Department of Forest Products Technology

Interactions of Chemical Variations and Biocide Performance at Paper Machines

Jani Kiuru

Aalto University

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Interactions of Chemical Variations and Biocide Performance at Paper Machines

Jani Kiuru

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Abstract

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Abstract

The objective of this thesis was to study the interactions of microbial activity, biocide usage and creation, and chemical changes in the papermaking process. The main focus was on oxidative biocide systems. In addition, new measurement and biocide production methods were applied to papermaking, and evaluated for the monitoring and control of the microbiological state and biocide usage. The measurement methods were based on portable handheld online equipments whereas the biocide production was based on electrochemical generation of biocides.

The trials were mainly performed in pilot scale with actual process samples and complemented with a few laboratory trials. Most of the pilot results were verified in several field studies at paper machines. In the studies also the applicability of monitoring tools were evaluated.

Biocide dosing itself, paper machine breaks, and poor management of broke generated chemical variations, which were detrimental to the papermaking process. Spoilage of broke due to poor broke management and poor biocide performance decreased the system pH, increased the conductivity, and caused the defects to the web. These chemical variations were also observed to cause variations in the cationic demand values. This probably caused unwanted particle flocculation generating the spots and holes to the web. Base paper defects were observed to cause runnability problems also at the coating machine. This cyclicity, where chemical variations cause breaks and breaks cause chemical variations, should be eliminated in order to restore good runnability.

When revealing many such cause-effect relations and hidden phenomena, hand-held instrumentation gives additional references for existing basic measurements such as pH, conductivity, and redox potential. This work also took in use measurements which have not been traditionally used in papermaking such as measurement of halogens, dissolved calcium, and dissolved oxygen contents. ATP content measurement using a portable luminometer was found to be useful and easy-to-use method for evaluating microbial activity and optimizing biocide performance at paper mills.

This thesis introduces a new biocide concept which can be used to prevent both microbial and biocidal problems described above. The results demonstrate how electrochemical on-site production can decrease chemical variations and improve biocide performance compared to current best practices offering an efficient and economically attractive alternative for microbial control.

Keywords Papermaking, wet end chemistry, variation, oxidizing biocide, microbial control, electrochemical treatment, online measurement, runnability, web break

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Tiivistelmä

Tämän työn tavoitteena oli tutkia mikrobiologisen aktiivisuuden, biosidien käytön ja valmistuksen sekä kemiallisten vaihteluiden välisiä vuorovaikutuksia paperinvalmistuksessa. Pääasiallisesti työssä keskityttiin hapettaviin biosidijärjestelmiin. Lisäksi uusia mittaus ja biosidin valmistusmenetelmiä sovellettiin paperinvalmistusprosessiin, sekä arvioitiin näitä menetelmiä mikrobiologisen tilan ja biosidiannostelun mittaamiseen ja hallintaan. Mittausmenetelmät perustuivat kannettaviin online-laitteisiin ja biosidien valmistus sähkökemialliseen tuotantoon.

Kokeet tehtiin pääosin pilot-mittakaavassa oikeita prosessinäytteitä käyttäen. Tuloksia täydennettiin muutamilla laboratoriokokeilla. Suurin osa pilot-kokeiden tuloksista todennettiin kenttäkokeilla paperikoneilla. Näissä kokeissa arvioitiin myös mittausmenetelmien käytettävyyttä.

Biosidin annostelu, katkot paperikoneella ja heikko hylyn käsittelyn hallinta aiheuttivat kemiallisia vaihteluita, jotka olivat haitallisia paperinvalmistusprosessille. Heikosta hylyn hallinnasta ja heikosta biosiditehokkuudesta johtunut hylyn pilaantuminen laski prosessin pH:ta, nosti johtokykyä ja aiheutti vikoja rataan. Kemiallisten vaihteluiden havaittiin myös aiheuttavan vaihteluita prosessin varaustilassa. Tämä todennäköisesti aiheutti ei-toivottua partikkeleiden flokkautumista aiheuttaen edelleen reikiä ja täpliä rataan. Pohjapaperin vikojen havaittiin aiheuttavan ongelmia myös päällystyskoneella. Em. syklisyys, jossa kemialliset vaihtelut aiheuttavat katkoja ja katkot aiheuttavat kemiallisia vaihteluita, pitäisi pystyä pysäyttämään hyvän ajettavuuden palauttamiseksi.

Osoitettaessa em. syy-seuraus suhteita ja piileviä ilmiöitä, kädessä pidettävät laitteet antavat lisäreferenssejä nykyisille perusmittauksille kuten pH, johtokyky ja redox potentiaali. Tässä työssä otettiin myös käyttöön mittauksia, kuten liuennut kalsium ja happi sekä halogeenit, joita ei yleisesti ole paperinvalmistuksessa käytetty. ATP pitoisuuden mittaus kannettavalla luminometrillä havaittiin olevan hyödyllinen ja helppokäyttöinen menetelmä mikrobiologisen aktiivisuuden arviointiin ja biosiditehokkuuden optimointiin paperitehtailla.

Tämä väitöskirja esittelee uuden biosidikonseptin, jota voidaan käyttää yllä mainittujen mikrobiologisten ja biosidilähtöisten ongelmien ehkäisyissä. Tulokset demonstroivat kuinka biosidien sähkökemiallisella on-site tuotannolla voidaan vähentää kemiallisia vaihteluita ja parantaa biosiditehokkuutta verrattuna nykyisiin menetelmiin. Sähkökemiallinen biosidien valmistus paikan päällä tehtaalla tarjoaa tehokkaan ja taloudellisesti kiinnostavan vaihtoehdon mikrobien hallintaan.

Avainsanat Paperinvalmistus, märkäosan kemia, vaihtelu, hapettava biosidi, mikrobien hallinta, sähkökemiallinen käsittely, online mittaus, ajettavuus, ratakatko

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CONTENTS

ABSTRACT 3
TIIVISTELMÄ 5
CONTENTS 7
LIST OF ORIGINAL PUBLICATIONS 9
THE AUTHOR'S CONTRIBUTION 10
ABBREVIATIONS 11
1. INTRODUCTION 13
2. THE OBJECTIVE AND THE OUTLINE OF THE STUDY 16
3. PAPER MACHINE AS ECOSYSTEM 17
3.1 Water systems at paper mills 17
3.2 Paper machine runnability 19
3.3 Detrimental substances in neutral papermaking 22
3.4 Chemicals and chemical interactions 23
3.5 Monitoring of process chemistry 25
4. MICROBES IN PAPERMAKING 33
4.1 Different types of microbes at paper machines 33
4.2 Formation of biofilm 34
4.3 Microbial problems in papermaking 35
4.4 Measurements of microbial activity 36
5. PREVENTION OF MICROBIAL GROWTH 40
5.1 Biocides 41
5.2 Good housekeeping 49
5.3 Boilouts 50
5.4 Alternative treatments 50
6. BIOCIDE EFFICIENCY AND PAPER MACHINE CHEMISTRY INTERACTIONS 51
6.1 Corrosion 52
6.2 Interference with additives and process chemistry 53

EXPERIMENTAL PART 57
7. MATERIALS AND METHODS 57
RESULTS AND DISCUSSION 70
8. GROWTH OF BACTERIA IN PAPERMAKING PROCESS (*Papers I and V*) 70
8.1 Development of anaerobic conditions 70
8.2 Pulp deterioration and wet end chemistry 71
8.3 Spoilage and end product quality 76
9. REVEALING HIDDEN PROCESS PHENOMENA WITH PORTABLE INSTRUMENTS (*Papers III and IV*) 77
9.1 Analysis of microbial activity 78
9.2 Measurement of biocide residues 79
9.3 Optimization of biocide dosage 82
9.4 Measurement of other chemical parameters 84
10. INFLUENCE OF BIOCIDES AND BIOCIDE INTERACTIONS ON PAPERMAKING PERFORMANCE (*Papers III and V*) 88
10.1 Chemical variations due to biocide addition 88
10.2 Effect of biocides on runnability and product quality 90
11. NEW CONCEPT FOR ELECTROCHEMICAL BIOCIDE GENERATION (*Papers I and II)* 94
11.1 Generation process 94
11.2 Efficiency in papermaking 96
11.3 Dual biocide concept 102
12. CONCLUSIONS 107
REFERENCES 111

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following scientific articles, which are referred in the text by their Roman numerals. In addition, some unpublished data are presented.

I **Kiuru J,** Tukiainen P, and Tsitko I. (2010). Electrochemically Generated Biocides for Controlling Contamination in Papermaking, *BioResources* 5(4), 2664-2680.

II **Kiuru J,** Sievänen J, Tsitko I, Pajari H, and Tukiainen P. (2011). A New Dual Biocide Concept for Fine Papermaking, *BioResources* 6(2), 2145-2160.

III **Kiuru J,** Peltosaari A, and Wathén R. (2011). Reviewing the Potential of Hand-held Sensors as Performance Indicators for Wet End Chemistry, *Ipw* 1/2011, 17-23.

IV **Kiuru J,** Tsitko I, Sievänen J, and Wathén R. (2010). Optimization of Biocide Strategies on Fine Paper Machines, *BioResources* 5(2), 514-524.

V **Kiuru J,** and Karjalainen S. (2011). Influence of Chemical Variations on Runnability of Paper Machines and Separate Coating Lines, *Ipw* 10/2011, 11-17.

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THE AUTHOR'S CONTRIBUTION

Publication I: Designed the experiments, interpreted the results, and prepared the first draft of the manuscript.

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Publication III: Designed the experiments, performed the analysis, interpreted the results, and prepared the first draft of the manuscript.

Publication IV: Designed the experiments, interpreted the results in part, and prepared the first draft of the manuscript.

Publication V: Designed the experiments, interpreted the results, and prepared the first draft of the manuscript.

ABBREVIATIONS

AKD	Alkylketene dimer
AOX	Adsorbable organic halogen compounds
ASA	Alkenylsuccinic anhydride
ATP	Adenosine triphosphate
BCDMH	1-bromo-3-chloro-5,5-dimethylhydantoin
BDC	BioDeposit control
BOD	Biological oxygen demand
CFU	Colony-forming units
CMC	Carboxymethyl cellulose
COD	Chemical oxygen demand
CTMP	Chemithermomechanical pulp
DBMH	3-dibromo-5,5-dimethylhydantoin
DCDMH	1,3-dichloro-5,5-dimethylhydantoin
DCS	Dissolved and colloidal substances
DOC	Dissolved organic carbon
EDXRF	Energy dispersive x-ray fluorescence
EPA	US environmental protection agency
EPS	Exopolysaccharide
ISE	Ion-selective electrode
MAF	Electrochemical microbial antifouling
MAR	Multivariate autoregressive
MPC	Model predictive control
NA	Nutrient agar
NSSC	Neutral sulfite semichemical
OBA	Optical brightening agent
PAA	Peracetic acid
PCA	Principal component analysis
PCM	Paper coating machine
PID	Proportional integral derivative
PM	Paper machine
PMEU	Portable microbial enrichment unit
RLU	Relative light unit

ROS	Reactive oxygen species
SPC	Sodium percarbonate
TOC	Total organic carbon
WES	Wet end simulator

1. INTRODUCTION

Conditions in a papermaking process are often favorable for microbes to grow (Kolari 2003). Microbes in the process can cause a multitude of production problems, from decreased production efficiency via impaired runnability and raw material spoilage to product safety issues (Edwards 1996; Ludensky 2003; Väisänen et al. 1998).

Because of their detrimental effect, microbes in the process are controlled with biocides. They act either by killing microorganisms (biocidal effect) or by inhibiting the growth of micro-organisms (biostatic effect). An ideal biocide should meet several requirements such as (Edwards 1996):

- Applicability over a wide range of operating conditions.
- No interference with other additives.
- Broad spectrum of activity towards microbes.
- Efficient and fast-acting.
- Environmentally friendly and non-toxic.
- Safe for the operator.
- Low-cost.
- Easy-to-handle.

Unfortunately, there is no biocide that can encompass all the requirements, and none of the biocides is suitable for all applications.

Annually, over 200 million Euros are spent on slime prevention by the paper industry in Europe. The total sales of (non-oxidizing) slime preventing chemicals (presented in Figure 1) has started to decrease after the peak in 2003 (Finnish Environment institute 2007). Contrary to the traditional biocides, in the last few years, the sales of oxidizing biocides have radically increased (Kolari 2007). The increased interest directed towards oxidizing biocides is due to their low cost. Oxidizing biocides also degrade faster, and the degradation products are not harmful or toxic, but environmentally sound. Typical biocide costs at paper machines vary between 1 and 4 €/paper ton. For average sized fine paper machine this means 0.5-1 million Euros in annual cost (Sievänen 2008).

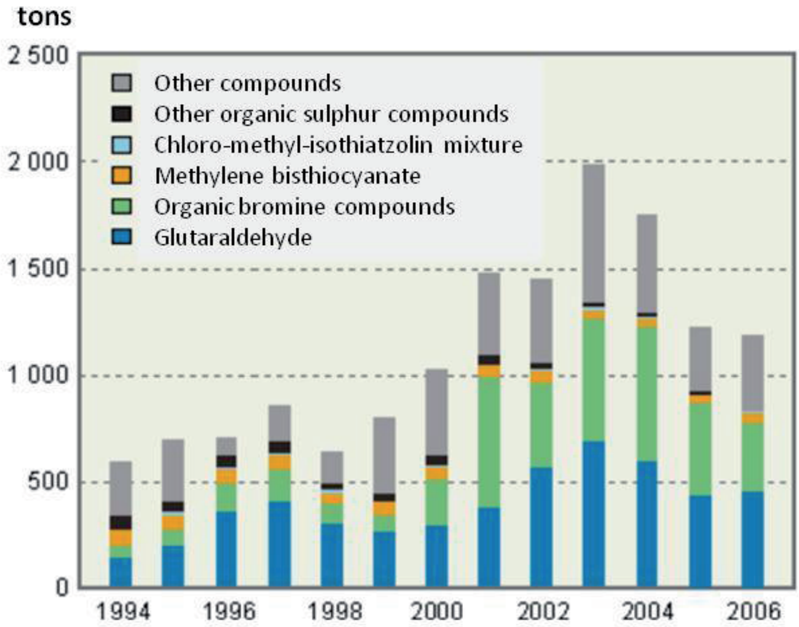

Figure 1 The total sales (tons) of non-oxidizing slime preventing chemicals in Finland (modified from Finnish Environment Institute 2007).

The development of a biocide strategy for a paper mill is always a compromise between the costs and performance. An insufficient use of biocides endangers the machine runnability and product quality (Blanco et al. 1996; Ludensky 2003). On the other hand, extensive use of biocides is not only expensive, but may result in unwanted interactions with the process and other chemicals (Casini 2003; Simons and da Silva Santos 2005). Papermaking is a dynamic process in a continuous state of change. Thus, evaluation of biocide performance is challenging. The results should be available instantly for reliable evaluation. This is not possible with traditional plating methods for determination of microbial counts. Indeed, more efficient methods would be beneficial.

During the past years the biocide development has been rapid. Reductive biocides were first replaced by strong oxidizers. After noticing the problems with the strong oxidizers (Simons and da Silva Santos 2005) the development has been towards weak oxidizers and stabilized halogens. Both continuous and batch additions of these biocides have been used (Schrijver ad Wirth 2007). During this development, in author's knowledge, in publically available literature basically no negative features of these biocides have been reported. This is rather surprising since these oxidizers are salts, they are dosed in certain pH, and they do interact with the process and with other chemicals.

Biocide usage and microbial growth both can cause chemical variations in papermaking processes. Interactions of biocides and chemical variations in a papermaking process are not thoroughly investigated. Having a clear understanding of the interactions would allow economically and environmentally efficient use of the biocides.

From the biocide treatment point of view the measurements are required in order to prevent errors in dosage. According to Hubschmid (2006) such measurements should not only include detailed monitoring system of biocide dosage but also:

- The type and quantity of other chemicals used in the process should be known, as well as physical data of the product to be treated such as temperature range, pH, redox potential and so on.
- Technical installations, such as agitator systems, re-circulation lines have to be evaluated with respect to choosing dosage points.
- It is important to determine the minimal inhibition concentration of the biocide to be used.

In fact, process measurements, diagnostics, and automation are widely being used in modern papermaking (Ruetz and Meitinger 1998). The mills are reducing personnel, and thus more measurements and analysis need to be performed automatically or quickly. On the other hand, more control loops are built, and measurements need to be continuous to maintain the control (Rantala et al. 1994; Artama and Nokelainen 1997; Bley 1998). Traditionally, process monitoring has been a combination of inline and online measurements and extensive laboratory work (Leiviskä 2000). These traditional inline sensors are real-time measuring equipment, but collected data is restricted due to the fixed sensor installation. Therefore, the measurement matrix is rather fixed and difficult to adapt to process changes, trial runs, etc. Having portable devices, which would be capable of performing all these necessary functions would allow adaptive monitoring and control. This would also meet the requirements for preventing errors in demanding biocide dosing.

2. THE OBJECTIVE AND THE OUTLINE OF THE STUDY

The objective of this work was to study the interactions of microbial activity, biocide usage and - creation and chemical changes in the papermaking process. Main focus was on oxidative biocide systems, because these systems have widely taken over the biocide markets and the interactions have not been studied adequately. Moreover the emphasis was on neutral/alkaline papermaking. In addition, new measurement and biocide production methods were applied to papermaking, and evaluated for the monitoring and control of the microbiological state and biocide usage. The methods were based on portable handheld online equipments. The biocide production was based on electrochemical generation of biocides, which enables on-site production of oxidative biocides.

Relevant scientific literature is reviewed in chapters 3-6. The review presents an overview of chemistry and microbiology at paper machines. It covers also the basics of prevention of microbial problems as well as potential interactions with the process due to these prevention programs.

In the experimental part in the results and discussion, chapter 8 concentrates on illustrating the growth of bacteria in the process and chapter 9 on measurement tools and philosophy to reveal the hidden phenomena occurring in the process. Chapter 8 shows the effect of microbial growth on paper machine chemistry and product quality, whereas chapter 10 shows how biocide program can affect those. Field data examples present the effect of biocides on runnability of paper machine as well as on web performance in converting processes.

Chapter 11 introduces a new biocide concept which can be used to prevent both microbial and biocidal problems described above. The chapter demonstrates how electrochemical on-site production affect chemical variations and biocide performance compared to current best practices. Chapter 12 gives the overall conclusions and suggestions for further research.

3. PAPER MACHINE AS ECOSYSTEM

"An ecosystem is a biological environment consisting of all the organisms living in a particular area, as well as all the nonliving, physical components of the environment with which the organisms interact" (http://en.wikipedia.org/wiki/Ecosystem). A good example of an industrial ecosystem is a paper machine, specifically chemical and microbiological phenomena and interactions occurring in the complex water circulations of the machine. Chemical stability in the water circulations goes a long way in establishing the whole efficiency of the paper machine process.

3.1 Water systems at paper mills

The papermaking process is basically a very large dehydration process. Consistency of the stock flow entering the paper machine headbox is typically 0.2%-1.0% (2-10g fiber per kg water). After drainage on the wire or forming section the web consistency increases to 15%-25%. Mechanical compression removes water on the press section. The web consistency increases to 33%-55% depending on the paper grade and press section design. After the press section, the web enters the dryer section where evaporation removes the remaining water. A small amount of moisture (5%-9%) remains in the paper even after the dryer section (Kuhasalo et al. 2000). In addition, in practice water leaves the paper mill also as wastewater to the wastewater treatment plant, which means that even in the most closed mill system, fresh water is needed to compensate this loss of water. Figure 2 illustrates the water balance of a typical paper mill.

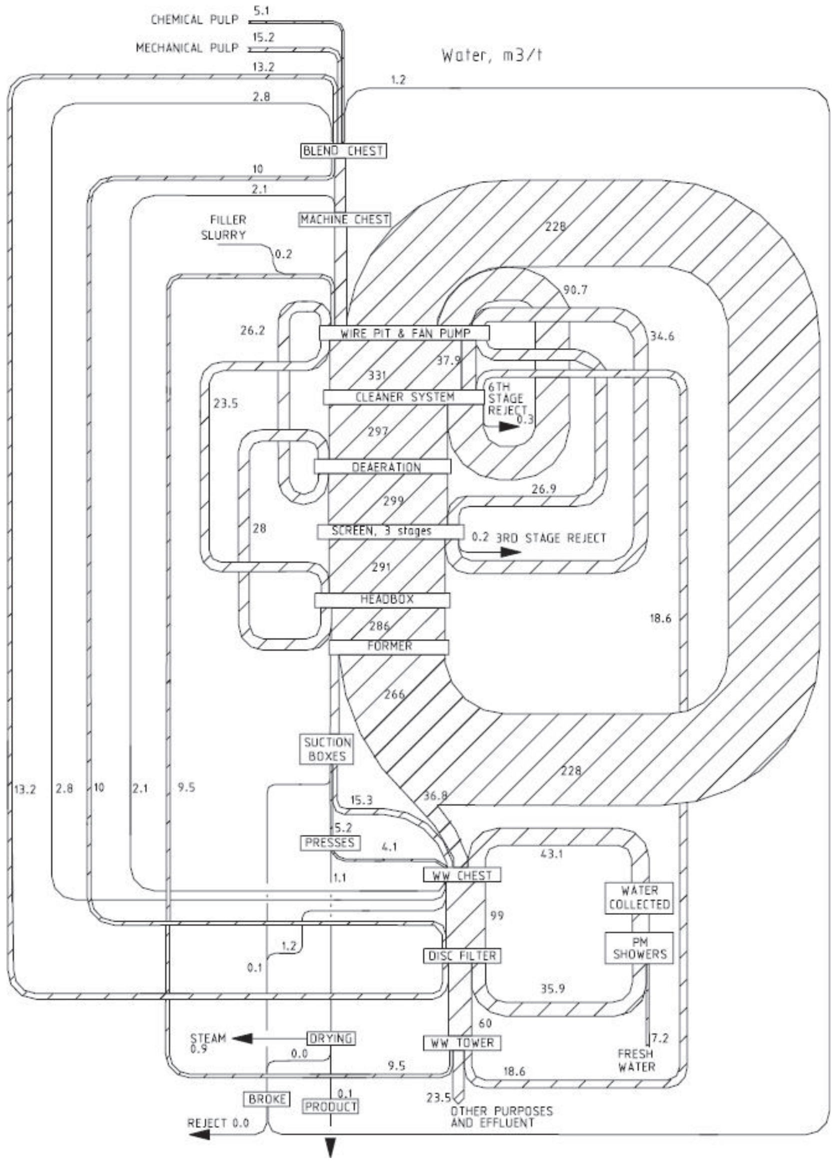

Figure 2 Paper mill's water household (Weise et al. 2000).

