium, Nord. Pulp Pap. Res. J. 14(3), 214-220.

Ulmgren, P., Rådeström, R. (1999b): Solubility of calcium oxalate in the presence of magnesium ions, and solubility of magnesium oxalate in sodium chloride medium, Nord. Pulp Pap. Res. J. 14(4), 330-335.

Ulmgren, P., Rådeström, R. (2000): On the formation of oxalate in bleach plant filtrates on hot storage, Nord. Pulp Pap. Res. J. 15(2), 128-132.

Ulmgren, P., Rådeström, R. (2001): Solubility and mechanisms of precipitation of calcium oxalate in D (chlorine dioxide stage) filtrates, J. Pulp Pap. Sci. 27(11), 391-396.

Utzman, S. (1993): Improved analysis of process liquors for the pulp and paper industry by ion chromatography, J. Chromatrogr. A 640, 287-292.

Varhimo, A. (2009): Wood raw materials. In: Papermaking Science and Technology, Vol. 5 Mechanical Pulping, Ed. Lönnberg, B., Paperi ja Puu Oy, Helsinki, 70-115.

Vuorinen, T., Fagerström, P., Räsänen, E., Vikkula, A., Henricson, K., Teleman, A. (1997): Selective hydrolysis of hexenuronic acid groups opens new possibilities for development of bleaching processes, 9th International Symposium on Wood and Pulping Chemistry (ISWPC 1997), Jun 9-12 1997, Montreal, Canada, M4-1-M4-4.

Vähäsalo, L., Degerth, R., Holmbom, B. (2003): The use of flow cytometry in wet end research, Pap. Technol. 44(1), 45-49.

Vähäsalo, L., Holmbom, B. (2005): Influence of latex properties on the formation of white pitch, Tappi J. 4(5), 27-32.

Vähäsalo, L. (2005): White pitch deposition. Mechanisms and measuring techniques, Doctoral thesis, Åbo Akademi University, Faculty of Chemical Engineering, Turku, Finland.

Wallace, D.W., Boerkamp, M., Lye, P.G., Lamb, D.W., Doherty, W.O.S., Fellows, C.M. (2008): Assessment of an intrinsic optical fiber sensor for in situ monitoring of scale-forming salts, Ind. Eng. Chem. Res. 47, 1066-1070.

Wang, L., Zhang, W., Qiu, S.R. Zachowicz, W.J., Guan, X., Tang, R., Hoyer, J.R., De Yoreo, J.J. and Nancollas, G.H. (2006): Inhibition of calcium oxalate monohydrate crystallization by the combination of citrate and osteopontin, J. Cryst. Growth 291, 160-165.

Willför, S., Sundberg, A., Sihvonen, A-L., Holmbom, B. (2000): Interactions between fillers and dissolved and colloidal substances from TMP, Pap. Puu 82(6), 398-402.

Willför, S., Rehn, P., Sundberg, A., Sundberg, K., Holmbom, B. (2003): Recovery of water-soluble acetylgalactoglucomannans from mechanical pulp of spruce, Tappi J. 2(11), 27-32.

Winestrand, S., Gandla, M.L., Hong, F., Chenc, Q.Z., Jönsson, L.J. (2012): Oxalate decarboxylase of *Trametes versicolor*: biochemical characterization and performance in bleaching filtrates from the pulp and paper industry, J. Chem. Technol. Biotechnol. 87, 1600–1606.

Yu, H., Sheikholeslami, R., Doherty, W.O.S. (2005a): Calcium oxalate crystallization in silica and sugar solutions-characterization of crystal phases and habits, Powder Technol. 160, 2-6.

Yu, L., Zhang, X., Ni, Y., Zhou, Y. (2005b): Oxalate-related scaling during peroxide bleaching of mechanical pulp, International Pulp Bleaching Conference (IPBC 2005), 14-16 June 2005, Stockholm, Sweden, 101-111.

Yu, J., Tang, H., Cheng, B. (2005c): Influence of PSSS additive and temperature on morphology and phase structures of calcium oxalate, J. Coll. Interface Sci. 288, 407-411.

Yu, L., Rae, M., Ni, Y. (2004a): Formation of oxalate from the $Mg(OH)_2$-based peroxide bleaching of mechanical pulps, J. Wood Chem. Technol. 24(4), 341-355.

Yu, J., Tang, H., Cheng, B., Zhao, X. (2004b): Morphological control of calcium oxalate particles in the presence of poly-(styrene-alt-maleic acid), J. Solid State Chem. 117, 3368-3374.

Yu, L., Ni, Y. (2005): Oxalate formation during peroxide bleaching of mechanical pulps, Appita J. 58(2), 138-142, 148.

Yu, L., Ni, Y. (2006): Decreasing calcium oxalate scaling by partial substitution of $Mg(OH)_2$ for NaOH in the peroxide bleaching of mechanical pulps, Tappi J. 5(2), 9-12.

Yu, L., Ni, Y. (2007): Partition of soluble and precipitated oxalate and its implication on decreasing oxalate-related scaling during peroxide bleaching of mechanical pulps, Pulp Pap. Can. 108(1), 39-43.

Zauner, R., Jones, A.G. (2000): Determination of nucleation, growth, agglomeration and disruption kinetics from experimental precipitation data: the calcium oxalate system, Chem. Eng. Sci. 55, 4219-4232.

Zerwekh, J.E., Drake, E., Gregory, J., Griffith, D., Hofmann, A.F., Menon, M., Pak, C.Y.C. (1983): Assay of urinary oxalate: six methodologies compared, Clin. Chem. 29(11), 1977-1980.

Zhang, J.X., Yu, E., Ni, Y., Zhou, Y., Joliette, D. (2002): Calcium oxalate in Tembec maple BCTMP line, African Pulp and Paper Week (APPW 2012), 8-11 Oct. 2002, Durban, South Africa.

Zhang, J.X., Yu, L., Ni, Y., Zhou, Y., Joliette, D. (2006): Calcium oxalate related scaling in a BCTMP line, Pulp Pap. Can. 107(1), 52-55.

Örså, F., Holmbom, B. (1994): A convenient method for the determination of wood extractives in papermaking process waters and effluents, J. Pulp Pap. Sci. 20(12), 361-365.

Åbo Akademi University
Department of
Chemical Engineering

PROCESS CHEMISTRY CENTRE

PAPSAT

ISBN 978-952-12-3076-9