Inside the paper mill the water is reused and cycled in several circulations. The water removed in the wire part of the paper machine is discharged into the wire pit. This water is used to dilute the stock fed to the paper machine. The diluted stock is pumped via centricleaners, air removal equipment, and screens to the headbox and ahead to the wire section. This system is called short circulation (Weise et al. 2000).

A part of the water removed in the wire and press section that is not led back into the headbox as described above, is utilized in the earlier stages of the papermaking process. These waters compose a long circulation of the paper machine. Water in the long circulation is used for example to adjust the consistency and to improve the material and heat economy (Ryti 1983). This water, which has been used at least once before is called white water and, is also processed using various means.

With an optimized water usage modern paper machines can operate with very low fresh water consumptions. Usually the degree of closure (fresh water added to the process) varies between 2 and 20m^3/t of produced paper depending on process and water processing technologies used (Weise et al. 2000). Low water usages lead to accumulation of various substances into water cycles. Especially the dissolved and colloidal fractions are difficult to separate (Wearing et al. 1985; Kokko et al. 2004).

3.2 Paper machine runnability

The fastest paper machines have an average running speed of nearly 2000m/min. The maximum width of paper machines is approximately 11 meters (Going 2008). Since the width increase would be expensive and difficult (vibration of the cylinders at high speeds), the production efficiency improvements are carried out by decreasing the downtime (breaks, web defects, broke volume) and increasing the production speed (Kurki et al. 2000).

The increase in production speed of a paper machine is often limited by increasing web breaks. In practice, reason (cause, location) behind web breaks need to be identified before speed increase is possible. In a study by Hokkanen (1996), the author showed that most of the web breaks occurred just after the press section when the paper web is wet (dryness 40-60%) (Figure 3).

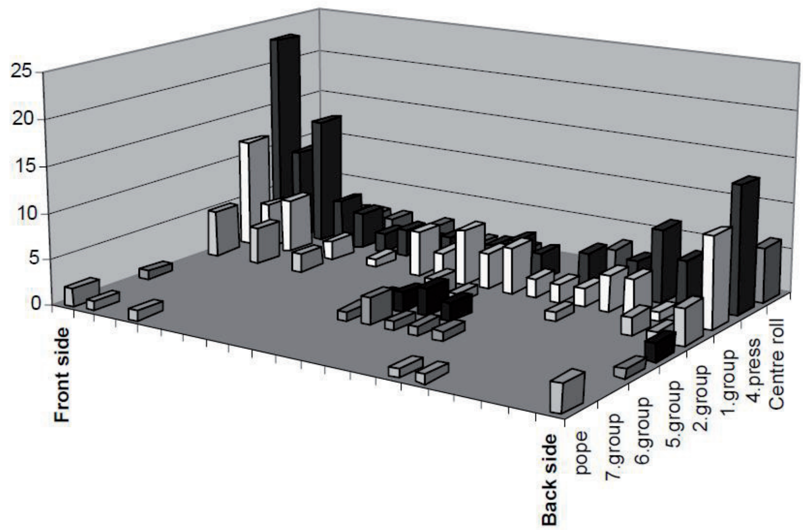

Figure 3 The location of web breaks during a six months follow-up study at a magazine paper machine in Finland (Hokkanen 1996).

Based on many published studies, web breaks can be explained by the high tension or low strength of the paper web. The studies suggest that web breaks are possible in the strength/tension range where these two distributions overlap. In practice, this means that statistical variation in tension and strength can cause the breaks (Wathén 2003; Wathén and Niskanen 2006; Roisum 1990a; Korteoja et al. 1998). The importance of minimizing periodical fluctuations of the process is therefore necessary for good runnability. The studies also suggest that the defects and the amount, size, shape, and position of the defects affect the break sensitivity (Wathén 2003; Uesaka 2005). The role of chemical stability and chemical variations has been acknowledged as a key to undisturbed paper production (Haapala et al. 2010; Hubbe et al. 2006; Sihvonen et al. 1998; Wathén 2007; Kallio and Kekkonen 2005). Therefore, it can be expected that significant amount of web defects have chemical background.

There can be numerous possible causes behind an individual machine break. Even thou the cause fundamentally have physical, chemical or microbial background (or combination of these), the actual brake can be related to pitch deposition, various chemical deposits, stickies and other adhesives in recycled paper processes and microbiological slime (Haapala et al. 2010). In addition, paper holes and spots, cuts and sheet breaks have been reportedly been cause by shives or flakes, bubbly gasses of droppings from the paper machine onto the web (Roisum 1990b). Also breaks due to mechanical problems, condensations droplets and many more have been reported.

Closing of the water circuits of paper machines leads to a situation when the amounts of dissolved and colloidal substances increase (Wearing et al. 1985; Kokko et al. 2004). These materials are derived from wood constituents like lignin, hemicelluloses and extractives. Many additives have effects on water properties as well. The studies have shown that contaminants in white water decrease the strength of paper (see Figure 4). Tay (2001) suggests that contaminants in white water make the fibrous material more hydrophobic and hinder the formation of bonds. This is seen as reduction in paper strength. Based on the important role of chemical stability, the same phenomena can cause web defects and breaks at a paper machine. Haapala et al. (2010) have shown that elevated conductivity, charge, and dissolved calcium levels increased the formation of defects on paper machine.

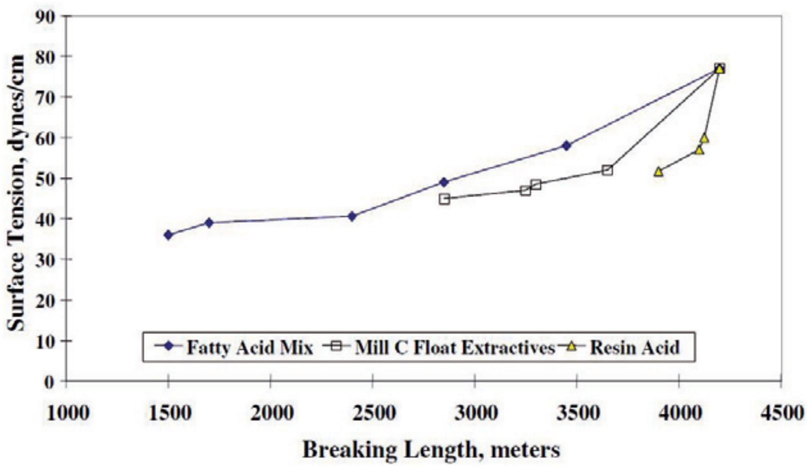

Figure 4 Relationship between surface tension and breaking length as a function of contaminant additions (Tay 2001).

Chemical stability has widely been acknowledged as a key to undisturbed and clean paper production. Production of chemical deposits has been attributed for example to variations in the process pH, temperature and the charge (Haapala et al. 2010; Hubbe et al. 2006; Sihvonen et al. 1998; Wathén 2007; Kallio and Kekkonen 2005). The importance of stable process is increased when water systems are closed, filler usage increased, and the amount of different substances in the process and water cycles has increased.

3.3 Detrimental substances in neutral papermaking

Substances detrimental in papermaking can enter the papermaking process with the fresh water, with the raw materials (pulp, chemicals) or from the machinery (Kanungo 2005). Although the factors such as water hardness and microbes in the fresh water or dissolved and colloidal substances from the wood can also directly cause problems, the difficulties are most often faced in the white water systems when these components accumulate.

White water in papermaking is described as water that has been used at least once before. It means that white water is never clean. It includes substances from fresh water, stock preparation, dissolution occurred during beating or pulp storage, additives, broke or microbiological activity. Because of the closed water circulations and twin wire machines the amount of detrimental substances have increased and caused problems in the papermaking.

Water from the pulp is removed in successive stages of dewatering by free drainage and other drainage elements in the wire section and is collected in the wire pit, seal pit, storage tank, and silo. Water removed from the web in the press section, along with shower water, is collected also trough the vacuum elements. Water collected from each stage of dewatering contains different proportions of fiber, filler, fines and other materials. These materials in water can be divided in two categories: suspended solids and dissolved and colloidal substances (Panchapakesan 1993).

Suspended solids are usually salts, fillers or fiber. High concentrations of suspended solids are of concern in terms of deposits, lowered filtration of the saveall, and plugging (Panchapakesan 1993).

Most detrimental substances are ionic dissolved and colloidal substances. They can absorb or precipitate onto the surfaces of fibers, fillers, and fines, which adversely affects fiber-to-fiber bonding, brightness, and the accessibility of the process chemicals. Table I lists the composition of dissolved and colloidal substances according to their origin.

Table I Composition and origin of dissolved and colloidal substances (Weise et al. 2000).

Chemical compound	Origin
Sodium silicate	Peroxide bleaching, deinking, recovered paper
Polyphosphate	Filler dispersing agent
Polyacrylate	Filler dispersing agent
Organic acids	Filler dispersing agent
Carboxymethyl cellulose	Coated broke
Starch	Recovered paper, broke, strengthening agents
Humic acid	Fresh water
Lignin derivates	Kraft pulp, mechanical pulp
Lignosulfonates	Sulfite and NSSC pulp, CTMP
Hemicelluloses	Mechanical pulp
Fatty acids	Mechanical pulp

Inorganic substances are mainly salts or cations and anions, of which those salts are composed. Inorganic substances can affect the swelling of fiber. They can also reduce fibers ability to bond. Organic substances include pitch, carbohydrates and lignin. They all derive from the wood. Pitch consists of fatty acids. Fatty acids are oxidized and polymerized to macromolecular compounds, which can cause pitch deposits. Carbohydrates and lignin can cause the raise of biological oxygen demand (BOD), chemical oxygen demand (COD) and the amount of total organic carbon (TOC). Deposits from latexes, ash and pitch from wood are called white pitch (Sirén 1996).

3.4 Chemicals and chemical interactions

Natural fibers are a major source of chemically reactive components in papermaking. Chemical additives are introduced into the pulp suspension with a view to alter the properties of paper (functional chemicals) or to improve the process (process chemicals). For these chemicals to perform properly, they must be able to react with or adsorb on the fiber. The mechanisms might differ considerably from case to case (Sten 2000).

A cellulosic fiber has a very hydrophilic surface, which chemically consists of hydroxyl groups. On the surface of the fiber, there are also some carboxyl groups. Due to its chemical composition and mechanical structure, the surface of the fiber is easily transformed by beating into a two-dimensional hydrocolloid of cellulose fibrils and microfibrils having a negative electrokinetic charge caused by the protolysis of the carboxyl groups (Sten 2000).

The chemicals which have effects on colloidal charged systems are added extensively into papermaking. Most common ones are:

- Retention aids added to dilute flow just before the headbox
- Fixatives added to thick stock near machine chest
- Defoamers added to water tanks to control foaming.
- Strength agents added usually to thick stock. The most common ones being starches but also chemicals such as CMC and chitosan have been used.
- Internal sizing agents (rosin sizes, AKD, ASA).
- Fillers and pigments, which usually are not charged but have significant effect on retention procedure.

Because most papermaking additives, pigments, sizes, etc., in water also form a negatively charged colloidal system, the majority of particles in the system repel each other. Due to this, there are two means by which to obtain an acceptable retention. Either the colloidal repulsive forces must be canceled, or the colloidal particles must be bridged together by long chain polymers (Hubbe and Rojas 2008; Sten 2000). Tens of different chemicals are added to the paper machines. Mostly these chemical affect this retention procedure three ways: by improving bonding (retention aids, fixatives, sizes), by adding more material to be bonded (fillers and pigments), or by just disturbing this bonding procedure (defoamers, biocides).

When interaction between ionic compounds (such as salts from oxidative biocides) and papermaking chemicals is considered the most critical point would be the coagulation procedure in the headbox and formation of the web followed by the headbox. Any effect of salt can cause disturbance in electrochemical stability and cause unwanted coagulation followed by deposits, web defects, web breaks etc. The effect of increasing salt concentration is to decrease the relative thickness of ionic double layers, thereby decreasing the forces between particles (Hubbe and Rojas 2008). This is related to tendency of increasing salt concentration to decrease zeta potential (Lindström and S9öremark 1975; Wang and Hubbe 2002). These particle interactions in different salt concentrations can be explained by the DLVO (Derjaguin and Landau, Verwey and Overbeek) theory (Derjaguin and Landau 1941; Verwey and Overbeek 1948). The theory explains how particles in aqueous system interact and how different forces affect the stability of the system and further the flocculation and coagulation. Figure 5 illustrates how different forces attract and repulse the particles, what is the effect of salt concentration, and what kind of the energy barriers have to be overcome in order to flocculate the particles. In the figure, when the interaction force < 0 (the secondary minimum basically) the particles attract each other and can flocculate. By increasing the ionic strength one may go from a kinetically stable colloidal dispersion to one that is coagulated. The theory is well referred in the literature (Donnan et al. 1981; Fröberg et al. 1999; Holmberg et al. 1997).

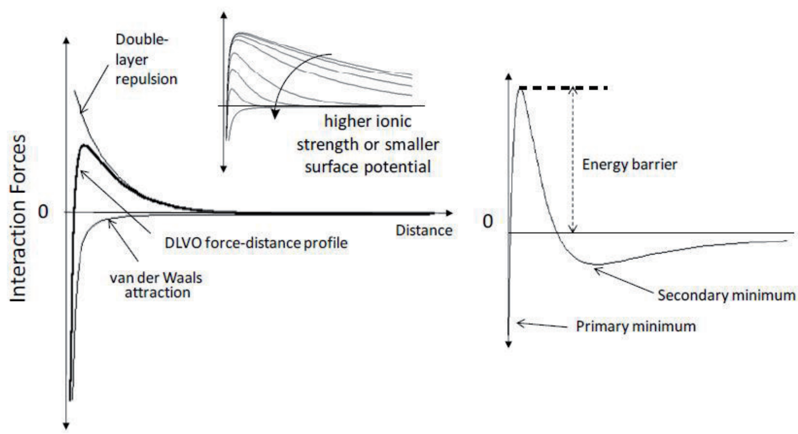

Figure 5 Forms of typical energies between particles according to DLVO-theory (left). Effect of increased salt concentration on interaction forces (left, inside). Energy minimums and barrier as a function of particle distance (right) (Hubbe and Rojas 2008).

3.5 Monitoring of process chemistry

Process measurements, diagnostics, and automation are widely being used in modern papermaking (Ruetz and Meitinger 1998). The mills are reducing personnel, and thus more measurements and analysis need to be performed automatically or rapidly. On the other hand, more control loops are built, and measurements need to be continuous to maintain the control (Rantala et al. 1994; Artama and Nokelainen 1997; Bley 1998). Traditionally, process monitoring has been a combination of inline and online measurements and extensive laboratory work (Leiviskä 2000). These traditional inline sensors are real-time measuring equipment, but collected data is restricted due to the fixed sensor installation. Therefore, the measurement matrix is rather fixed and difficult to adapt to process changes, trial runs, etc. For control maintenance the fixed instruments are suitable – as long as the measurements are maintained properly.

In continuous monitoring, in practice, the measurements at paper mills are still rather limited. Basic parameters such as pH and conductivity are measured, but usually even these parameters are not measured for multiple enough locations (Tornberg 2000). pH variation detected from the headbox is a valuable piece of information but it would be more valuable to detect the same variation also from the earlier process stage. Very seldom all necessary incoming flows to paper machine are equipped with online chemical measurements. The problem is not the availability of the measurements. There is a great number of online analyzers of chemical parameters available, but probably high price, laborious maintenance, regular need of calibration, and lack of resources to interpret the results is limiting the usage of the devices.

Chemical online measurements installed to a typical "well-equipped" paper machine include pH, conductivity, temperature, and cationic demand measurements. Sometimes pH, temperature, and conductivity are measured from several positions. Usually the machine is also equipped with air content analyzer, which can in some cases be considered as a measurement of chemical phenomenon (Kahala and Koskinen 2007). Sometimes also redox potential is measured from the machine. Everything else is often measured by a chemical supplier or sometimes a special analysis group. Typical online measurements these researchers often use are (Kahala and Koskinen 2007; Wathén 2007):

- pH, redox potential and conductivity.
- Cationic demand analysis. Zeta potential.
- Air content and content of dissolved oxygen.
- Measurement of individual ions, in most cases dissolved calcium content.
- Online analysis of organic compounds. Usually just TOC analysis. Sometimes also analysis of dissolved starch.

As mentioned earlier, the amount of performed laboratory analysis at a typical paper mill has been reduced during the last decade. Earlier the laboratory analysis was performed regularly. At present the analysis is basically carried out only when it is too late. In principle, a laboratory measurement cannot be considered as process monitoring. It is not possible to detect sudden changes or periodical fluctuation using laboratory methods. In process monitoring the laboratory analysis are utilized to calibrate online instruments. Also analyses that cannot be performed online reliably or with a reasonable work are performed in laboratory. Deposit analysis and analysis of waste waters (AOX, COD, BOD, etc.) are examples of such analysis (Levlin 2000). The purpose of these is not process monitoring but troubleshooting or occasional follow-up of regulations. Also different kinds of microbial analysis are often performed. These will be described later in this review.

Due to increased amount of subcontractors at the paper mills, increased optimization, and the utilization of multiple control loops - there is a need for new kinds of online measurement instruments. These instruments could be installed to a paper machine for short periods of time to be intended for solving problems related mainly to wet end chemistry. The same instruments could be used also for trial runs and process optimization. This approach enables an inexpensive, easily transferable and convertible field laboratory for point to need use. This idea was demonstrated in this study using several instruments and several chemical parameters.

Below are listed the most important online measurable chemical parameters. Also mechanisms how these parameters are related to process stability are reviewed.

Temperature

Temperature increases accelerate the chemical reactions and the solubility of substances (Jaycock 1997). In general, a decrease in temperature creates precipitates of dissolved substances. The deposition of components found in extractives occurs at a temperature slightly below the melting point, where a solid becomes tacky. An increase in temperature reduces the viscosity of resin acids and thus decreases the adherence to smooth surfaces, but it largely increases the stickiness to press felts (Holmberg 1999).

At higher temperatures, dewatering on the wire sections is better, because of the lower viscosity (Norell et al. 2000). An excessively high drainage rate may lead to poor formation. In some case there is also a limit in increasing temperatures. For instance, the AKD sizing agent’s melting point is 50°C.

Temperature exercise has a great influence on the existing microbial population. Normal papermaking conditions are suitable for the growth of many kinds of microbes. The temperature in the papermaking systems usually varies from 30°C to 60°C. Fungi and yeasts generally do not tolerate temperatures above 40°C. Contrary to this, many bacteria thrive well in the high temperature range (Jokinen 2000). Optimal temperature ranges for different types of microbes listed by Blanco et al. (1997) are listed in Table II in chapter 4.1.

A stable temperature is the requirement for a stable papermaking process; changes of 1-2 degrees can be significant. This fact is sometimes overlooked, despite its simplicity. When measuring any parameter, it is always of importance to also know the temperature (Holmberg 1999). In fact, most of the sensors also measure the temperature, in addition to a desired parameter.

pH

pH, a logarithmic value of the molar hydrogen ion concentration affects almost everything in the wet-end. pH should be controlled well, from pulping onwards, and it is important to keep the pH variations as small as possible (Holmberg 1999).

pH regions which paper machines use, can be divided into 3 categories: acid (pH 4.5-6.5), neutral (pH 6.6-7.5) and alkaline (pH 7.5-8.5). The process pH strongly affects the solubility of wood components, especially the phase change of dissolved material. pH increase boosts the solubility of wood components and thus the amount of anionic disturbance substance is also increased. The surface charge of fibers and other components increases. Also, the resin solubility increases and the bacteria activities accelerate. When pH decreases, precipitates are usually formed which are practically non-soluble and significantly disturb the process (Aloi and Trsksak 1998).

For pH control, sulphuric acid, SO_2 water, and alum have been used as acids to decrease pH, while NaOH usually has been used as a base. During the last decade, more and more mills have started to use CO_2, or a combination of CO_2 and NaOH. CO_2 systems are usually based on CO_2 production from sodium bicarbonate or application of liquefied gas that provide CO_2 (Aloi and Trsksak 1998; Jansson and Ortiz-Cordova 2011; Ogston et al. 2010). In some cases the CO_2 has also been obtained from exhaust gases from combustion. As the effect of temperature is sometimes overlooked, so is the quality of the chemical used for pH control. It is important to be aware of possible quality changes, to ensure a functioning control system (Aloi and Trsksak 1998; Jansson and Ortiz-Cordova 2011).

Conductivity

Conductivity is defined as the conductance of a material between opposite sides of a cube with 1cm side length. Conductivity is mainly caused by inorganic ions in the process water. Small ions such as Na^+, Cl^-, SO_4^{2-} often cause most of the conductivity, pH-control chemicals and bleaching chemicals being the most remarkable source of conductivity in the paper process. The conductivity of electrolytes increases with increasing temperature (Holmberg 1999). High concentrations of ions may lead to precipitation, and in general high conductivities are signs of an unclean process (Kanungo 2005).

Redox potential

Redox potential is a measure of electronegativity. Substances having stronger electronegativity than hydrogen have a positive redox potential, they are capable of oxidizing. When the redox potential of a system changes, the amount of oxidative or reductive agents in the process changes (Gray 1982). This will, sometimes with delay, lead to changes in for example the microbial state or pH of the system.

Air content and dissolved oxygen

Air in the papermaking process can be very detrimental, compromising product quality, pumping efficiency, and water removal, for example. Dissolved air consists of molecules of nitrogen, oxygen, CO_2, and other gases that are part of the liquid phase (Weise et al. 2000). Dissolved oxygen is relevant also to the aerobic microbial activity in the process. If all the dissolved oxygen is consumed, anaerobic bacteria growth is very likely to proliferate in the process (Rice et al. 2009; Blanco et al. 1996).

Dissolved oxygen can be measured online using two different methods, electrochemical and optical. An electrochemical method based on Clark's cell (Rayleigh 1885) is affected by conductivity. The system measures the current associated with the reduction of oxygen which diffuses through a Teflon membrane, and this current is proportional to the partial pressure of oxygen in the solution being evaluated. Optical measurement is based on constant movement of oxygen through a diffusion layer. Diffused oxygen interacts with a luminescing element when the luminescence changes. Conductivity of the samples must also be taken into account with the optical method (YSI incorporated 2006). Air content can be measured by pressing the air bubbles out from the process sample. In commercial analyzers this result is correlated with the ultrasound analysis of the sample flow, which is known to correlate with the air content (Savcor Process Oy 1999).

Turbidity

Turbidity is a measure of the ability of an aqueous sample to scatter light, indicating the relative amount of fine, suspended materials in the sample, as well as particle size. Turbidity is used to follow the changes in fine suspended matter in white water or in filtrate obtained by passing furnish samples through a specified screen. It has been used for investigating the effect of retention aids and flocculating agents. Turbidity is not an exact measurement but in some studies it has been found to correlate with the changes in charge (Schneider et al. 2001).

Dissolved calcium

Being aware of the amount of dissolved calcium is important at mills using calcium carbonate $CaCO_3$ as filler, as well as at mills using recycled fibers as raw material. Calcium carbonate dissolves into Ca^{2+} and CO_3^{2-} ions as pH decreases below neutral or the temperature decreases. An apparently natural way to decrease the dissolving of $CaCO_3$ is to increase the pH in the system, since the dissolving of $CaCO_3$ above pH 8 is negligible.

Calcium ions contribute to compression electrostatic double layer around disturbing substances, causing them to come closer together and agglomerate. Calcium ions also form insoluble soaps with fatty acids and resin acids. This can lead to deposits in pipes and on machinery, which in turn can lead to the need for extra shutdowns for cleaning. Agglomerates and insoluble calcium soaps can also lead to formation of spots and holes in the paper, which leads to reduced paper quality and can cause breaks. Calcium ions block anionic charges on fiber surfaces. Cationic process chemicals have to compete with calcium ions to adsorb onto the fiber surfaces. This means that adsorption of for example cationic starch and wet strength resin will vary when the concentration of dissolved calcium ions vary. Varying process water hardness and conductivity can thus cause variations in paper strength (Jansson and Ortiz-Cordova 2011).

Online measurement of dissolved calcium is based on online sample pretreatment and elemental analysis. Sample treatment is usually performed with ceramic filtrations whereas the analysis is based on Energy Dispersive X-ray Fluorescence (EDXRF) technology. Ion-selective electrodes have also been studied to measure calcium from a wood pulp suspension (Vázquez 2001). However, these applications have not become commercially utilized in such purposes.

Halogen compounds

The main halogen compounds found in papermaking waters are chloride, Cl^-, and bromide, Br^- (Aromaa 1999). One Cl^- source is chlorine dioxide, which is used in the bleaching of pulp or as a biocide. The halogens are considered highly corrosive by papermakers (Jokinen 2000). Chlorine measurement is beneficial when determining the correct amounts of biocides and bleaching agents based on chlorine dioxide or sodium hypochlorite. Also bromide ions enter the papermaking streams via the biocides. The online measurements are based on ion-selective electrodes and require sample filtration before the analysis if measured from the process.

Charge and ionic conductivity

Pulp contains a large amount of solid particles, such as fibers, fillers, fines, dissolved and colloidal substances (DCS). Particles usually acquire a certain charge when they are dispersed in water. In the absence of chemical additives, almost all of the particles have a negative charge in a water suspension. DCS has plenty of anionic charge capacity (Norell et al. 2000). Nowadays excessive anionic charge is neutralized with small molecule mass and high charge density cationic polymers. Another option is to wash away the anionic water phase using wash press, and to replace it with cleaner water.

The most common methods for measuring the total net charge of suspensions are titration procedures. The anionic charge of a sample is titrated against a positively charged standard polymer, or the sample is first treated with an excess of positively charged polymer, followed by back-titration with a negatively charged standard polymer. Online methods are based on measuring the zeta-potential or streaming potential of a fiber pad (Holmberg 1999).

A charge condition disturbance can lead to a many difficult problems in the process. For example, underdosage of fixing agents can lead to poor retention and retention control. Overdosage can lead to a charge reversal and further formation build-up of precipitates, spots, emergence of holes, bad drainability and formation, and problems in the center-roll release. Fixing agents are cationic synthetic polymers, which build up agglomerates with colloidal material in the water phase, and attach themselves to fibers, so that they end up in the final paper (Holmberg 1999).

Organic compounds

Organic compounds have a significant role in papermaking. Compounds like dissolved starch, rosin acids, fatty acids and carbohydrates can be detrimental to machine runnability and product quality. Organic material also decreases the efficiency of oxidizing biocides since biocides react with organic material at the same time with microbial action (Edwards 2003). Even though the measurements are important, they still are rather seldom measured. There are basically no online methods available. The only online possibility is to measure the total amount of organic material (TOC). The measurement is based on CO_2 analysis of wet-oxidized samples and it is rather complex requiring sample pretreatment, acidification, UV-exposure and detection. However, the method is available as an online application (Holmberg 1999).

Process control

Another factor, after applying an online measurement, is in maintaining a stable process with a functioning control. Traditionally the controls have been based on PID-controls (Proportional Integral Derivative). In controlling the fast phenomenon with multiple controls this type of control has proved to be inadequate in maintaining the stable conditions. Especially during the grade changes and start-ups the PID-control is too slow. Mainly the machine suppliers have developed new solutions, MPC-controls (Model Predictive Control), where mathematical modeling is utilized in control loops. The idea is to use modeling to teach the control to perform the adjustments optimally and more rapidly compared to the traditional means (Dietz et al. 2007; Laitinen et al. 2007).

4. MICROBES IN PAPERMAKING

Due an aquatic environment, a temperature of 30-60°C, and a pH range of 4.5-9.0, paper machines offer an ideal environment for microbes to grow and reproduce (Kolari 2003). In addition, cellulose and various degradable additives present in paper machine waters offer a good source of nutrition for microbes. The reduction of fresh water consumption and closing up the water cycles causes the buildup of dissolved organic material used by microbes as nutrition. This, together with increased usage of recycled fibers and the move from acidic to neutral or alkaline paper manufacturing processes, are factors that have increased the amounts of microbes in paper machine systems, as well as the extent of problems related to these microbes (Blanco et al. 1997).

4.1 Different types of microbes at paper machines

The microbial flora of a paper machine covers a wide range of microbes. It includes spore-forming aerobic bacteria, non-sporulating aerobic bacteria, and anaerobic bacteria. Molds, yeasts, and algae may also occasionally be present (Väisänen et al. 1998). The most common types of microbes found in the paper machine wet end are aerobic bacteria belonging to the genera *Bacillus, Burkholderia, Pantoea, Ralstonia* and *Thermomonas* (Kolari 2003). The factors affecting the growth of microbes are listed in Table II.

Table II Factors affecting the growth of microorganisms (Blanco et al. 1997).

	Optimal temperature, C	Light	Oxygen	Optimal pH	Water
Bacteria 0.5-1 µm	Psychrophiles 15 Mesophiles 35 Thermophiles 55	No effect	Aerobic > 4ppm Anaerobic < 4ppm Facultative: no effect	6.5-7.5	Essential
Fungi 10µm	22-30 Molds T_{max} = 65 Yeast T_{max} = 45	Could affect spore germination	Molds > 4ppm Yeast no effect	5.0-6.0 4.0-5.0	Non-essential
Algae >100µm	< 35 for green algae	Essential	O_2 needed to start photosynthesis	4.5-9.0	Essential
Protozoa 10-100µm	20	No effect	Aerobic > 2ppm Anaerobic < 2ppm	6.5-7.5	Non-essential

4.2 Formation of biofilm

Free-swimming (planktonic) bacteria, even when present in the process water in large numbers, do not always affect machine operation or end-product quality. Problems usually arise when bacterial cells become attached to the surfaces of tank walls, pipes or other paper machine parts and form colonizations (Väisänen et al. 1998). These colonizations are called biofilms (scientific) or slimes (in practice). The build-up of a biofilm is often demonstrated using a five-stage model (Figure 6). The formation of a conditioning layer is considered to be one reason why microbes are attracted to the surface. A conditioning layer consists of organic matter such as polysaccharides present in the papermaking process waters. Such material is readily adsorbed onto different surfaces, altering their properties and their interactions with microorganisms. The increased nutrient concentration attracts planktonic bacteria toward the surfaces. The actual formation of a biofilm starts when "primary biofilm formers" become attached to the surface. The microbes attached to the surface produce an extracellular polymer layer to protect it and then start to reproduce. This extracellular polymer layer consists of a variety of different polymers that make the biofilm slimy. An exopolysaccharide (EPS) layer attracts other microbes, which deposits particles on the surface with the result that the biofilm gets thicker. Once the biofilm reaches a certain thickness the cells of the inner part of the biofilm start to die due to lack of nutrients. The slime loses its capacity to attach itself and single cells or larger clumps start to become detached from the surface by the shear forces to which they are subjected. The detached clumps of biofilm colonize other parts of the paper machine or drift into the end product, causing specks and holes in the paper. Microbes growing in a biofilm are generally more stable than free-swimming planktonic bacteria (Schenker et al. 1998, Ludensky 2003).

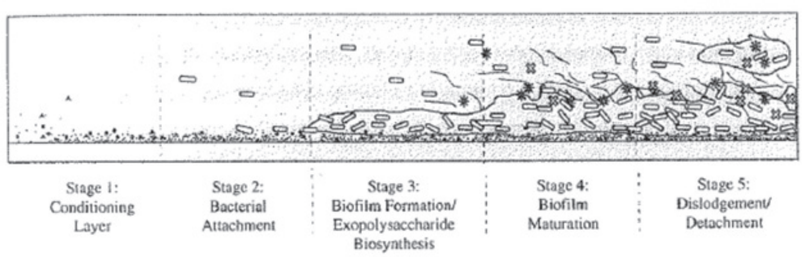

Figure 6 Model of biofilm formation on paper machine surfaces (Schenker et al. 1998).

4.3 Microbial problems in papermaking

If the growth of microbes is not controlled, problems can occur in the papermaking process. These include runnability problems, poor end-product quality and deterioration of the raw material (Edwards 1996). Bad odor and premature wearing of machine parts such as felts are also common problems caused by excessive microbial growth (Ludensky 2003). Table III presents a list of microbial problems encountered in papermaking.

Table III Microbiological problems encountered in papermaking (Edwards 1996).

	Production	Quality	Raw material
PROBLEM	Slime deposits Breaks Corrosion Felt plugging Odors Reduced flows	Holes and Spots Sheet odor Machine esthetics Discoloration Brightness losses Increased dirt count	Fiber degradation Additive contamination Odor Reduction in strength properties Coating mass deterioration Fouling of probes

Slime deposits can cause plugging and fouling of felts, showers and pipes, resulting in paper machine runnability problems. It has been estimated that 10-20% of paper machine downtime is caused by slime problems (Blanco et al. 1996). Microbes can also cause problems in cooling towers. Biofilms formed in cooling towers lead to increased frictional fluid resistance and heat transfer resistance in power plant condensers and process heat exchangers. Biofilms also cause premature wearing out of process equipment and increase the need for replacement (Ludensky 2003).

If care is not taken over mixing and the correct ventilation of chests, extensive growth of anaerobic bacteria can cause production of volatile fatty acids, which are the reason for bad odor. Sulfate-reducing bacteria use volatile fatty acids as nutrients and produce H_2S. Sulfuric acid is also formed, and this can cause corrosion of the surfaces of machine parts (Blanco et al. 1996).

Microbes can use additives such as starch or retention and sizing agents as nutrients, leading to total or partial loss of their activity. Long storage of pulp without proper microbe control can also lead to spoilage of fiber material. Microbial spoilage of raw material and additives can cause problems in web formation and adversely affect the strength properties of the end product. Detached parts of slime deposits can find their way into the end product, where they can result in spots and holes (Blanco et al. 1996).

Unchecked microbial growth causes a variety of problems in coating and raw materials related to coating as well. The problems are similar to wet-end: viscosity increase in pigment slurries as the dispersant is degraded, pH drop, brightness losses and odor problems due to anaerobic growth, starches and protein lose viscosity as they are degraded (Woodward 2009).

4.4 Measurements of microbial activity

Papermaking conditions are favorable for the growth of various microbes. Since paper mills do not operate under sterile conditions, there is always microbial population in the wet-end. High microbial activity in papermaking may causes problems with slime formation, seriously compromising productivity and even product quality. Coated broke due to a large amount of starch in furnish may have a high content of bacteria, which causes a decrease in pH and dissolving of $CaCO_3$ (Molin and Puutonen 2004). That is why monitoring of the bacteria content is so critical.

Cultivations

So far, the main method for monitoring bacterial population in industrial samples is cultivation on agar. The existing standard plate count procedure requires several days for quantification. Bansal et al. (2010) has well described the complex cultivation procedure with important precautions. There are many modifications of the methods, such as Petrifilm, contact or dipslide systems (Envirocheck®, Hygicult®, and Rida®Count) designed to simplify the sampling and plating. However, days are yet needed for bacterial colonies to be counted. Moreover, many bacteria require specific media for growth, and therefore can be overlooked when only one rich medium is used. There is a need for rapid enumeration of bacteria in a papermaking process. Such a method would enable paper mills to make well-timed decisions.

Mentu et al. (2009) present a Portable Microbiological Enrichment Unit (PMEU) for paper machine microbiological control. The device is a case, which eliminates a need of microbiological laboratory. Even though this is a good effort towards rapid analysis it requires at least 24 hours and is thus still too slow. However, the whole procedure looks easier and gives also additional information compared to conventional plating.

ATP analysis

ATP, adenosine triphosphate, is an energy-rich compound and is the primary energy "currency" in living cells (Figure 7). Therefore, it can be considered as a biomass indicator and has been used in biological studies for the enumeration of bacterial mass. The average ATP content for gram-negative and gram-positive bacteria is approximately $1.5 \cdot 10^{-18}$ and $5 \cdot 10^{-18}$ mol/cell respectively, giving a ATP content ration of 1:4-5 (Hattori et al. 2003; Mujunen et al. 1998). The amount of ATP in cells, moreover, is directly connected to the activity status of the cells. Metabolically active cells in the environment rich with nutrients have a higher ATP content than starving cells. It should be noted that bacterial spores have a very low ATP content. Therefore, the ATP assay will definitely overlook spores in the process samples. ATP is stable in the pH range 7-9, but it will quickly decompose in acid conditions. Thus ATP analysis cannot be used in monitoring acidic processes.

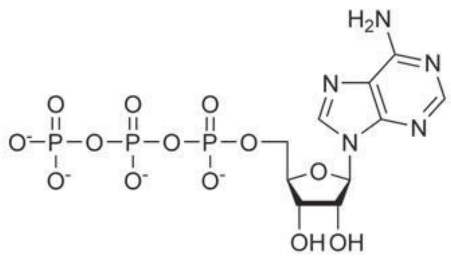

Figure 7 Adenosine 5'-triphosphate (ATP), chemical structure.

The quantification of ATP has been used in industries as a bacterial cell viability assay method (Kramer et al. 2008; Najafpour 2007). In their studies related to the paper industry Mentu et al. (1997) concluded that the measurement of biomass using an adenosine triphosphate (ATP) assay gave results immediately but was only suitable for high levels of microbial contamination due to the low sensitivity of the assay. During recent years, the sensitivity of ATP assays has significantly improved. There are several portable devices that make ATP measurement easy to perform. Contrary to traditional plating, which takes three days, the results of the ATP assay are received in less than one minute. These devices have been developed mainly for the hygiene monitoring, and have not yet been widely used in papermaking.

There are different methods available for ATP measurements. Among them, an enzymatic method based on bioluminescence is the most sensitive. The easiest and the most rapid to use is a portable luminometer with different sampling dippers. This system was designed for hygiene monitoring, mostly in the food industry. The correlation between ATP and the total bacterial count in paper broke have been studied in pilot trials (Figure 8). The ATP content correlated with the total amount of aerobic heterotrophic bacteria. ATP, thus, can be used as an estimate of microbial activity in papermaking process samples (Kiuru et al. 2008).

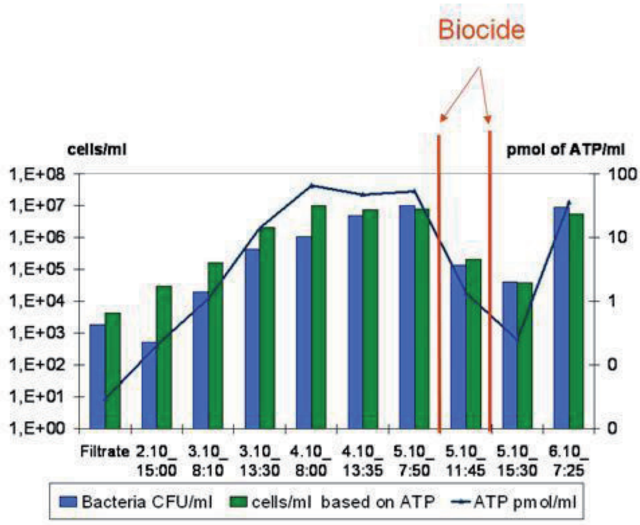

Figure 8 Correlation between ATP and the bacterial count in wet broke (Kiuru et al. 2008).

In above mentioned study the ATP content was measured in microtiter plate using ATP biomass kit. In this laboratory method, after light emission measurement the ATP standard solution (10^{-7} M) is added into each sample and luminescence re-measured to calibrate the light emission. The measurement of ATP with portable device is, however, one-step process with no correction with internal standard. When ATP content in real process samples is measured with the portable device, the results may be influenced by chemical and physical factors. The same total number of aerobic heterotrophic bacteria in different process points (broke, mixing chest and wire water) may give slightly different RLU values.

Indirect methods

Microbiological activity is also being monitored using indirect methods. Different tasting and smelling sensors have been utilized into paper machine diagnostics (Keppler et al. 2007; Lindberg 2005; Savolainen and Pitkänen 2000). These measurements are usually based on analysis of volatile compounds such as fatty acids, hydrogen sulfide, halogens from the biocides etc. The compounds are detected using special sensors. The methods basically always include complex multivariate calculations where sometimes also other papermaking parameters are included. In principle the methods offer continuous online monitoring and even a possibility to build control loops with the measurement. There are several installations at paper machines but probably due to laborious maintenance and complex data interpretation the methods have not become successful.

Biofilm measurements

Measurement of biofilm forming tendency and the analysis of free-swimming bacteria can at least sometimes differ since the biofilms often contain different bacteria than those swimming freely in the white water (Kolari 2007b). The analysis of biofilms is even more difficult and time consuming than the analysis of process waters. Kemira has developed a "Hedgehog" test, which is basically an efficiency test for anti-biofilm agents. The test includes immersion of plate films into the process followed by sufficient contamination time (from 1 day up to 2 weeks). After the contamination the plates can be exposed to anti-biofilm agents and the analysis of biofilm viability can be performed (Kolari 2007b). Such a test can be suitable tool for optimizing the biocide program especially in the case of high biofilm-forming tendency. It is not useful for continuous monitoring or troubleshooting when the corrective actions should take place rapidly. Kemira has also developed a new monitoring technique targeted at measuring the primary biofilm formers called the PiBa assay (Pigmented Biofilm-Forming Bacteria assay) (Keegan et al. 2010).

Basically all the biocide suppliers have developed their own biofilm or deposit control measurement – for instance Kolb's BioDeposit Control (BDC), Nalco's OxiPRO Technology, and Ashland Hercules' Decutec.

The Kolb´s device measures thickness of the biofilm. Measurement principle is based on deposition's insulating feature when the deposit is in contact with water medium. Due to the measurement principle the device can be operated online, which enables early detection and quick response to the problems (Bunk et al. 2006).

Ashland Hercules' Decutec method relies on the microscopic analysis of coupons. An online unit that monitors deposits on a stainless steel surface is also available. A sensor is placed in a bypass chamber or built into any chest or channel way in the paper machine. Analyses of light scattering in the deposit layer provide data on its thickness, growth speed, and density (Jerusik and Davis 2010).

Nalco's OxiPRO system obtains real-time data on deposit formation and microbial activity from the paper machine. Optical fouling and biofilm growth in addition to other parameters such as redox potential and pH are measured. The actual analysis is performed in a separate software (TrendGen) using multivariate tools (Meier 2009).

5. PREVENTION OF MICROBIAL GROWTH

While it is practically impossible to eliminate completely all the microbes in the papermaking process, it is essential to keep the number within tolerable limits. The microbial flora associated with papermaking is reported to consist of both aerobic and anaerobic bacteria. The total aerobic counts are normally between 10^4CFU/ml for machines producing high-grade papers with effective biocide control and 10^8CFU/ml for less controlled lower grade papers, such as brown paper or cardboard. At most mills slime is considered to be under control if the bacteria content of the white water is less than 10^6CFU/ml. In cooling towers 10^4CFU/ml and below can be regarded as a tolerable microbe level (Ludensky 2003).

5.1 Biocides

Biocides are products used to control the growth of microbes. They act either by killing microorganisms (biocidal effect) or by inhibiting the growth of micro-organisms (biostatic effect). An ideal biocide should:

- Be applicable over a wide range of operating conditions, such as pH and temperature.
- Not interfere with other paper mill additives.
- Have a broad spectrum of activity towards microbes.
- Be efficient and fast-acting.
- Be environmentally friendly and non-toxic (no organic solvents, heavy metals, dioxins or furans) and also safe for the operator.
- Be low-cost and easy-to-handle.
- Be cost-competitive.

There are no biocides that can encompass all the requirements, and none of the biocides is suitable for all applications. The selection of biocides must always be made site-specifically (Edwards 1996). Proper estimation of reduction in the microbial count and in the number of fungi is essential parts of a successful biocide program.

Biocides can be divided into three groups based on their activity towards microbes (Blanco et al. 2002):

- Agents that inactivate the enzymes of the cell (quaternary ammonium compounds, methylene bisthiocyanate).
- Electrophilic agents, which act on the the nucleophilic material of cells (for example dithiocarbamates).
- Agents that act through oxidative decomposition of microorganisms (oxygen, ozone and peroxides), also called oxidizing biocides.

Another way to classify biocides is based on their function in the process. Slime-prevention biocides are dosed into the circulation water to prevent the build-up of slime on pipes, tank walls and other parts of the paper machine. Short persistence is an advantage in such cases. When the reaction takes place already in the paper machine, the effluent going for biological treatment is non-toxic. The short half-life of oxidizing biocides makes them suitable for slime prevention. At paper mills biocides are also used in storage tanks, where they protect the slurries from biological spoilage (preservation aids). For this purpose long persistence is often preferred, and rapidly degrading oxidants are therefore not suitable (Kolari 2007).

Oxidizing biocides

Nowadays, vast amount of various commercial products containing oxidizing biocides are available on the market. Moreover, intensive work is going to improve the stability and performance of the known oxidizing biocides. Oxidants are considered to be quick-killers; they do not have good preservation qualities (Woodward 2009).

Ozone, hydrogen peroxide, chlorine, chlorine dioxide and bromine are the oxidizing agents most commonly used as biocides. Performance on the oxidizers can be evaluated based on reaction potentials. Standard potentials of the most common oxidizers are presented in Table IV.

Table IV Standard potentials of common oxidizers at 298 K (Bard et al. 1985; Lenntech 2011)

Oxidant	Half reaction	E°, V
Ozone (acidic)	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	+2.07
Hydrogen peroxide (acidic)	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.76
Hypochlorous acid	$HOCl + H^+ + e^- \rightarrow ½Cl_2 + H_2O$	+1.63
Hypobromous acid	$HOBr + H^+ + e^- \rightarrow ½Br_2 + H_2O$	+1.60
Chlorine	$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	+1.36
Ozone (alkaline)	$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	+1.25
Chlorine dioxide	$ClO_2 + e^- \rightarrow ClO_2^-$	+0.95
Bromine	$Br_2(l) + 2e^- \rightarrow 2 Br^-$	+1.07
Hypochlorite anion	$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	+0.89
Hydrogen peroxide (alkaline)	$HO_2^- + 2e^- + H_2O \rightarrow 3 HO^-$	+0.87

The effectiveness of an oxidant as a biocide is not always related to its oxidation potential. For instance, hydrogen peroxide is a strong oxidizer but weak biocide. The biocidal efficiency of oxidizing agents depends on many factors:

- biocide factors (concentration, contact time and temperature)
- microorganism factors (type of organisms, their growth rate and amount, spores or vegetative cells, mode of growth: plankton or attached growth, stages of biofilm development, clumps)
- environmental factors (pH, organic matter load, transition metals, temperature)

Chlorine

Chlorine in its several forms is the most widely used disinfectant in public and industrial water supplies, waste waters and has many domestic applications. Common forms of chlorine compounds for these applications are: chlorine gas, calcium hypochlorite ($Ca(OCl)_2$) and sodium hypochlorite (NaOCl).

Commercial grade sodium hypochlorite products may contain as much as 15% free available chlorine. The stability of a sodium hypochlorite solution is greatly affected by concentration, light, pH, and temperature. Increased hypochlorite concentration, elevated temperature and storage time adversely affects the strength of sodium hypochlorite solution (Casson and Bess 2003). Liquid hypochlorite products typically have a pH between 11 and 13. In basic solution, hypochlorite anion (OCl^-) decomposes to form toxic chlorate anion (ClO_3^-). The decomposition of hypochlorite may be catalyzed by transition metals. Therefore, storage conditions and handling of hypochlorite stock are very important for prevention of losses during the storage period. The most stable hypochlorite solutions are those of low concentrations (10%), with pH of 11, with metal contents of less than 0.5mg/l, stored in darkness and at cool temperature (White 1999).

Chlorine gas reacts with water to form hypochlorous and hydrochloric acids:

$$Cl_2 + H_2O = HOCl + HCl.$$

The production of acids leads to a drop in the pH of the water. The active agent of sodium hypochlorite is hypochlorous acid which is generated by hydrolysis of hypochlorite:

$$NaOCl + H_2O = HOCl + NaOH$$

The activity of hypochlorite greatly depends on pH. Hypochlorous acid has a stronger bactericidal effect than OCl^- anions. Hypochlorous acid is uncharged and small and therefore relatively easily penetrates the bacterial cell membrane. At pH lower than 7 most of the biocidal activity is provided by hypochlorous acid (Figure 9). Above pH 8.0, biocidal efficacy is noticeably reduced due to production of OCl^- ions: $HOCl = OCl^- + H^+$. Thus, the pH range for the best biocidal activity of hypochlorite is between 6.5 and 7.5. Note, that dissociation is a temperature dependent process (Deborde and Gunten 2008).

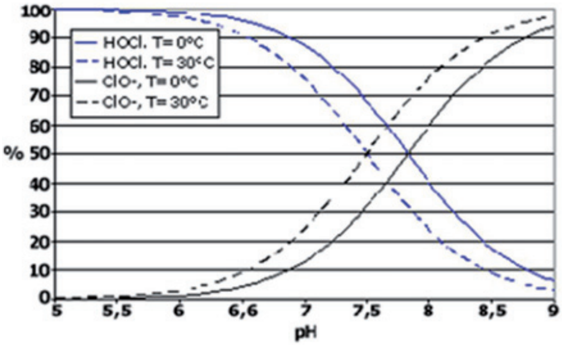

Figure 9 Dissociation of hypochlorous acid at various pH values (http://www.electrolyseur.com/images/hypochlorite.jpg)

Haloamines

The chloramine is a mixture of monochloramine (NH_2Cl) and dichloramine ($NHCl_2$). Chloramine is a weaker disinfectant than chlorine, but is more stable. Chloramine is not as reactive as chlorine with organic material in water, and thus produces less disinfection by-products. As the chloramine residual is more stable than free chlorine, it provides better protection against re-growth of bacteria, which can be important for storage tanks and places with dead-ends. However, at the same time slow decay rates can result in higher biocide residues in the end product (Elsmore 1995; Paulus 2005).

Chlorine Dioxide

Chlorine dioxide is a comparatively strong oxidizer but it has a lower oxidation potential than ozone or chlorine. The optimal pH for ClO_2 is between pH 6.0 and pH 10.0. Chlorine dioxide is generally more effective against microorganisms at pH above 8.0 than chlorine (Knapp and Bettisti 2001). In water, ClO_2 is converted to chlorite (ClO_2^-), predominant end-product (50-70 %), and to chlorate (ClO_3^-) and chloride (Cl^-) (Baribeau et al. 2002). The main advantage of using ClO_2 is that it reacts less with ammonia than chlorine. Chlorine dioxide shows good biocidal activity against bacteria, fungi, protozoa and algae. In bacterial cells it inhibits protein synthesis and damages membranes (Knapp and Bettisti 2001).

ClO_2 is the strong oxidizing agent but is not very effective against established biofilms. For instance, when used at a concentration of 25ppm

ClO_2 failed to remove a biofilm thicker than 100 µm (Jang et al. 2006). Chlorine dioxide is being increasingly used in public water treatment facilities, as a cellulose bleaching agent and for water disinfection at paper manufacturing plants. Generation of chlorine dioxide on-site can be carried out with Eka ClO_2 Purate® technology by Eka Chemicals Systems. The technology is based on on-site generation of ClO_2 from sodium chlorate, hydrogen peroxide and sulfuric acid in Eka's SVP-Pure® generator (Koepenick 2010).

Bromine

The biocidal potential of bromine is similar to that of chlorine. Bromine is frequently added as a bromide salt and generated by the reaction with chlorine. Sodium bromide is not a biocide itself, therefore it must be used together with an activating agent such as chlorine gas, hypochlorite, or ozone. The reaction results in the generation of hypobromous acid:

$$HOCl + NaBr = HOBr + NaCl.$$

Sodium bromide may also be activated by electrical current resulting in the generation of hypobromous acid. The electrochemical generation of oxidizers is discussed later in this review. Similar to hypochlorite, hypobromite hydrolyzes in water to form hypobromous acid (HOBr). HOBr dissociates to form H^+ and OBr^-, but the reaction happens at a higher pH than in case of hypochlorite. This means that at pH 8.5 hypobromite has higher biocidal efficiency than hypochlorite when applied at equal concentrations (Elsmore 1995).

Halogen-Release Biocides

The halogen-release biocides are organic biocides that release hypochlorous and/or hypobromous acids in contact with water. For example, chlorinated isocyanurates release chlorine and hydantoins release chlorine and bromine. Examples of these halogenated compounds include: 1,3-dibromo-5,5-dimethylhydantoin (DBMH), 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH), and 1,3-dichloro-5,5-dimethylhydantoin (DCDMH). The main advantage of these compounds is their stability. They are however, adversely affected by organic matter even though at a lower degree than chlorine (Bloomfield and Miller 1989). Halogenated hydantoins are used in swimming pool, hot tub disinfections, water cooling tower disinfection and toilet bowl cleanser. The number of hydantoin based products is available for use in papermaking to control slime development (SYKE 2006).

Ozone

Ozone is a strong oxidant and disinfectant. Ozone decomposes in solution producing hydroperoxyl ($\bullet HO_2$), hydroxyl ($\bullet OH$), and superoxide ($\bullet O_2^-$) radicals. Partly the reactivity of ozone is due to strong oxidizing power of these free radicals (Kim et al. 1999). The main advantages of ozone are that it is one of the most potent sanitizers known; it decomposes rapidly to produce oxygen and leaves no residues in the final product. Due to its high reactivity it is needed only in low concentrations. Similarly to all oxidizing biocides ozone has some disadvantages such as instability and high corrosion potential. Some factors such as temperature and pH affect solubility, stability, and reactivity of ozone. The pH greatly affects the stability of ozone in aqueous solutions. Stability of ozone in solution is the greatest at pH 5.0 and decreases as pH is increased (Kim et al. 1999).

In the paper industry, ozone is mainly used for pulp bleaching, water disinfection and as a final treatment of effluents. A laboratory study on the possibility to use ozone in the paper industry to control bacteria in recycled white water showed its high efficiency (Korhonen and Tuhkanen 2000).

Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is a very strong oxidizing agent but much less effective biocide than, for instance, hypochlorite. The bactericidal action of hydrogen peroxide is due to formation of hydroxyl radicals ($\bullet OH^-$) which oxidize thyol groups in proteins (Russell 1998; Denyer and Stewart 1998). Hydrogen peroxide generates oxygen from solution when reacted with organic matter. It reacts with most materials including metals and therefore it is rapidly consumed by organics and non-organics. Some commercial products have additives that enhance bactericidal action of the biocides. Hydrogen peroxide is used in the paper industry often as commercial products that are mixed with other (e.g. PAA) oxidizing biocides (Bjorklund 2000).

Peracetic acid

Biocides based on peracetic acid (PAA) are strong oxidizing agents formed from an equilibrium mixture of acetic acid, hydrogen peroxide, PAA and water. There are many different commercially available PAA-based biocides. PAA is used widely for cold sterilization and disinfection. It is also effective for both drinking and waste water treatment (Kitis 2004; Rossi et al. 2007). It is a strong oxidizing agent and has rapid bactericidal activity against different vegetative organisms and spores (Baldry 1983). Temperature and pH affect the bactericidal effectiveness of PAA (Cords and Dychdala 1993). The presence of organic compounds adversely affects the biocidal activity of PAA. PAA is effective over a broad pH range (pH 1.0 - pH 8.0); however the optimum antimicrobial activity occurs in acidic environment. The activity of PAA decreases when the pH is greater than 8 (Cords and Dychdala 1993; Sanchez-Ruiz et al. 1995).

PAA based biocides are known to be effective for controlling microbial populations in papermaking process waters (Bjorklund 2000; Maunuksela 1995). Since PAA is consumed rather fast and does not leave any toxic residue it can be an attractive biocide for mill producing food grade paperboard. At the same time, acetic acid present in high amount in PAA-based biocides may have a negative effect on the pH stability of a papermaking process. Another disadvantages associated with PAA disinfection is the increase of organic content and the potential microbial regrowth due to remaining acetic acid (Kitis 2004).

Mixed oxidants

Oxidizing agents may have some synergetic effect when are mixed together. Below are several examples of such mixtures.

A mixture of hydrogen peroxide and sodium hypochlorite was shown to be an effective biocide even against spores (DeQueiroz 2004). In such a mixture generation of singlet oxygen was monitored and reported to be crucial for sporicidal action of the mixture (DeQueiroz 2004).

Mixed oxidants Cl_2/O_3 (1ppm), Cl_2/ClO_2 and Cl_2/ClO_2- were up to 52% more efficient against *B. subtilis* spores than Cl_2 alone (Son et al. 2005).

Mattila et al. (2006) described a method to inhibit the growth of microbes in fresh and circulating water in board- and papermaking processes. The patented formulation, Bimodes (BIM Kemi), combines sodium hypochlorite (NaOCl) and BCDMH. This mixed biocide is well suitable for processes with pH of 4 to 9, though the efficiency increases with increasing pH.

A method to control the growth of microorganisms in aqueous systems using synergistic mixtures of haloamines is described in a patent by Mayer and Singleton (2007). The haloamine mixtures discussed in the invention consist of chloramines and bromamine. It is claimed that the mixture of has enhanced biocidal activity as compared to that of the individual components. Apparatus for producing an aqueous solution containing synergistic combinations of chloramines and bromamine is presented in a patent of Singleton et al. (2007).

Several years ago ammonium bromide-based biocides for use in papermaking industry were proposed (Davis and Casini 2003). Patented technology was based on the blending of ammonium bromide and sodium hypochlorite (Barak 1999). The biocide is described as "bromide activated chloramine":

$$NH_4Br + NaOCl = \{Br^- \bullet [NH_2Cl]\} + Na^+ + H_2O.$$

The biocide is marketed as Spectrum® Ammonium Bromide Technology by Ashland Hercules. The biocide is unstable and therefore must be produced on-site. The biocide mixture is considered to be mild and, since it does not react with fiber, it is useful in broke or with recycled fibers (Davis and Casini 2003). It effectively reduces the total microbial community within a system where the pH is neutral to alkaline. The optimal pH for this biocide is in the range of pH 7 to 9.

Electrochemically generated oxidants

Electrochemically generated biocide is created by electrolysis of diluted salt solutions in an electrolysis cell. Most of the available information is dedicated to biocides electrochemically generated from brine (NaCl) solution. Salts such as KCl and $MgCl_2$ can also be used (Buck et al. 2002). Since sea water or even tap water contain chloride, it is also possible to obtain free chlorine using such water by electrolysis (Casson and Bess

2003; Nakajima et al. 2004). Main biocidal component in all these applications is hypochlorite.

On-site generated biocides are used for water treatment, and in hospitals for washing medical devices. It has also become very popular in vegetable and fruit processing. In 2002, Japan had officially approved electrolyzed water as a bactericidal agent for food (Huang et al. 2008 and references therein). Electrolyzed water generator has also been approved for applications in the food industry by the US Environmental Protection Agency (EPA) (Park et al. 2002).

In publically available literature, there is very little information on use of electrochemically generated biocides in pulp and paper industry. As mentioned above the electrochemically generated biocidal solutions have been studied intensively in terms of using them in food industry, drinking water and waste water sanitation and hospitals. In author's knowledge, so far there is only one example on electrochemical production of oxidative biocides and their use in paper industry (Särkkä et al. 2007; Särkkä et al. 2008). In their studies Särkkä et al. (2007; 2008) used isolated bacteria and synthetic paper machine water. Thus their approach is not applicable as such and lots of open questions still remain. In addition a few recent patents on electrochemical generation of oxidants have been applied (Savolainen 2006; Cheng et al. 2008).

5.2 Good housekeeping

An important requirement in the overall management of microbial problems is good housekeeping. This includes controlling contaminants entering the process and performing regular boilouts of pipelines and tanks.

Without the implementation of good housekeeping practices, even the best biocide program will be stressed to maintain microbial control of the process. Basic housekeeping starts with the classic "first in, first out" rule (Woodward 2009). To avoid extended storage times, this should be basic rule for all the containers, especially for the chemicals since they might be stored by the machine for weeks. An important issue is also the washing of the hoses when filling the tanks and containers. Other good housekeeping manners include aspects such as sufficient agitation and recirculation, tank cleaning on routine basis, and at least annual system-wide boilouts. If the time and temperature in boilouts are restricted the usage of special chemicals or enzymes could be considered (Woodward 2009).

Good housekeeping can also be automated at least in some extend. Online cleaning can be applied to basically any position in papermaking process. The simplest solution is to use an electric driven water pump which uses the cleanest return water available from the process (clear filtrate). The commodity items are the spray nozzles and the joint piping connections permitting ease of piping travel through elevation and direction changes to continuously clean for example - the entire wire channel with a single flow. This type of automated mechanical cleaning have been reported to reduce manual cleaning, diminish paper quality issues like spots and tears, reduce need for unexplained, unplanned re-feed and re-start exercises, reduce waste amount and improve paper quality. Also reduction in biocide usage has been reported (Parks 2007).

5.3 Boilouts

Even biocides and good housekeeping are not always enough to control the microbes and the problems they cause. Eventually the process gets contaminated so that it must be stopped for a total boilout (exhaustive cleaning). Schwamberger and Wormsbaker (2006) point out the importance of well-planned boilouts and the advantages they offer. The boilout must include careful washing of the whole system and removal of any deposits or biofilms. The chemistry must be carefully optimized during the boilout for optimal washing and successful start-up. Careful washing without considering the chemical interactions might cause significant problems in start-up. The authors mention problems such as wrong pH level and excessive foaming. Boilouts can significantly increase the runnability (less breaks) and product quality (less defects) (Schwamberger and Wormsbaker 2006).

5.4 Alternative treatments

Besides biocides, there are other methods for managing microbe-related problems in papermaking processes. One method is to use dispersants to reduce the size of dispersed particles, reducing the possibility of the formation of microbiological deposits (Blanco et al. 1997). Other possibility is the use of enzyme-based biodispersants to control slime build-up. These agents reduce the formation of biofilms and improve the penetration of biocides (Dykstra and Stoner 1997; van Haute 2003). Oxidizing enzymes, such as glucose oxidase and lactoperoxidase, have biocidal effects against microbes (Siika-aho et al. 2000) while hydrolyzing enzymes can degrade EPS (exopolysaccharide) to soluble products with lower molecular weights (Kolari 2007). In practice, these enzyme treatments are not yet effective enough to replace biocides. The synergistic effect of combined enzyme and biocide treatment can lead to better surface cleanliness with reduced chemical usage.

Electrochemical microbial antifouling (MAF) technology for the prevention of biofilm and inorganic deposits on stainless steel surfaces is based on polarization of the steel surface. A preventive current is fed from an electrode to the (metal) surface to be protected through an electrolyte, leading to oxidation and reduction reactions. These reactions momentarily alter the pH of the metal surface, creating conditions that repel microbe attachment. Since 2000, full-scale MAF systems have been installed at several UPM mills with a positive outcome (Häkkinen et al. 2004).

6. BIOCIDE EFFICIENCY AND PAPER MACHINE CHEMISTRY INTERACTIONS

It is not easy to meet the requirements of an efficient biocide. The biocide should not only be efficient, fast-acting, and applicable over a wide range of operating conditions, but also not to interfere with other papermaking additives (Edwards 1996). In practice, this means that any interaction between the biocide efficiency and paper machine chemistry is unwanted. These interactions are often categorized as microbial problems but actually they are biocide problems - problems with the papermaking chemistry.

6.1 Corrosion

The biocidal effects of the biocides always have an impact also on the chemical resistance of metals. The main metals in the white water systems of paper machines are stainless steels and the corrosion resistance of these steels is most often adequate. However, oxidizing agents may cause an increase in corrosion of stainless steels by either increasing the concentration of harmful anions, for example halides, or as they increase the redox potential, which may raise the potential of stainless steels in a region, where the passivity of stainless steels is no longer stable (Aromaa 1999).

Probably due to sensitivity of the subject not much information about the corrosion problems at paper machines is published. However, the risk of local corrosion in presence of biocide solutions is high (Outokumpu 2004). For instance, with hypochlorite rather low local concentrations (200ppm) can cause corrosion especially on free surfaces (Neville et al. 1998). Hydrogen peroxide is one of the most powerful oxidants, but it is not considered highly corrosive. At paper machines peroxide can assist chloride-induced corrosion but may inhibit thiosulfate-induced pitting (Aromaa 1999). The knowledge about paper machine corrosion (Aromaa 1999), problems it can cause (Hedlund 2002), and the available methods to control the corrosion (Svensson et al. 2005) point out that it is obvious that corrosion is a great concern at paper machines.

Not only the biocides - but also the salts they are dosed with - can cause corrosion. Especially halogens, chloride and bromide, are known to be corrosive. According to Yamamoto (1995) Br^- ions show lower corrosivity in pitting and crevice corrosion compared with Cl^-- ions. Stainless steels are more prone to pitting in bromide solutions than in chloride solution, when the temperature is low. On the other hand, at a higher temperature (e.g. 65°C) the situation is reversed (Virtanen 1999). It seems that bromide is slightly more aggressive on stainless steels in white water than chloride.

Another corrosion aspect is the corrosion induced as a result of metabolic activity, which is generally associated with the microbiological deposits. The corrosion can be originated by different types of micro-organism, including bacteria, fungi and algae. Main types of micro-organisms causing corrosion according to Blanco et al (1997) are sulfate reducing bacteria, fermentatives, nitrite reducing bacteria, hydrogen producers, methanogenic bacteria, organic acid producers, thiobacillus, and iron oxidizers. The sulfate reducing bacteria are considered the main ones responsible for the corrosion induced by microorganism.

6.2 Interference with additives and process chemistry

For good runnability, it is especially important to prevent chemical variations which easily lead to uncontrollable agglomeration and which may further cause deposits, defects, breaks, poor formation etc. (Norell et al 2000; Holberg 1999; Kanungo 2005). The role of biocides in this matrix is twofold: They are added to the system to prevent microbial growth. Microbial growth itself causes chemical variations. On the other hand, biocides themselves can cause chemical variations such as pH shocks. Due to this, biocide types and their dosing strategies must be carefully selected according to the process.

Interference of traditional "non-oxidative" biocides on process chemistry and additive performance has been studied widely. The biocides have been reported to interfere with basically everything from fixing and retention to sizing. These interactions eventually lead to problems with runnability and product quality; typical detrimental effects being reduced filler retention, decreased strength properties, and destroyed sizing. (Raymond et al. 2006; Huber et al. 2010). These biocides which include chemicals such as acetophenoles, benzothiazoles, benzylammoniums, bromonitrostyrenes, carbamates, glutaraldehydes, isothiazolins, polyoxyalkenes, quaternary ammonium salts, and sulfones are mostly cationic and therefore it is obvious that they interact with the other charged chemicals and disturb the flocculation mechanisms. Besides the high price of the biocides this was probably the main reason for invasion of oxidative biocides into markets.

Unfortunately oxidative biocides have similar features. Application of strong oxidizers into wet-end of a paper machine may lead to unexpected detrimental effects. Strong oxidizers are not selective in their reactions but react with all kind of organic material present in papermaking process such as fibers, starch, and papermaking additives. To gain maximum efficiency using strong oxidizers they need to be overfed leading to higher chemical costs. Other negative aspects include excessive cost due to the consumption of additives, increased corrosion, and reduced felt life. (Casini 2003; Simons and da Silva Santos 2005). Especially over the past 10 years the trend in oxidizing biocides has drifted from strong oxidizers such as sodium hypochlorite towards weak oxidizers and stabilized halogens. Stabilized halogens are mostly applied by combining an ammonium salt and hypochlorite. These concepts have decreased the problems mentioned above, but at the same time more attention to process and biocide dosing strategies are needed (Simons and da Silva Santos 2005).

While market share of stabilized halogen systems have increased, very few negative features of these biocides have been reported. This is rather surprising since these oxidizers are salts, they are dosed in certain pH, and it would be rather surprising if they did not interact with the process and with other chemicals. Obviously the suppliers are aware of these risks but understandably they are not too enthusiastic to speak about the concerns. At the paper production units it is also very difficult to show these concerns into practice – especially when the chemical systems are mostly in the hands of the suppliers. These risks are neglected by describing the features such as low concentrations, low dosages, quick degradation etc. instead of describing the actual causes (Koepenick 2010).

Oxidative biocides break down double bonds of the cells by binding their other electron. Oxidizing potential (or redox potential) is a value that describes atoms ability to gain or lose their electrons. When the oxidation value increases it is easier for atom to gain electrons. Strong oxidizer reacts fast and it loses the selectivity that may also cause unwanted side effects. A biocide with low oxidizing potential has minimal negative side effects on other additives, but it is admitted, that even the weak oxidizers can interfere the additives (Edwards 2003). However, mostly the potential problems with these biocides are related to their effects on chemical conditions in papermaking – not on direct interference with other additives.

The main process chemistry interference of stabilized halogens is the conductivity increase they cause. It is a fact, that all the biocide systems add mostly salt to the process. Even in the most optimal on-site dosing system the amount of active substance is less than the amount of salt. Type of salt depends on the biocide system. Usually the dissociated cations include Na^+ and/or NH_4^+ whereas the anions are typically halogens (Cl^- and Br^-). Usually these biocides are dosed in batches, which mean that the system is opposed to conductivity shocks in regular basis. Conductivity variations are known to cause serious problems in papermaking, even though they have not been earlier linked to the biocide programs.

Another major papermaking chemistry concern is the pH of the dosed biocide. The suppliers do not usually adjust the pH of the biocide according to the process. Almost always the biocide is dosed in a significantly higher pH, which creates a sudden increase of process pH. This affects the whole chemical balance and is reported to be detrimental as well (Göttsching and Pakarinen 2000; Jansson and Ortiz-Cordova 2011)

The third possible threat is the oxidation potential of the biocides. The biocides are oxidative and that limits the usage of reductive chemicals. Evidently this is so obvious, that no reductive additives are used when oxidative biocide system is installed.

Oxidative biocides can also be expected to oxidize other biomaterials besides microorganisms and can therefore be expected to increase the amounts of bound aldehyde and carboxylic acid groups. The mechanism behind this effect is expected to be similar to periodate oxidation of starch when manufacturing dialdehyde starch (Bates et al. 2000) or in pulping process when carboxylic groups are introduced through oxidation of hydroxyl groups in the cellulose molecule (Norell et al. 2000). When carboxylic acid groups are created as a result of such oxidation, one can expect that the cationic demand will be higher. At paper machine this change should have an effect on how wet-end chemicals perform. For instance, it is possible that the demand for retention aid will increase, or first-pass retention will fall as a result of oxidation of the suspended materials in a paper machine system.

By accounting these possible process interactions with the biocides, the process efficiency could be improved. There is potential to reduce defects amount in the paper which would further decrease the down-time of the paper machine and any converting processes after it. Careful optimization of biocide performance and dosing would also reduce the needed amount of other additives since the system would be stabilized. Also positive impact on fresh water and energy consumption could be possible. Detrimental effects of biocides and new solutions to measure and analyze them are required. For optimization and also to increase knowledge and awareness, it is important to show how biocides work in papermaking process, how different dosing strategies affect, and what are the implications of biocides on process chemistry and product quality.

Optimization alone would not eliminate the whole problem. There would still be salt addition to the process even thou the biocide addition would be performed in a more controllable way. Therefore, there is a demand for new biocide solutions. Development of concepts and technologies how oxidative biocides could be generated on-site and added to the process with minimal impact on the process and other additives would be beneficial. With electrochemistry the share of active substances in the biocide suspension can be increased on a higher level than it is possible with current commercial solutions. Electrochemistry offers also possibilities to develop new biocides which would also have other positive features in addition to controlling microbial growth. These could further reduce the detrimental effects such as pH variations and corrosion. This development is necessary when paper industry is seeking for economically and environmentally more positive solutions.

EXPERIMENTAL PART

7. MATERIALS AND METHODS

Overview of the experimental procedures including trials and analysis used in this study are described in this chapter. Materials and methods are arranged according to the structure of the results and discussion chapter. Detailed descriptions of the materials and the methods are found in the original publications, referred to by their Roman numerals (I-V).

Chapter 8: Growth of bacteria in papermaking process (Papers I and V)

Pilot trials (Paper I)

Experimental pilot simulator

A Wet End Simulator was used in this study. The device is a miniature version of a paper machine's short and long circulations. It includes online data logging with more than 100 online measurements. For microbial studies the tanks of the simulator can be used as pilot broke towers. The detailed information on the simulator has been presented earlier by Kiuru et al. (2003), Seppälä (2003), Kiuru et al. (2008), and Rice et al. (2009).

Materials

Materials for the trial were dry broke consisting of a coated fine paper (kaolin/carbonate ratio approximately 20%/80%) and a clear filtrate. The clear filtrate was clean (very low microbial count) when sampled at the mill. Upon its receipt, the filtrate was kept in containers stored for a few days to promote spoilage.

Preparations

Dry broke and clear filtrate was disintegrated in several 150L batches for 10 minutes. The target consistency in the pulper was 3%. Prior to disintegration the filtrate was preheated to 40^{o}C. After the disintegration the pulp was pumped to one of the broke towers. The temperature was maintained at 40^{o}C throughout the trial. After the disintegration, the pulp was stored in a pilot broke tower.

Microbial cultivation

Enumeration of bacteria was carried out by a conventional plating technique from serially diluted (10-fold dilutions) samples. Tryptone Glucose Extract Agar (Fluka) and Reinforced Clostridial Agar (Oxoid) were used for the enumeration of total heterotrophic and anaerobic bacteria, respectively. For bacterial spore counting, the samples were heated at 80°C for 20 min before plating. For anaerobic bacteria enumeration, plates were incubated in an anaerobic atmosphere (Anaerogen; Oxoid Limited, Basingstoke, England). Colony forming units (CFU) were counted after cultivation for 72h at 40^{o}C (relevant for paper machine).

Analytical Methods

During a pilot trial on-line measurements of pH (Foxboro 874, glass electrode and Ag/AgCl reference), redox potential (Foxboro 874, platinum electrode and Ag/AgCl reference), and conductivity (Kemotron conductivity sensor Type 4224) were performed.

Zeta potential was estimated by measuring streaming potential using a Mütek SZP-06 (BTG Group, Germany) according to manufacturer's instructions. Dissolved calcium content (wet digestion and ICP measurement after filtration through 0.45μm filter) was measured using Iris Intrepid (Thermo Scientific, USA). Conductivity, pH, and the charge were determined according to standards SFS-EN 27888:94, SFS 3021, and SCAN-W 12:04, respectively. Total organic carbon (TOC) was measured from samples filtered through 0.45 μm membrane filters according to SFS-EN 1484 standard using TOC-5000A (Shimadzu, USA). Absorbable organic halogen compounds (AOX) was determined based on standard EN-ISO 9562:04.

Standard deviations for zeta potential, charge, TOC, and AOX were less than 10%. The tests were repeated twice, and if the deviation was larger than 10%, a third measurement was performed. For pH and conductivity the deviation was 6%. Calcium measurement was repeated ten times with 5% uncertainty in the measurement.

Handsheet Properties

Laboratory handsheets were made from the broke samples according to EN ISO 5269-1 standard. Target grammage of the sheets was 60g/m^2. Sheet properties were determined using standard ISO-methods: tensile strength, tensile index, and stretch (EN ISO 1924-2), the tearing strength and the tear index (ISO 1974), and the bending stiffness (ISO 5629). The zero-span tensile index was determined according to (ISO 15361), the grammage and bulking thickness (EN ISO 536), and the bulk (ISO 534). ISO-Brightness, CIE-whiteness (D65/10˚), D65-brightness (D65/10˚), color (C/2˚), L*, a*, b*, and yellowness (C/2˚) were measured according to ISO 2470, ISO 11475, SCAN-P 66, ISO 5631, and DIN 6167 standards, respectively. Ash content, 525˚C and Ash content, 900˚C were determined based on ISO 1762 and, ISO 2144 standards, respectively. Ten parallel measurements were performed from all sheet properties. Two parallel measurements for ash content were performed. The results are given as averages of parallel measurements.

Mill trial (Paper V)

Case mill

The study was performed at a paper machine (PM) with a separate coating machine (PCM) located in Finland. The mill produces medium weight coated (MWC) paper from kraft pulp and groundwood pulp. The kraft/groundwood ratio is approximately 50/50. The production capacity of the paper machine is approximately 300.000t/a. The paper machine uses 10-15% calcium carbonate as filler.

The biocide program at the machine was based on weak oxidizers, which were used to treat the low consistency flows. The biocide was dosed in batches:

- White water dose 23 minutes followed by 4 hours dosing delay
- Shower water dose 5 minutes followed by 130 minutes dosing delay

The amount of commercial biocide added was approximately 200g/t of produced paper.

Measurements

The data for the analysis performed in this study was mainly taken from the mill's database. Data from both paper and coating machines were used. The data was mostly taken from the fixed online instruments. The number of the measurements used in the analysis was approximately 400. Collection interval for the data points was 60 seconds. In addition to conventional online instrumentation following parameters were measured: ULMA 100/200 Web Imaging Solution (ABB, Switzerland) for web defects, Foxboro 871pH (Invensys, USA) for pH and redox potential measurements, Kemotron Type 4224 (Metso, Finland) for conductivity measurements, and Mütek PCT20 (BTG, Germany) for charge/cationic demand analysis.

Analysis tools and methods

Data were analyzed using Savcor Wedge software (Kajanto 2002). Analysis methods included principal component analysis (PCA), multivariate auto-regression (MAR), waveform matching, and soft sensor calculations. The methods are described in details by Eriksson et al. (2006). The calculations were performed in Matlab (MathWorks, USA), which was used by the Wedge software. The density trends for break signals were calculated according to Matlab equations 1 and 2.

```
start_of_break(t) = 1, when d/dt (machine_running(t)) = -1        [1]
                    0 otherwise
break_density(t) = c * integral_tau_from_minus_inf_to_plus_inf    [2]
                   start_of_break(t) * exp(- d * (t – tau)^2) dtau
```

Parameters c and d in Eq. 2 were selected individually for each signal (based on a signal level) to scale the y-axis. Discrete calculation was used. The same equations were also used to calculate the density signal from the defect data. In practice, these equations were used to convert a binary signal (value 1 or 0 depending if the machine is running or not) into a continuous trend signal. This conversion was needed for analytical purposes.

Runnability at paper and coating machines was evaluated based on unplanned breaks at the machines (both number and duration of the breaks). At the paper machine each break was evaluated individually. The cause of the break was categorized based on the state of the process before the break. Planned breaks and stoppages were left out from the analysis. At the coating machine the break density calculated using the equations 1 and 2 was correlated with the parameters measured from the paper machine. Runnability analysis at the coating machine was emphasized on the breaks without any obvious reason.

Chapter 9: Revealing hidden process phenomena with portable instruments (Papers III and IV)

Laboratory Trials (Paper IV)

Bromine-based biocide was used in the laboratory trials for dosage optimization. The biocide was generated from sodium bromide (NaBr) (Sigma-Aldrich, Finland) by electrolysis. The electrolysis was carried out using Electro MP Cell® (ElectroCell, Denmark) according to manufacturer's instructions. NaBr concentration in electrolyzed solution was 0.3M. The solution was pumped through the cell with a flow rate 8L/h. The applied current density was 1.5kA/m^2. The main active compound in the product was sodium hypobromite (NaOBr). Active bromine content was measured according to manufacturer's instructions using a Dulcotest DT1 (Prominent, Finland) portable microprocessor-controlled photometer.

Laboratory experiments were conducted using a clear filtrate sample from a fine paper machine after a disc filter. Experiments were performed in 250ml flasks with 50ml samples. After addition of biocide the samples were incubated on rotary shaker at 37°C for 30min. After 30min contact time sub-samples were taken for ATP content determination and bacterial count. The results from the laboratory experiments are presented as an average of at least three measurements.

The effect of biocides on the ATP assay was tested in the clear filtrate. Bacteria were removed from the sample by filtering through a sterile 0.45µm filter (Whatman GmbH, Germany) and ATP ($5 \cdot 10^{-9}$M) was added. The ATP levels were measured after 4 and 15 minutes of exposure to different amounts of hypochlorite.

The amount of total heterotrophs and bacterial spores in paper machine samples was determined as described above.

Mill Trials (Paper IV)

Trials were carried out at paper and board mills producing fine paper under neutral/alkaline conditions. During these trials 3 different biocide concepts were reviewed: an oxidative system based on hypochlorite and hydantoin, an oxidative system based on hypochlorite, and a reductive system using glutaraldehyde and DBNPA (2,2-Dibromo-3-nitrilopropionamide). Data were analyzed using the Wedge software (Kajanto 2002) and Microsoft Excel tools. The ATP measurement at each point of time was performed at least twice. The validity of the data was followed by comparing the results from the sequential measurements.

Field measurements (Papers III and IV)

ATP Measurement

Total and free ATP contents were measured by using an Aquasnap™ testing device (Hygiena, USA) according to manufacturer's instructions. The Aquasnap collects 100µl of water sample in a honeycomb-shaped dipper. The sample is placed into a chamber in which reagents that react with ATP are released. The device measures the ATP contents in the solution and uses no internal or external standards. Both total and free ATP was measured. The Aquasnap for free ATP lacks the enzyme needed for cell lysis and therefore measures only free ATP. The Hygiena Aquasnap sampling devices were chosen for this study based on the information provided by the producer, that the devices are suitable for different industrial applications (Easter 2009).

The dipper collects only the water phase from the sample and therefore no filtration is needed. The light was measured and displayed in relative luminescence units (RLU) with a SystemSURE II portable luminometer (Hygiena, USA). The range of this assay was from 10^{-11}M to 10^{-7}M ATP as determined based on calibration using known amount of ATP.

pH, conductivity, temperature, redox potential and dissolved oxygen

For basic measurements, multi-parameter sensors proved to be feasible. Multi-parameter sensor YSI-556 MPS (YSI Incorporated, USA) was used in most of the trials. This portable commercial multi-parameter measuring device is capable of measuring pH, conductivity, temperature, redox potential and the amount of dissolved oxygen. The device has an internal memory which can store up to 49000 data sets. Dissolved oxygen measurement is carried out using membrane technology and thus variations in conductivity might disturb the measurement. Another multi-parameter sensor in mill trials was YSI-6920 V2 (YSI Incorporated, USA). It is rather similar to YSI-556 MPS. In addition, it is equipped with optical dissolved oxygen and turbidity probes.

Calcium, chloride and ammonium

Calcium, chloride and ammonium ion concentrations were measured using ion-selective electrodes (ISE). The ion-selective electrode technique measures the ionic concentration in an aqueous solution. The method is based on an ion-specific membrane, which allows particles of a certain size to diffuse through the membrane. The sensor converts the activity of a certain ion to an electrical potential which is compared with the reference electrode. The problem with ISE sensors is the interfering ions, which have a molecular size similar to the measured ion, thus they are able to diffuse through the membrane together with the measured ion. ISE sensors were reviewed in this work because of their significant potential. ISEs are not commonly used in papermaking, and no single ions are measured from the process either, even though there might be great benefits in doing so. Some studies with promising results have been carried out (Vázquez 2001), but the applications have not become commercialized and the methods have not been utilized in online monitoring.

Dissolved calcium content was measured with ion selective russel electrode. The logging device was Consort C933 (Consort nv, Belgium). The sample needed to be pretreated before the measurement. Measurement of chloride and ammonium ions is based on ISE technology available with the YSI Professional Plus multi-parameter measuring device (YSI Incorporated, USA). The chloride sensor was also found to be sensitive to bromide - and presumably other halogens - because of their similar molecular size. Therefore, it can be efficiently used for monitoring changes in the amount of both chloride and bromide, as long as these ions do not co-exist in the measured solution.

Filtration and pretreatment

Measurements of dissolved compounds (in this study calcium, chloride and ammonium) require a filtration of the sample before the measurement. For papermaking processes ceramic cross-flow filtering has been utilized earlier for online measurements of ions with capillary electrophoresis (Kokkonen et al. 2002). A ceramic cross-flow filter connected to an online flow chamber met our needs for this kind of sampling/filtering system perfectly. The filter itself de-pressurizes the sample, as filtrate is extracted from the stock flow (Figure 10). The filtrate is sequentially directed to flow chamber in which the measuring probes are attached. Naturally, when using ceramic cross-flow filters, only the dissolved amounts in the filtrate could be measured.

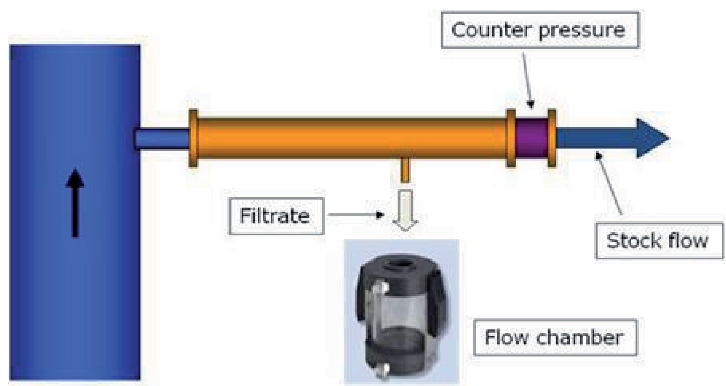

Figure 10 Ceramic filter connected to a flow chamber for filtrate.

Some measurements (e.g. Dissolved oxygen (DO), ISEs) were found to work incorrectly if there is no flow (particle movement) in the measured substance. During the cross-flow filter trials, it was noted that the filter did not always provide enough filtrate flow to the flow chamber for the probes to operate reliably. For these kinds of situations, a flow chamber with an auto-stirring function was designed and built (Figure 11). The chamber is equipped with a small pump which circulates the sample within the chamber. This provides the needed stable and continuous flow for the probes to operate.

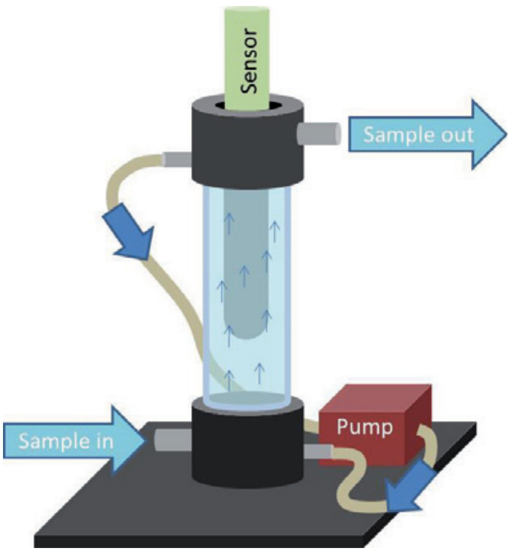

Figure 11 Flow chamber with auto-stirring system.

Chapter 10: Influence of biocides and biocide interactions on papermaking performance (Papers III and V)

The experimental setup as well as the measurements and analysis principles were performed as described above.

Chapter 11: New concept for electrochemical biocide generation (Papers I and II)

Biocide Production

Oxidative biocides were generated with the Electro MP Cell® electrolytical device (ElectroCell, Denmark). The cell is a multipurpose plate and frame cell and intended for laboratory-scale experiments. The electrodes in the undivided cell were a boron-doped diamond anode and a titanium cathode. The effective areas of the electrodes were 0.02m².

For the generation of biocides the following salts were used: NaBr (Fluka) - for hypobromite (NaOBr); NaCl (Suprasel) - for hypochlorite (NaOCl), and sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) (J.T. Barker, Merck) - for sodium percarbonate (SPC). The pH values of hypochlorite and hypobromite solutions were 9.9 and 10.7, respectively. The pH of the SPC solution was adjusted to 8.5 (pH of papermaking process) with 1M HCl. The parameters for the production of electrochemically formed biocides are presented in Table V. The term halogen-containing biocide refers to hypobromite and hypochlorite in this study.

Table V Parameters for the Electrochemical Generation of Biocides

Biocide	Raw material	Concentration of salt, M	Current density, A/cm²	Current efficiency, %	Flow rate, l/h	Concentration of active substance, ppm***
Hypochlorite	NaCl	0.3	0.15	50	8	2600
Hypobromite	NaBr	0.3	0.15	70	8	6300
SPC*	Na_2CO_3 + $NaHCO_3$**	0.75 +0.75	0.125	18	4	700

*) Active substance - hydrogen peroxide. **) For SPC generation sodium silicate (15mmol/L) and magnesium sulphate (0.3mmol/L) were added to stabilize the peroxide. ***) Concentration here and the dosages further in the text are given as the amount of active substance: free active halogen for hypochlorite and hypobromite, and hydrogen peroxide for sodium percarbonate.

The anodic reactions and their standard reduction potentials for generating oxidative biocides are collected in Table VI. The potential of the oxygen evolution reaction is pH-dependent. With an oxygen evolution reaction, the reduction potential is 1.3V, 0.8V, and 0.4V at pH=0, pH=7, and pH=14, respectively and from a thermodynamic point of view oxygen evolution is more favorable than other anodic reactions.

Table VI Anodic Reactions and Standard Reduction Potentials (Vanysek 2006)

Anodic reaction *	Product	Standard reduction* potentials, V
$2Cl^- \rightarrow Cl_2(aq) + 2e$	hypochlorite	1.40
$2Br^- \rightarrow Br_2(aq) + 2e$	hypobromite	1.09
$2CO_3^{2-} \rightarrow C_2O_6^{2-} + 2e$	SPC	ca. 2.0**/0.42***
$2H_2O \rightarrow O_2(g) + 4H^+ + 4e$	oxygen evolution	1.23

*) These are the actual electrode reactions but for the standard reduction potentials they should be written the other way around; **) Oloman 1996; ***) Zhang and Oloman 2005.

Trial setup

Trials were performed in the laboratory and with a semi-pilot Wet End Simulator (WES) at 37°C temperatures. Samples for the trials were obtained from Finnish paper mills producing fine paper. The samples used in the laboratory trials are presented in Table VII. For the WES trials, the samples were a clear filtrate and a broke. The broke was prepared by disintegrating a dry broke paper in clear filtrate to 3% consistency. The initial bacteria count for the clear filtrate was $7 \cdot 10^5$CFU/ml and for the dry broke $8 \cdot 10^2$CFU/g. The clear filtrate was sampled after a disc filter from the water circulation at the paper machine. The machine circulates the water and uses fresh water approx. 10-15m^3/t of produced paper. This leads to an accumulation of material to the water circulations. This accumulated material consists of compounds containing also nutrients such as nitrogen and phosphorous, which potentially causes microbial problems. The samples were selected to represent the papermaking process and different delays and retention times in the process. Wire water and headbox samples present the short circulation with rather short delay (approx. 30 minutes). Clear filtrate presents the water cycles with similar approx. 30-60 minutes delay. Mixing tank and broke samples present the pulp cycles with longer delays varying from an hour to more than 10 hours.

Table VII Samples for the Laboratory Trials

Sample	Total bacteria (CFU/ml)	Spores (CFU/ml)	Consistency (%)*	Ash content (% of sample volume)**
Clear filtrate	$1.2 \cdot 10^6$	<10	0.01	0.01
Wire water	$9.6 \cdot 10^5$	<10	0.3	0.2
Headbox	$1.2 \cdot 10^6$	<10	0.9	0.5
Broke	$5.3 \cdot 10^6$	10	3.3	1.0
Mixing tank	$7.2 \cdot 10^6$	$3.7 \cdot 10^2$	4.0	0.5

*) The consistency was measured by filtering the sample and drying it at 105 °C. The dry matter content of the sample was calculated based on the weight of the dried sample. **) The ash content was analyzed by heating the sample at 525 °C and measuring the weight of the residue.

The biocides and the samples were mixed together either in a rotary shaker (dilute samples, consistency <0.3%), magnetic stirrer (medium consistency 0.3 to 1.0% samples) or with a mixer (high consistency >1.0% samples) to ensure proper mixing regardless of the sample consistency.

The optimization of dosing strategy for a combination of halogen-containing biocide and SPC was carried out with the clear filtrate and the broke (at 3% consistency) in the WES. The final optimal dosing scheme for the dual biocide system was as follows: halogen-containing biocide was added first, followed by SPC after a 20 minutes delay. Samples for biocide efficiency checks were taken in 30 minutes after SPC addition. The biocides were added to a flow before a pump that was circulating the broke in the tank. The broke was continuously mixed.

When single biocides were tested either in laboratory or with the WES, the contact times were 30 minutes for halogen-containing biocides and 40 minutes for SPC. Contact times were selected based on preliminary trials (results are not shown). The contact times were selected so that the differences between the trial points would be as large as possible. The difference in contact times is due to different reaction times between halogen-containing biocides and SPC.

The effect of mixing on biocide performance was tested with the WES. The amount of hypochlorite added to the clear filtrate was 1, 2, or 3ppm. One of the tanks was continuously well mixed with a mixer. The other tank was unmixed until the sampling for the cultivation. The contact time for hypochlorite was 30 minutes.

The effect of dosing mode was examined by comparing the differences between continuous biocide addition and batch addition. The trials were conducted using clear filtrate. Clear filtrate was heated up to 44°C and afterwards treated with 3.5ppm of electrochemically formed hypobromite. After the initial treatment, the clear filtrate was divided into two tanks each with volume of 90 liters. Untreated clear filtrate was pumped continuously into the tanks at the same rate (0.5L/min) as pretreated filtrate was pumped out. Details of the trial setup are presented in Figure 12 and Table VIII.

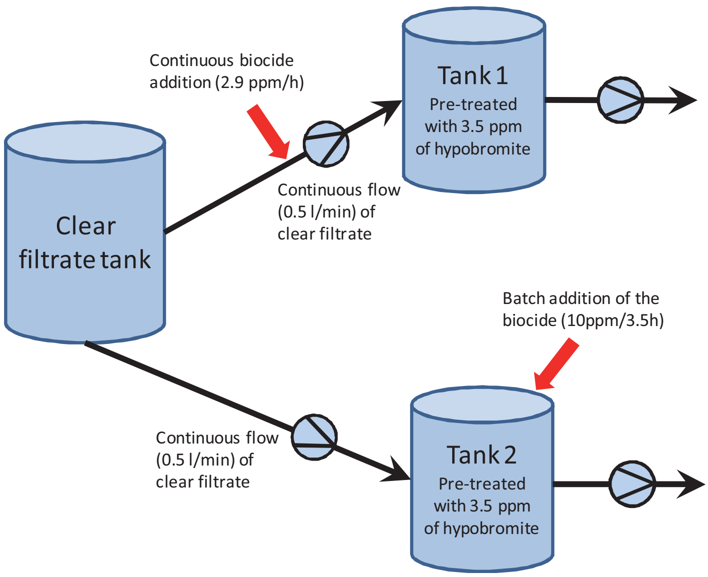

Figure 12 Trial setup for the determination of the effect of dosing mode. Flow rates of the pumps were synchronized so that the clear filtrate levels in the tanks 1 and 2 were constant.

Table VIII Setup for the Dosing Mode Trials

	Tank 1	Tank 2
Retention time in tanks	3 h	3 h
Dosing sequence	Continuous, 2.9ppm/h	Batch, 10ppm every 3.5 hours
Sampling	Beginning and once every hour	Beginning, before, and after biocide dosage

The decomposition of the halogen-containing biocides was tested in the laboratory trials. For this, microbes were removed from the clear filtrate by filtering the samples through a 0.45µm membrane filter.

Active chlorine and bromine contents were measured using a Dulcotest® DT1 (Prominent) portable photometer. The analysis of active compound in SPC, hydrogen peroxide was performed based on the oxidation of iodide by hydrogen peroxide to iodine and further titration of the liberated iodine with sodium thiosulfate ($Na_2S_2O_3$). The measurement at each sampling point was performed at least twice. The validity of the data was followed by comparing the results from the sequential measurements. The amount of total heterotrophs and bacterial spores was determined by conventional plating technique on Nutrient Agar (Merck KGaA) as described above.

RESULTS AND DISCUSSION

8. GROWTH OF BACTERIA IN PAPERMAKING PROCESS (*Papers I and V*)

In pilot trials pulp was spoiled in a pilot broke tower while the spoilage was followed with online measurements such as pH, redox potential and conductivity. Implications of the spoilage on chemistry were further analyzed in laboratory by measuring chemical parameters such as charge. The effect of spoilage on end product quality was evaluated by producing laboratory sheets from the spoiled pulp and by measuring the paper properties of the sheets. The phenomena and implications are clarified by presenting the consequences of broke spoilage at production machine environment. These results are based on online measurements performed at the mills.

8.1 Development of anaerobic conditions

In paper and board machine systems the broke towers are usually the places where hydraulic retention times of pulps are the longest. These huge towers have usually poor mixing, which enables anaerobic conditions to develop. Retention time of broke in the broke tower is usually around 10 hours (from a couple of hours up to 20 hours). Short breaks at the paper/board machine lead to increased retention time of broke in the broke tower.

Web breaks heavily increase the production of broke, and on the other hand no broke is consumed during the break. This case is difficult to control because such breaks are always unplanned. During longer planned production brakes (stoppages) such as planned wire or felt changes it is possible to treat the broke in the tower using biocides before the break. It is also possible to try to decrease the broke volume before the breaks. Both cases are even more complex when the broke systems are integrated together with other paper/board machines in the same mill.

The raw material spoilage trials were performed using broke. The amount of heterotrophic bacteria in dry broke used in the trials was only 60CFU/g. After the spoilage period the total amount of microbes in the clear filtrate was over 10^6CFU/mL (see Figure 13). Similar growth in the amounts of heat resistant spores and anaerobes were measured as well.

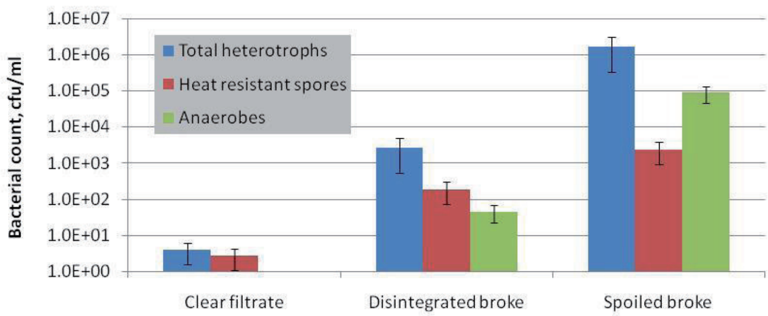

Figure 13 Growth of bacteria (plate counting) during 50 hours broke storage period. Error bars represent deviation between 5 parallel platings. *Modified from Paper I.*

Figure 13 indicates that the increase in bacterial count in the trial is mostly due to increase in the numbers of anaerobic bacteria and thus the spoilage is caused by the development of anaerobic conditions. This is quite common situation and has been well documented with its consequences in the publically available literature (Edwards 1996; Blanco et al. 1996; Ludensky 2003). Implications of this microbial activity are documented and discussed in the next chapter.

8.2 Pulp deterioration and wet end chemistry

In the pilot trials, acid formation due to microbial growth resulted in notable pH reduction. This led to dissolution of $CaCO_3$, which increased conductivity (Table IX). This is highly detrimental feature because calcium ions can give rise to tacky fatty acid soaps or can form calcium sulfate

(Holmberg 1999). Increased conductivity has also a tendency to affect the ionic attraction forces between the polymers and fibers potentially causing retention, formations etc. problems (Gess 1998). This is related to consequence of increasing salt concentration to decrease zeta potential (Lindström and Söremark 1975; Wang and Hubbe 2002). Any variations in these chemical parameters are also considered as a detrimental effect and will potentially cause production or end product quality problems.

Table IX Laboratory analysis performed on the broke samples.

	Disintegrated broke	Spoiled broke
Dissolved calcium, mg/L	23	150
Adsorbable organic halogen, mg/L	0.5	0.6
Colloidal charge, μeqv/L	-244	-138
Dissolved organic carbon, mg/L	71	220
pH	8.0	6.6
Conductivity, mS/m	49	112
Zeta potential, mV	-29	-27

The level of DOC (amount of dissolved organic carbon) in the broke tower increased notably during broke spoilage period. This was attributed to volatile acid accumulation due to microbial growth. In many cases, increased levels of volatile fatty acids indicate problems caused by high microbial activity in the system. These acids are produced in the anaerobic metabolism of microbes (Robichaud 1990; Jokinen 2000). Thus, the level of DOC may be a good indicator, even though indirect, of microbial metabolite accumulation.

Increased amount of organic material is also detrimental for the chemistry of the system. In addition to microbial problems such as slime deposits and odors, fatty acids are known to cause unwanted phenomena such as foaming and decreased sizing performance. Other implications of increased DOC can be deposit formation, dewatering problems and strength and brightness losses in the paper web (Holmberg 1999).

Large increase in calcium content caused by the pH drop was observed during the spoilage. After 50 hours spoilage conductivity of the broke was significantly higher. Considering calcium to be even more harmful than sodium, it is clear that inhibition of microbial growth is very important, not only for the microbiology, but also for the chemistry. The same effects were also seen in charge values during the spoilage. The pH of the broke decreased and the latex particles of broke became less anionic, which was seen as an increase in colloidal charge values.

The detrimental effect of calcium is based on the DLVO theory presented earlier. Calcium induced conductivity increase is considered to be more detrimental compared to conductivity increase due to monovalent cations such as sodium. The effect of increasing calcium concentration is to decrease the relative thickness of ionic double layers, thereby decreasing the forces between particles (Hubbe and Rojas 2008). Multivalent cations cause for instance deposit formation in significantly lower concentrations compared to monovalent cations (Sundberg et al. 1994).

Figure 14 illustrates the changes in the values of the chemical online parameters redox potential, pH, and conductivity during the spoilage.

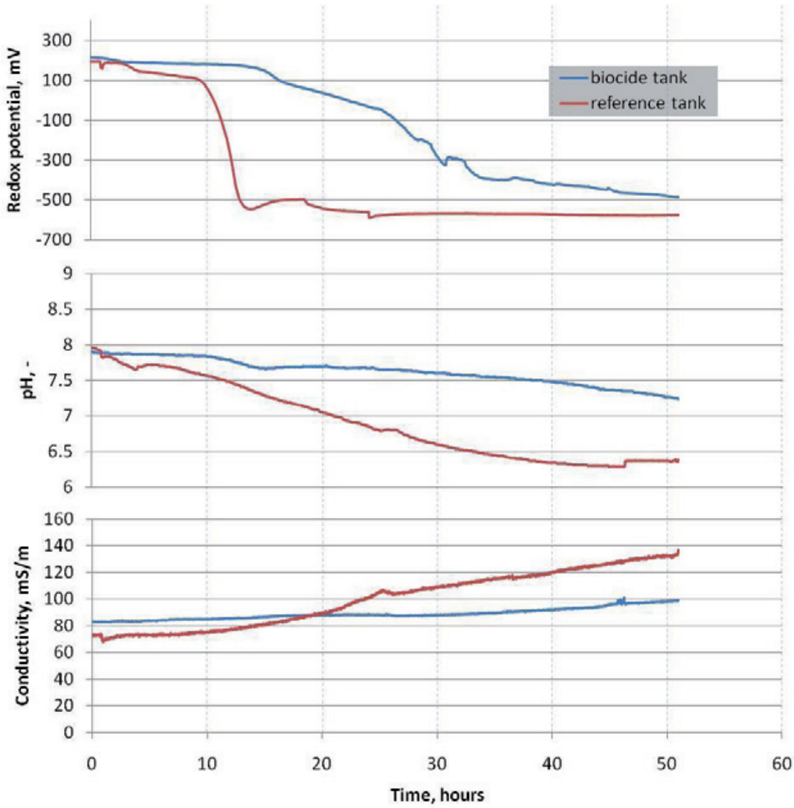

Figure 14 Online trends from the broke spoilage trial. Online measurements of pH (Foxboro 874, glass electrode and Ag/AgCl reference), redox potential (Foxboro 874, platinum electrode and Ag/AgCl reference), and conductivity (Kemotron conductivity sensor Type 4224) were performed. Biocide treatment (28ppm, measured as free active chlorine, electrochemically generated hypochlorite solution) to the biocide tank was performed just before the monitoring started. No biocide was added to reference tank. *Modified from Paper I.*

The redox potential started to decrease heavily after five-hour spoilage, reaching the lowest reading in 15 hours. This change was accompanied with a reduction in the pH level due to acid formation (also seen in laboratory measurements). The figure shows also a significance of biocide usage as an inhibitor to microbial growth. In the biocide treated tank it took more than two days to reach the same redox potential level. In the reference tank, the pH drop was almost 2 pH-units and in the biocide tank only 0.4 units. After two-day spoilage the pH difference between the tanks was more than one unit. The biocide effects are discussed in details in chapter 11.

The same phenomenon contributing to pH drop and conductivity increase in the pilot trials was also seen in the mill trials as shown in the Figures 15 and 16. At the mill conditions the broke spoilage was also seen to have an effect on the quality of paper web. As shown in Figure 16, broke deterioration affected to web adhesion and web release from the cylinders. This may also have influence on machine runnability. Web attachment forces to increase draws which may promote the web to break.

However, a more significant factor contributing to runnability problems and web breaks is the occurrence of defects in the web. This is also coupled to the adhesion and draws since the web tends to break from the weakest point – defects. The mechanism of web defect formation due to broke spoilage is probably due to changes in charge. The particles flocculate easier when the charge is increasing (approaching to zero). This increase – in this case in Figure 15 – is due to the spoilage of broke. The connection of defects to web adhesion causes problems especially when the draws between the cylinders have to be increased. Increased fatty acids concentration due to spoilage might also play a role in this matrix. Precipitation of fatty acids in the presence of calcium ions may influence the defects as well as the adhesion. The basics of the adhesion phenomena have been well documented in the publically available literature (Kurki et al. 1997; Pye et al. 1985).

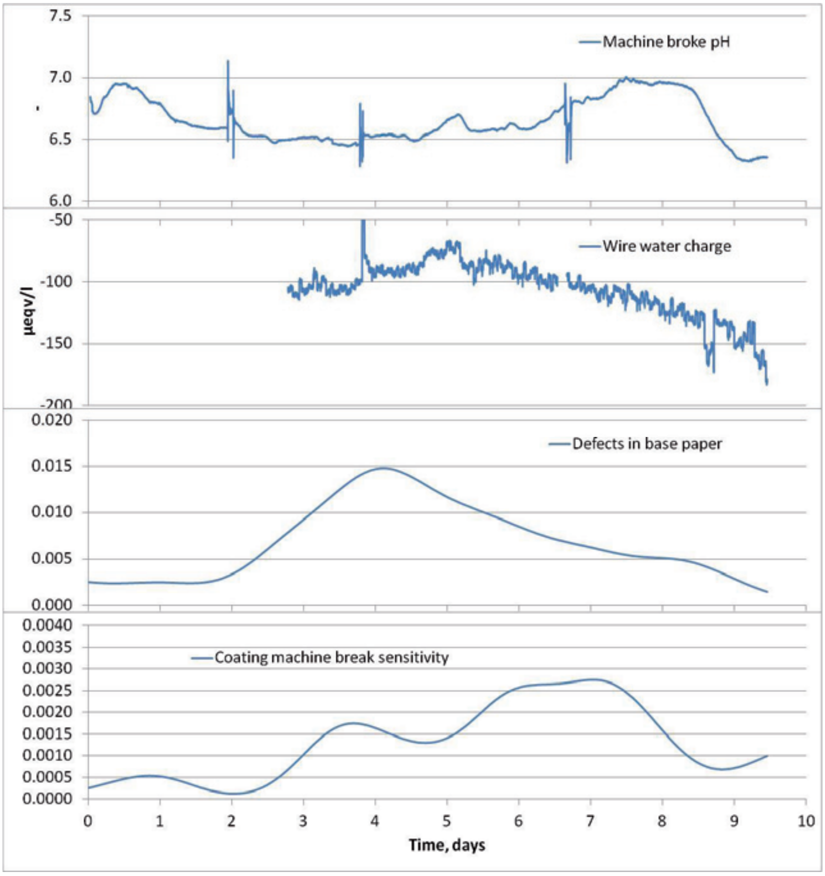

Figure 15 Observed chemical variations at a paper machine and their influence on paper defects and runnability in coating. Break sensitivity and defects curves are calculated according to equations 1 and 2. Modified from *Paper V*.

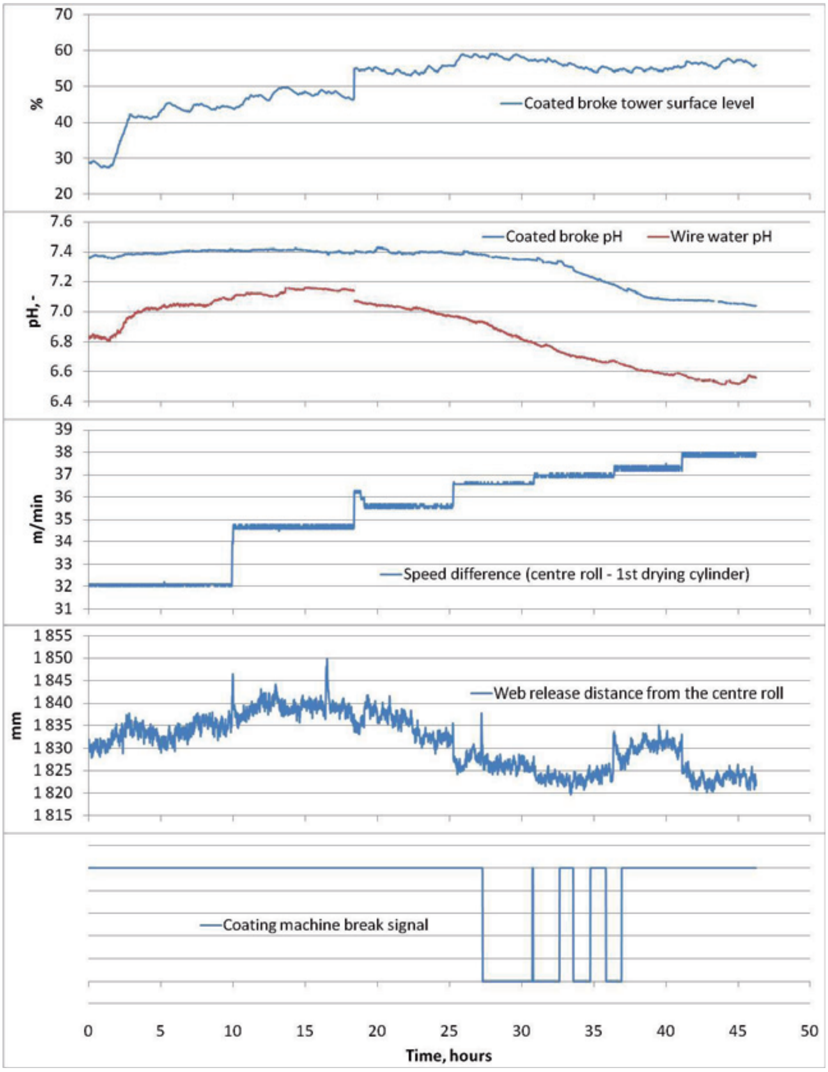

Figure 16 Effect of broke spoilage on web adhesion and coating machine runnability. *Paper V*.

8.3 Spoilage and end product quality

In addition to the defects count and adhesion properties, the spoilage of broke had very little effect on the paper properties measured from the broke sheets. Mostly the effects can be explained with the dissolution of filler. The most significant effect was decreased brightness. Approximately 1.5-units brightness drop was measured due to the spoilage. The root cause is unknown but there are several possible reasons to the brightness drop. Reduced filler content in the sheets can decrease brightness (Krogerus 2000), microbial activity can affect optical additives such as dyes and brighteners, or reductive reactions taking place during spoilage can affect brightness (Baumgartner and Spedding 2010).

Strength properties, which depend on interfiber bonding, decrease when fillers are introduced into the sheet structure because fillers are unable to form significant bonds to fibers (Krogerus 2000). When fibers are substituted by fillers, strength properties will decline also because of less fiber in the network per unit volume. In the trials an opposite phenomenon of this was observed. Dissolution of filler due to pH drop caused a minor strength improvement. This is logical since the handsheets were prepared to target basis weight.

In the mill trials, significant effects of broke spoilage on product quality were observed. Especially the amount of defects, spots and holes, in the base paper were observed due to the broke spoilage (as described above). These effects are very detrimental – and on the other hand – very difficult to observe in the laboratory. According to Jokinen (2000) harmful deterioration of product quality can also result on account of spots or holes when microbes get loose from the actual growth place and these freely moving cells are removed in dewatering.

9. REVEALING HIDDEN PROCESS PHENOMENA WITH PORTABLE INSTRUMENTS (*Papers III and IV*)

Idea of utilizing handheld instruments in process diagnostics arises from the inadequate level of instrumentation at paper mills. Handheld instruments can easily be located into most important positions, and if the position turns out to be wrong – relocating the device takes only minutes. These new measurement positions can also give important new information about the process. Especially useful the handheld instruments are for troubleshooting cases, process checks or when monitoring trial runs and extra information is needed. Since the handheld devices are not meant to be measuring for years at the machine their durability can be poorer and therefore also the price can be lower. Also new measurement techniques can be applied, which gives possibilities for new measurable parameters. Basically handheld instruments combine the positive features from laboratory and online devices. More parameters can be measured from numerous locations but still the data is collected continuously in order to detect rapid changes and periodical fluctuations.

9.1 Analysis of microbial activity

As described in chapter 4.4, the online measurement of microbial activity is challenging. No direct online measurement is available. The good and reliable indirect measurements of microbial activity including dissolved oxygen content, redox potential, pH, and conductivity are also available as handheld measurements. Actually they all are available in one multi-parameter probe.

Another indirect method studied was a portable luminometer for ATP analysis. A test was carried out in which oxidative biocide (hypochlorite from a container) was added with batch dosing to a short loop of a fine paper machine producing specialty papers. Both free and total ATPs were measured from the wire water (filtrate as the paper is formed).

The effect of the biocide feed on the ATP content of the wire water is presented in Figure 17. The figure shows that 40 minutes of batch feed of the biocide was able to decrease the microbial activity to a slightly lower level. However, the level started to increase instantly after the dosing was stopped. Based on a theoretical calculation, the drop in cell counts was not very significant (Hattori et al. 2003; Mujunen et al. 1998). The level before the biocide feed was around 10^7CFU/ml, and it dropped to slightly above 10^6CFU/ml.

The results also indicate that the biocide program could be further optimized. Dosing batches should be applied more frequently, or pulp should be treated better before it enters the short loop. The wire water is probably not the best point to apply the biocide in this case.

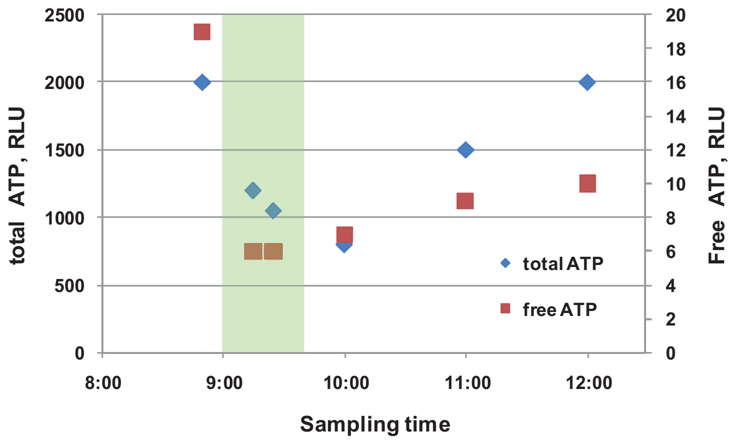

Figure 17 ATP (free and total) measurements on wire water to monitor the effect of biocide performance. Coloring presents the dosing of biocide (hypochlorite was added for 40 minutes time). *Paper IV*.

Some authors have shown that exogenous ATP may persist for a long period of time even under harsh conditions (Schuerger et al. 2008), resulting in overestimation of microbial mass. As seen in Figure 17, the level of free ATP in our trial was low. A very low amount of free ATP indicates that total ATP represented mostly the cellular ATP. The low level of free ATP in the process water could be due to rapid consumption of ATP by bacteria. As shown for Antarctic mineral soil, even at a temperature of 15°C ATP was utilized by microorganisms within 30 minutes (Cowan and Casanueva 2007).

9.2 Measurement of biocide residues

Ion-selective electrodes (ISE) offer a possibility to measure concentrations of individual ions from the process. In papermaking, the ions of interest are in dissolved and colloidal fraction, which means that the sample must be pretreated before the analysis. In practice, in case of online measurement, this means online sample pretreatment. To detect biocide residues, ISE-technology was tested for ammonium and halogen ions.

Ammonium in biocides is normally used in combination with halogens, for example in ammonium bromide systems (Martensson 2005). Halogens are also used without ammonium, for example hypochloride (NaOCl) and hypobromide (NaOBr). Thus, knowing the halogen concentration would add value to the ammonium measurement or replace the need for it.

Halogens are also known to cause corrosion (Koepenick 2010), and online monitoring the content could provide an alert signal for a critical concentration.

Ammonium is known to be a nutrient for microbes, and is therefore a very sensitive measurable parameter for biocide residues. An ion-selective electrode can be a useful tool for optimizing biocide usage. Laboratory trials indicate that when ammonium was added to a clear filtrate sample from a paper mill the sensor gave linear response to the ammonium concentration (Figure 18). Online surveillance for ammonium measurement was not tested in this study.

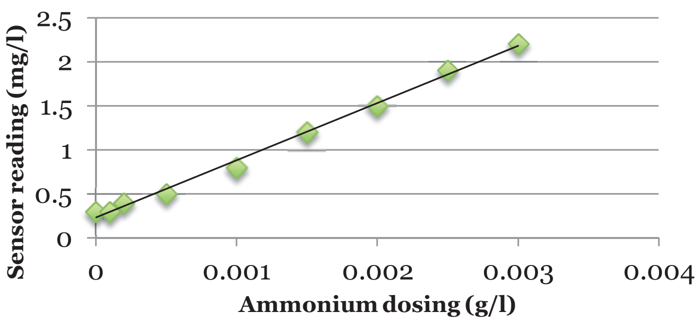

Figure 18 Response of ISE ammonium measurement (YSI Professional Plus) to ammonium dosing into process water sampled from a paper machine.

At fine paper mills, the halogen measurement was applied in the broke system. The measurements of bromide were, in this case, performed during two separate periods. In the first case, the paper mill was using a reductive biocide system with a batch-wise dosing system. When biocide was fed in batches, the dosing could easily be detected by the fluctuation of the measured data (see Figure 19 upper). After a few weeks, the mill switched the biocide system to a continuous feed of oxidative biocide. When the biocide feed was continuous, the measured data from the halogen probe was relatively constant (see Figure 19 lower).

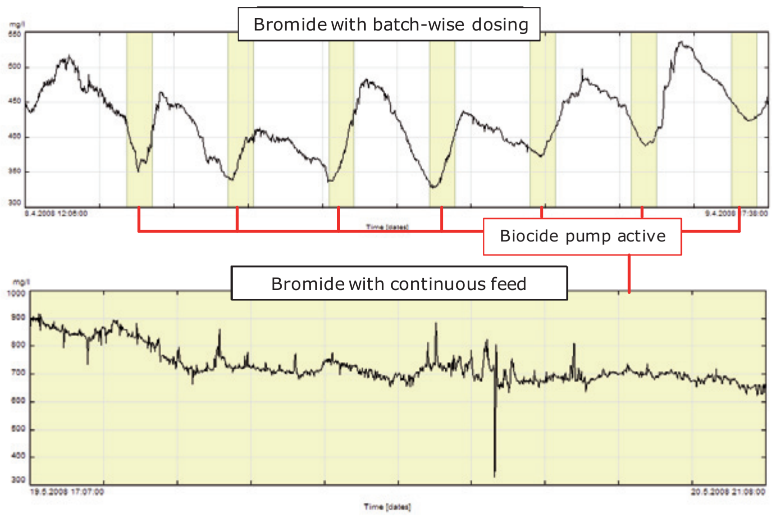

Figure 19 The change in the amount of bromide detected by a halogen electrode (YSI Professional Plus) illustrated during biocide dosing periods. Colorings present dosing of biocide. *Paper III*.

The batch-fed biocide dosing also seemed to have an effect on the pH of the broke system. An examination of measurement data provided by the mill revealed visible changes in the pH of the broke flow during the biocide feeding periods (Figure 20). This indicates that a discontinuous feed of biocide can cause chemical variations.

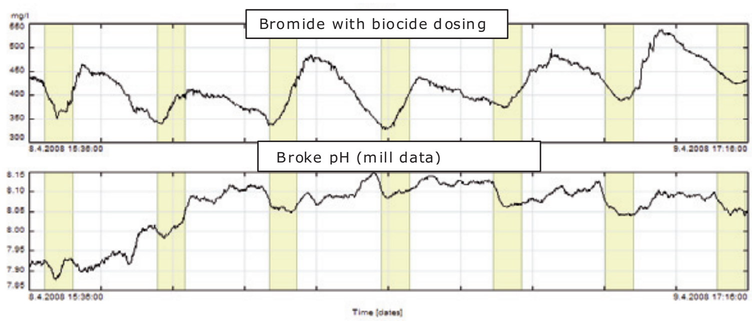

Figure 20 Biocide feeding generates chemical variations in the process. Bromide concentration was measured with YSI Professional Plus. Colorings present the dosing of biocide. *Paper III*.

It is known that biocides have a strong effect on the dissolved oxygen measurement since the measurement is sensitive to ions released from the biocides (YSI Incorporated 2006). Oxidative biocides especially increase the oxygen amount chemically and, on the other hand, the oxygen amount increases due to elimination of anaerobic bacteria. However, the effect is probably mainly due to disturbance in the measurement. Figure 21 shows how a batch-wise fed oxidative biocide is presented in the dissolved oxygen data from a wire pit.

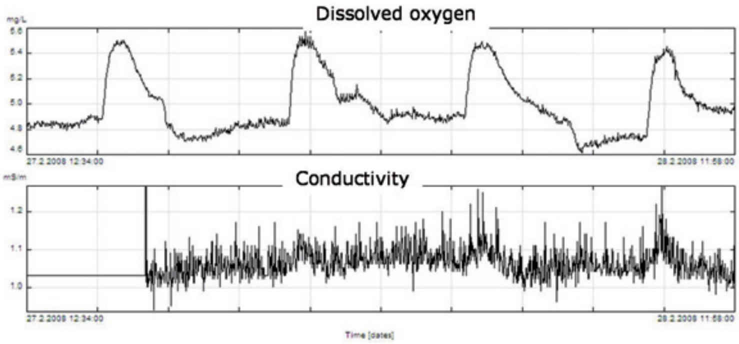

Figure 21 The effect of biocide feed on dissolved oxygen and conductivity measurements. Both parameters were measured with YSI 6920V2. *Paper III*.

The figures show how sensitive the dissolved oxygen measurement is for disturbances. The feed of biocide is barely seen in conductivity, and the effect seen in conductivity seems to disappear rather quickly. A long-term influence of biocide is seen in the dissolved oxygen measurement. This could actually be used for biocide optimization. This example is also another good indication of how a biocide feed can cause chemical variations in the wet end.

Measurement of halogen and ammonium residues in combination with dissolved oxygen, pH, and conductivity is already very useful package for optimizing biocide performance and chemical interactions at paper mills. More value can be added by performing the at-line ATP analysis.

9.3 Optimization of biocide dosage

The rapid ATP measuring method is also suitable for on-site optimization of the biocide dose. These experiments were carried out to demonstrate that the optimization of biocide dose can be conducted at a laboratory scale with actual mill samples. The water sample was taken from a sampler just before the biocide addition to the clear filtrate at the paper machine. Different dosages of bromine-based biocide were added to the sample. Total ATP contents were measured and compared to total viable and spore count (Figure 22).

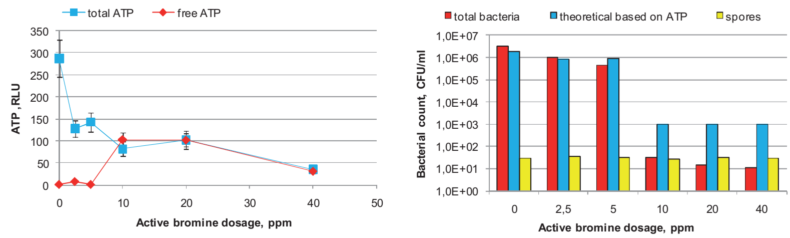

Figure 22 Optimization of biocide dosage with a portable ATP luminometer. Biocide was dosed to fine paper machine's clear filtrate. Viable bacteria were calculated on the basis of intracellular ATP, which was estimated by subtraction of free ATP from total ATP content. ATP values are averages of at least three measurements. *Paper IV.*

Figure 22 shows that 10 ppm of a bromine-based biocide was able to reduce the amount of bacteria in a clear filtrate sample from 10^6 to 10^1CFU/ml. It can be seen that the optimal dosage range was very narrow. A dosage of 10 ppm of the biocide was able to reduce the amount of culturable bacteria to the limit of detection (10CFU/ml), whereas a 5ppm dosage only decreased the bacteria amount slightly. Thus, an optimization is important in order to avoid overdosing, while maintaining proper efficiency. In practice, dosages of more than 10ppm are not realistic. Normally the dosages at paper machines are in a range of a few ppm's.

A decrease in the total ATP content was seen already after a 2.5ppm biocide addition, while free ATP level remained low. When the biocide was added at an amount of 10ppm the level of free ATP increased, indicating cell lysis. The concentration of intracellular ATP depends upon the cell size and the metabolic activity (Nilsson et al. 2002; Russel and Cook 1995). A small amount of biocide can disturb the activity of bacteria and reduce the cell volume, reducing the ATP level per cell.

The amount of culturable cells has been reported to range from less than 1% to more than 50% of total viable bacterial cells in different environments (Colwell and Grimes 2000; Hammes et al. 2008; La Duc et al. 2007; Yoshida and Hiraishi 2004). The bacterial population may differ between paper machines and depend on many factors such as degree of closure, type of fibers, and production conditions (Öqvist et al. 2008; Desjardins and Beaulieu 2003; Lahtinen et al. 2006). Therefore, one may expect the number of viable bacteria (measured based on ATP level) to be much higher than that of culturable cells. Unexpectedly, in our study we found that the ATP level in the clear filtrate correlated with bacterial count. This means that in this case most of bacterial population was represented by bacteria that were culturable on NA. The only disagreement between the two methods was at high dosages of the biocide. However, the biocide at high dosages has a negative effect on the ATP assay. When performing such optimization trials, one should always calculate a correlation factor for a given paper machine. The correlation factor describes the relation between ATP and bacterial count and is specific to each process. It is possible to replace the cultivations and utilize the full potential of rapid ATP assays by using this factor. Both methods, viable cell estimation based on ATP and bacterial counting, are biased.

9.4 Measurement of other chemical parameters

According to Schneider et al. (2001) the charge measurement correlates with colloidal turbidity in the wet end of a paper machine. A high anionic charge means a stable wet end, and is recorded as low turbidity values. This correlation between turbidity and charge can expected to be highly process specific and therefore turbidity can be used only as an indicative measurement. There are plenty of different kinds of devices for online measurement of charge. All are rather expensive and difficult to install. In terms of size, these devices are not mobile. They also need continuous maintenance and addition of chemicals.

In the course of this study, turbidity was measured in the wire water. The result indicates that it is possible to measure colloidal turbidity using optical turbidity measurement device. Figure 23 shows a significant correlation between turbidity and charge values. In this case the online turbidity measurement measures the amount of colloidal turbidity since the solid particles are filtered out prior to the measurement by the membrane included in the measurement head of the device.

For a machine without a charge analyzer the benefits of the turbidity measurement are obvious:

- Easy sampling.
- No chemicals needed.
- The measurement is easy to interpret.
- The price is significantly lower than for a conventional measurement.

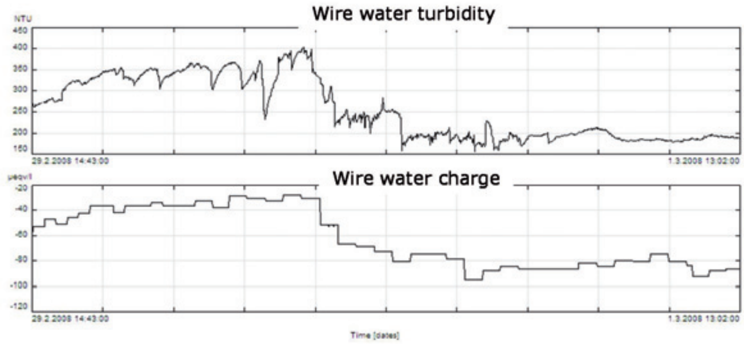

Figure 23 Online turbidity (measured with YSI 6920V2) and charge (with Mütek PCT20) measured from a flow after the wire pit. *Paper III*.

At a fine paper mill, the amount of dissolved calcium was measured from wire water using ISE-technology. The sample was taken continuously from a sampling tap and filtered through a 0.8µm ceramic filter. Colloidal calcium compounds do not pass the filter, only dissolved ions do. The calcium measurement was compared with data from the mill's inline-installed conductivity probe (see Figure 24) showing obvious correlation.

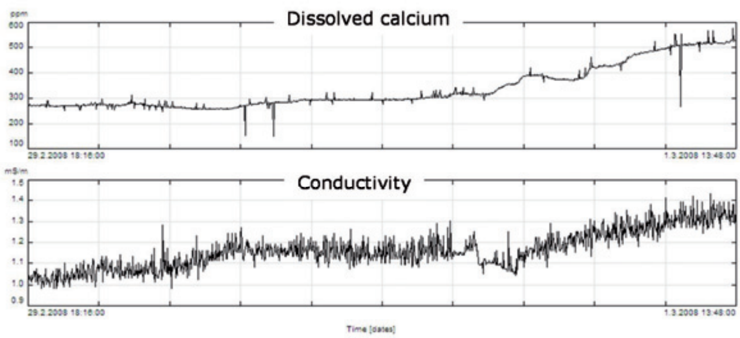

Figure 24 Conductivity (with YSI 6920V2) and the amount of dissolved calcium (with Consort C933 equipped with online sample pretreatment) measured in the wire pit. *Paper III*.

Calculations based on the ionic conductivity of calcium ions reveal that the increase seen in the calcium content should increase the conductivity by 35mS/m (Vanysek 2008). The conductivity increases from 100mS/m to 135mS/m. This indicates that all variations in conductivity are due to the variations in the amount of dissolved calcium. The effect of dissolved calcium on conductivity is ~38%, when the conductivity is around 100mS/m. When the conductivity increases to 135mS/m, calcium causes ~54% of the conductivity.

In this case it was possible to show that the source of all variations in conductivity during the measurement period were due to variations in the calcium content. These variations are most likely a result of the dissolution of filler. The result emphasizes the importance of pH stability for controlling the dissolution of calcium carbonate and maintaining stable conditions in the wet end. By monitoring the dissolved calcium content, it is possible to separate conductivity variation due to dissolution of filler from other possible variation sources. This gives important information for the wet end control.

The handheld instruments are also very suitable for detecting process delays. The multi-parameter probes are especially useful, because they can detect the delays of various methods from the same position. Delays can be detected also in combination with the mill's own, fixed sensors. In a mill trial, a sudden increase in pulp chest conductivity was monitored through the entire machine (see Figure 25). By delaying the signal, it is possible to focus the parameter time axes. This way it is easier to see the cause-effect relation - time delays no longer complicate the analysis. Also, the effect of changes on process delays is easier to study. This might be important, for instance for chemical optimization.

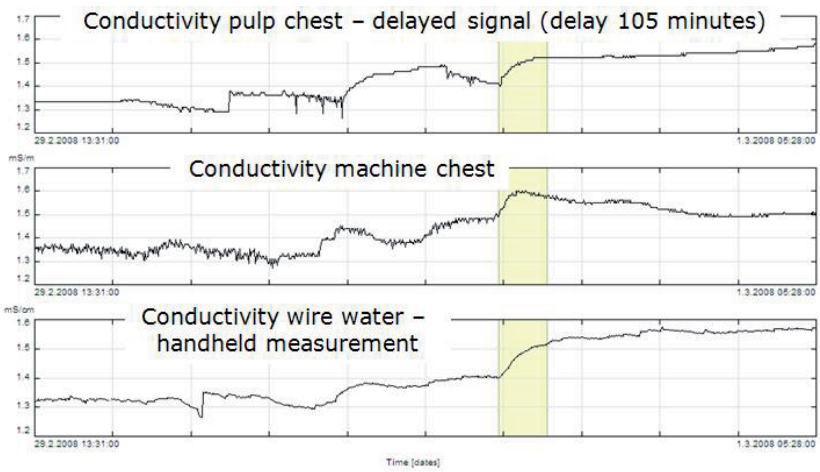

Figure 25 Detection of process delay based on handheld devices (YSI 556MPS). Delayed signal is generated in process analysis software by shifting the time axis. *Paper III*.

The same multi-parameter instrument was utilized also to detect periodical fluctuations (Figure 26). Process water was removed from the process through a certain chest at one of the case mills. To reduce the fresh water consumption, this water should be circulated back to the process, but there was uncertainty if this was safe due to chemicals from the daily washes of felts also going to the same chest. The chest had no measurements, so it was not known if the chemicals affect the quality of the water. A multi-parameter probe was installed in this chest for 2 days. The result in Figure 26 reveals how the washing cycles affected the pH. During night time, the washing of 5 felts can be seen as a fluctuation. This indicated that water cannot be used further in the process during washing.

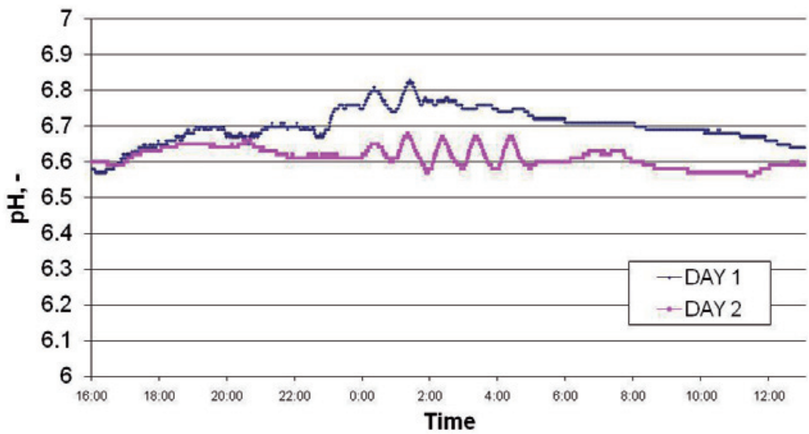

Figure 26 pH in the water removal chest during felt washing measured with YSI 556MPS. *Paper III.*

The importance of the multi-parameter probe installation can also be seen in Figure 27. The same washing cycles cannot be seen in the conductivity measurement as they were seen in pH measurement in Figure 26. The process has a strong periodical fluctuation in conductivity which covers the effect of the washing chemicals. In fact, this is also a good example of how handheld measurements can give valuable data quickly and easily. The periodical fluctuation in conductivity could be an additional phenomenon to tackle into. The result was seen after measuring for just a couple of hours.

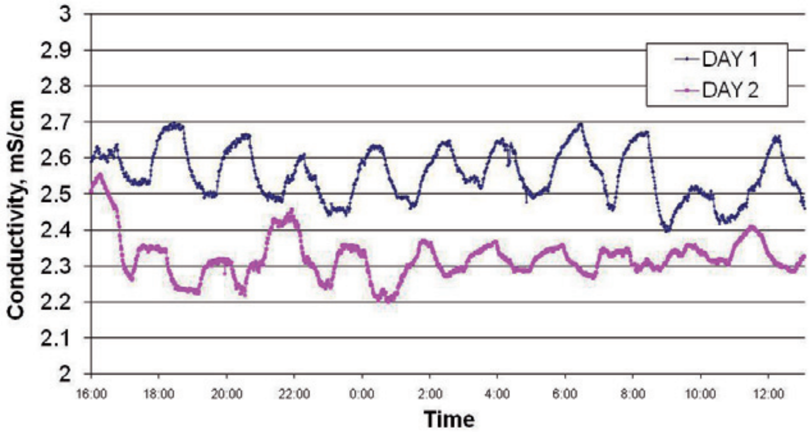

Figure 27 Periodical fluctuations in water removal chest conductivity (measured with YSI 556MPS). Same time period and measurement location is presented as in the Figure 26. *Paper III*.

10. INFLUENCE OF BIOCIDES AND BIOCIDE INTERACTIONS ON PAPERMAKING PERFORMANCE (*Papers III and V*)

10.1 Chemical variations due to biocide addition

Several paper machines and four different oxidative biocide programs (plus one reductive system) were diagnosed. Mostly the strategies were very similar. Biocide programs were usually based on a batch addition of the chemicals. Moreover the strategies were based on a treatment of rather dilute fractions such as white water and shower water. In some cases also broke system was treated. And – most importantly – all the strategies were detected to cause chemical variations.

At one of the case mills the duration of the biocide batch to white water was 23 minutes followed by 4 hours delay before the next batch was dosed. The efficiency of the system was based on the usage of stabilized halogens. The killing mechanism was based on oxidative stress to the microbes (Kolari 2003), which was seen as an increased redox potential of the system due to the biocide batch as described in the literature part. The effect of biocide dosage on the chemical variations in the short circulation is presented in Figure 28. The figure shows that the biocide batch increases short circulation pH with approx. 0.1 units during 23 minutes dosing time. After the batch the pH starts to recover back to a lower stable level. This result suggests that the pH of the biocide is too high compared to the pH of the process. The shown increase in conductivity due to the biocide addition illustrated the effect of the salt added to the process with the biocide.

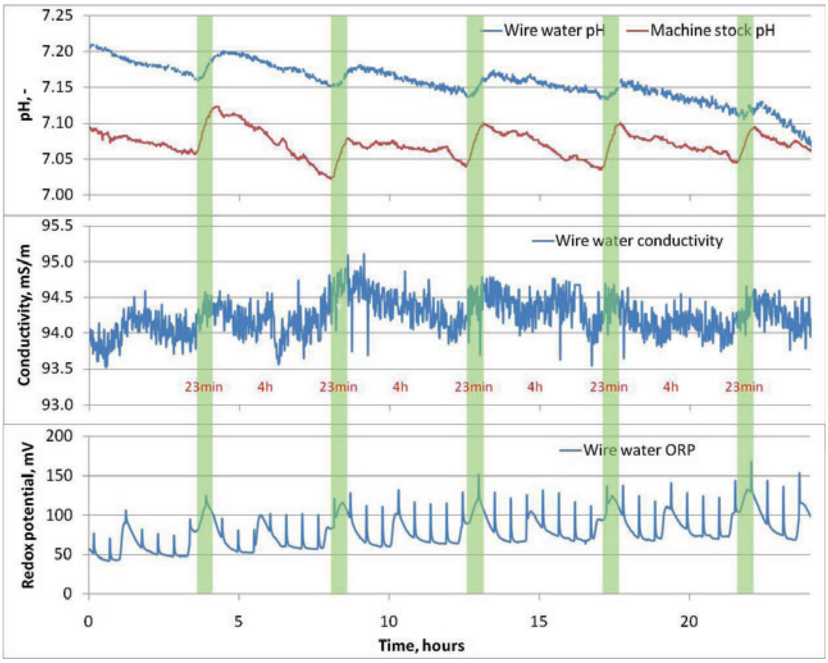

Figure 28 Chemical variations in the short circulation due to the biocide addition. Colorings present the batch-wise added biocide dosing. *Paper V.*

As mentioned in the previous chapter, dissolved oxygen measurement is sensitive to salts and oxidative biocides. The benefit of the measurement is the response time of the assay when it is compared to redox potential and pH (see Figure 29). The yellow color in the figure presents the time when the feeding pump of the oxidative biocide was on. The dissolved oxygen measurement is capable of showing the detrimental and biocidal effect 30 minutes earlier than when using redox potential measurement. pH, in this case, does not give any significant response. This example shows that traditional measurements are not necessarily capable of showing all the chemical variations and moreover, not early enough. Since colloidal stability is closely linked to these measurements and can also be evaluated with charge analysis, additional 30 minutes response time at a paper mill could be enough to perform needed corrective actions to avoid problems. Chemical variations due to biocide addition can also be seen in the concentrations of individual ions as shown in chapter 9.2 (Figures 19 and 20). Since in this case the halogen-containing biocides increase the chloride and/or bromide concentrations the measurements are valuable to avoid corrosion and to control the load to waste water treatment. These ions are also increasing the conductivity and therefore the separate measurement of certain compounds composing the conductivity provides information when solving problems related to chemical interactions.

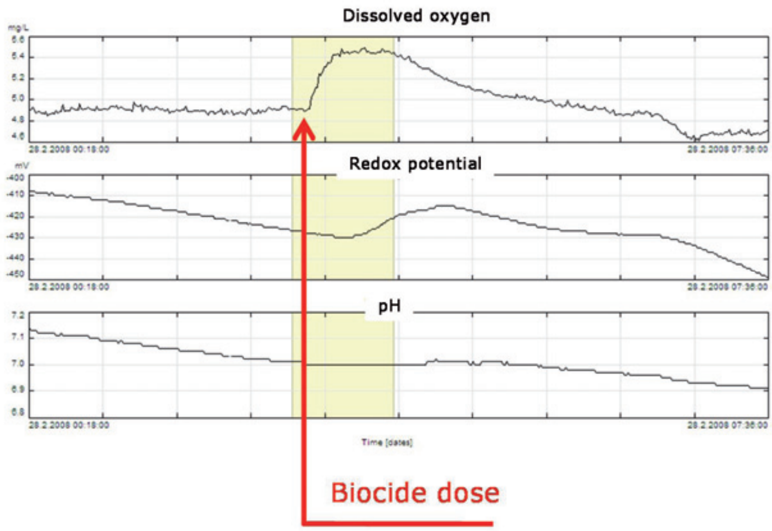

Figure 29 The effect of oxidative biocide feed on dissolved oxygen, redox potential, and pH measurements (measured with YSI 6920V2). A coloring presents the dosing batch of the biocide. *Paper III*.

10.2 Effect of biocides on runnability and product quality

Based on the results from the mill trials, fluctuating wet-end chemistry, due to biocide interactions had clear implications on the runnability of the paper machine. In one of the trials more than 1/3 of the unplanned breaks at the paper machine occurred instantly after the oxidative biocide dosing batch. Statistically the result is relevant. Each PM break was explored individually. In practice, more than 1/3 of the breaks occurred 30-50 minutes after the start of biocide dosing batch. This 20 minutes time window in 263 minutes dosing interval represents less than 8% of the production time. However, the same time window caused almost 40% of the breaks. Typical effect of biocide dosage (shown here as pH increase) on machine breaks can be seen in Figure 30.

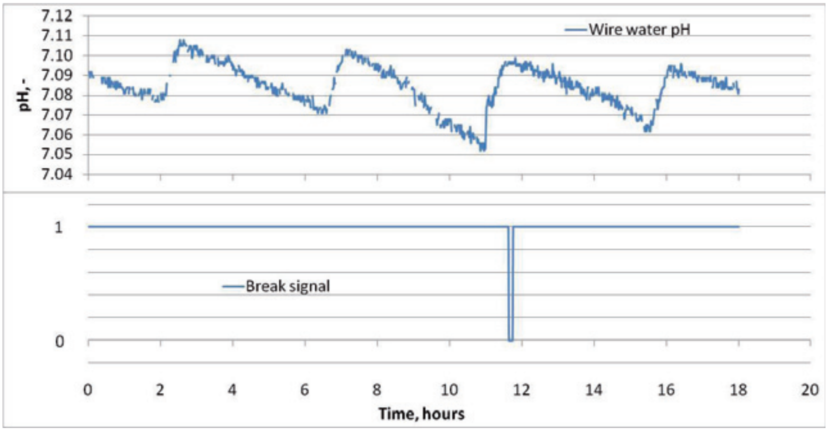

Figure 30 Occurrence of web breaks at PM due to a pH shock generated by the biocide dosing. *Paper V.*

Mechanism behind the web break can be rather complex and was not deeply studied in this research. However, it is well known that there is a strong correlation between pH stability and paper machine runnability (Almegård 2004). Sudden pH increase can influence on performance of the chemicals such as retention aids, fixatives, defoamers etc. and it influences directly to the electrochemical balance between the particles (Norell et al. 2000). Actually, even small variation in pH can disturb the chemical balance exponentially (Kanungo 2005). This can be seen for instance in cationic demand and zeta potential values. All this can have effects on flocculation, retention, web adhesion etc. All these, even alone, can cause production breaks at the paper machine (Haapala et al. 2010; Hubbe et al. 2006; Sihvonen et al. 1998; Wathén 2007; Kallio and Kekkonen 2005).

These results points out the importance of pH stability in the paper production. Especially sudden changes in the pH should be avoided. In this case the biocide should be dosed in a lower pH. Also more frequently added smaller biocide batches or continuous dosing could improve the situation. There may also be a possibility to feed the biocide to a position where its impact on chemical parameters would be less dramatic; the shock would have more time to stabilize before entering to the short circulation.

Even more detrimental effect of the biocide was its implications on product quality and further to the web performance in the converting processes after the paper machine. In an extensive process analysis including more than 400 parameters from paper and coating machines the most significant factor affecting coating machine runnability was found to be paper machine's chemical stability. Figure 31 presents a measurement period of one month. The first two weeks of the period the coating machine runnability was good (break time 2.9%) whereas during the second half of the period the runnability was poor (break time 18.6%). The figure clearly shows how the chemical variations at the paper machine are connected to the runnability at the coating machine. The breaks at coating machine increased the amount of coated broke in the system and therefore increased the broke delays in the towers resulting to pH drop. The figure shows that the chemical variations due to pH drop were seen as poor runnability.

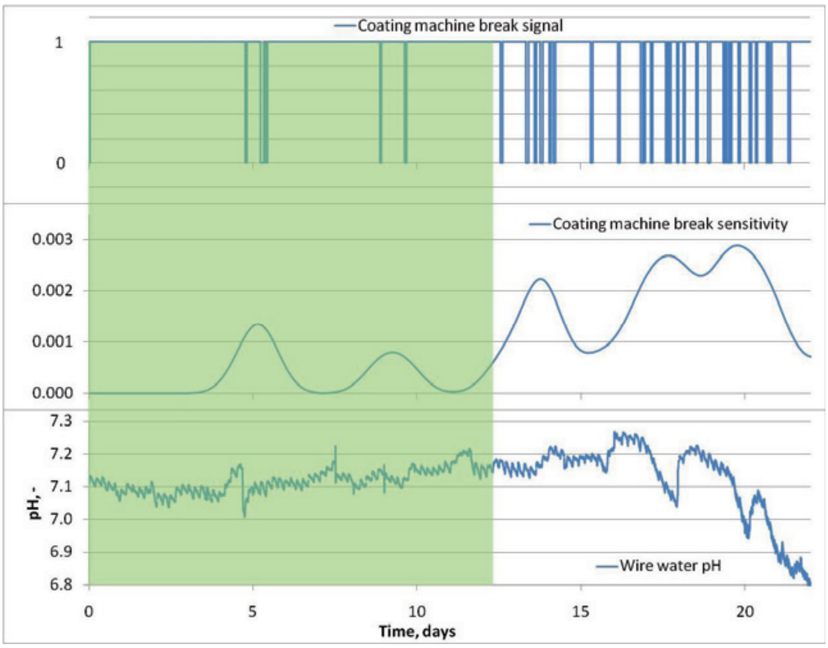

Figure 31 Relations between coating machine´s runnability and paper machine´s chemical stability. The part with color presents the period with good runnability. Break sensitivity is calculated from the break signal according to equations 1 and 2. *Paper V.*

It can be discussed, whether the previous example is considered to be biocide or process management problem. In the author's opinion, it is a biocide management problem. Biocide generates directly chemical variations and breaks at the paper machine. Biocide program is also an essential part of broke management. And as shown, poor biocide performance leads to spoiled broke, web defects and further problems with the web performance in coating (see Figure 32). There is also strong, statistical evidence available in the literature, that improved broke preservation and consistent chemical characteristics of the broke contribute to the reduction in hole counts observed on the paper machine (Rice et al. 2009).

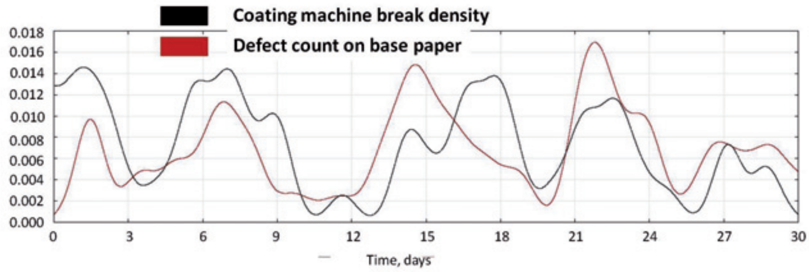

Figure 32 Correlation between base paper defects and coating machine runnability. Break density and defect count are calculated according to equations 1 and 2. *Paper V.*

There are also some indications that paper machine breaks (partly caused by the biocides) would directly cause also breaks at converting processes. A break or planned stoppage at the paper machine always disturbs chemistry of the machine. Chemical flows are disturbed and the broke cycles are burdened. Figure 33 shows the implications of a paper machine break to chemical stability and coating machine (PCM) runnability. A paper machine break itself disturbs the chemistry and causes a break at PCM with a quite short delay. The paper machine break further increases the broke volumes, causes extended delays in the broke towers and enables increased microbial growth in the broke towers. This microbial activity can be seen as a continuous decrease in pH values. This microbial disturbance causes chemical variations which finally causes a series of breaks at PCM. Since only the paper web is transferred to the converting processes, the mechanism of the PCM breaks is due to web properties as described above. In practice, this means that defects cause local variations in web tension and strength and further cause the breaks (Wathén 2003; Wathén and Niskanen 2006; Roisum 1990a; Korteoja et al. 1998).

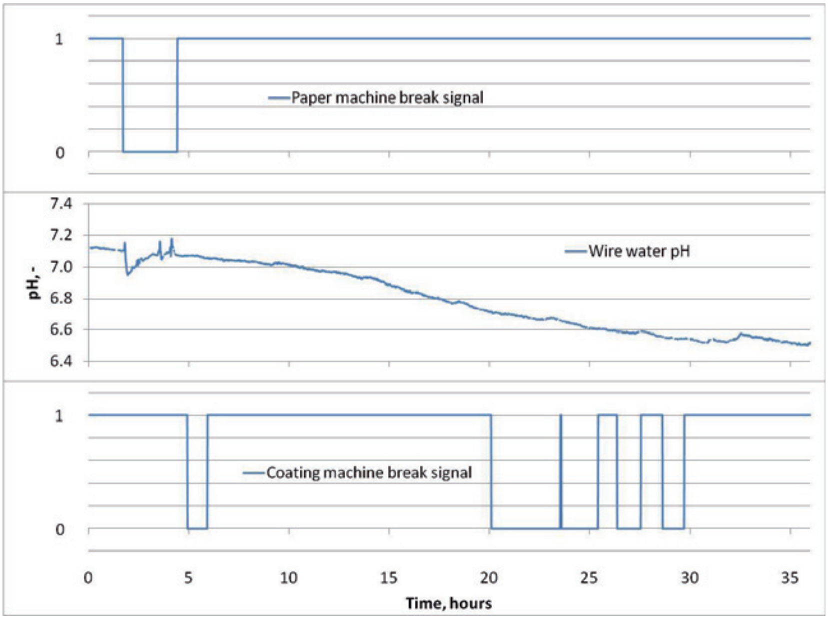

Figure 33 The effect of PM break on chemical stability of the PM wet end and PCM runnability. *Paper V.*

11. NEW CONCEPT FOR ELECTROCHEMICAL BIOCIDE GENERATION (*Papers I and II*)

11.1 Generation process

Based on several mill studies and trials in laboratory and pilot as well as available literature, it is obvious, that current commercial biocide programs are causing problems (Casini 2003; Simons and da Silva Santos 2005; Edwards 2003). These problems are twofold: biocides are salts, they generate chemical variations, and chemical variations cause runnability and product quality problems. In addition effects on surface activity, oxidative effect on the creation of charged groups, and dispersing effect possibly causing slime to be released are possible. On the other hand, poor biocide performance causes process deterioration, which causes similar problems: raw material spoilage, process variations, production efficiency losses, etc. (Koepenick 2010; Baumgartner and Spedding 2010). Process deterioration can be handled with proper measurements, analysis, and control. Optimization of the biocide programs is possible with current technology as shown in the Chapter 9.3. After the optimization, the problem of biocides being salts still remains. One possible approach to improve this situation is application of electrochemically generated biocides.

Electrochemical generation of biocides enables on-site production. Onsite-generated biocides are low-cost solutions because their production is based on actual need, not on estimated ones. Onsite oxidant production eliminates the transportation and storage of biocides, reducing the cost substantially. Moreover, due to the short time between the production and use, the degradation of the active compounds can be minimized, which would reduce chemical variations. This synergy would further decrease the total chemical costs at paper mills. And most importantly – it is possible to reduce the amount of salt added to the process using this technology.

As halogen ions are detrimental to the corrosion behavior of stainless steels, in biocide production the conversion of halogen ion to the corresponding hypo-compound should be as high as possible. In commercial hypochlorite solutions used in most of the oxidative programs at least in some stage, the "conversion" is <50%. When the hypochlorite is made by reacting chlorine gas with aqueous sodium hydroxide ($Cl_2(g) + 2NaOH \rightarrow NaOCl + NaCl + H_2O$), the molar ratio of sodium hypochlorite and chloride ion in the product is one. And this “conversion” drops constantly during transportation and storage. In electrochemical generation, when other variables are constant, the conversion to hypo-compound can in principle be increased by increasing the electric current, decreasing the feed concentration of the salt, and decreasing the flow rate. On the other hand, these changes usually decrease the current efficiency, which then leads to lower conversion. This can be seen in Figure 34. It is difficult to get higher conversions than about 60% with the cell configuration used in this work. Since no conversion optimization was carried out, it is expected that higher conversions can be reached by cell design, electrode selection and by optimizing the operation parameters. However, we managed to exceed the theoretical maximum biocide concentration of conventional hypo-product by more than 20%.

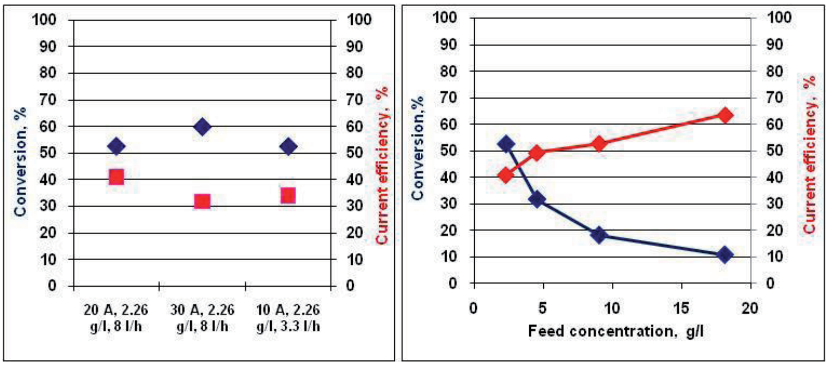

Figure 34 Conversion and current efficiency at different operating conditions (left) and the effect of NaCl feed concentration on conversion and current efficiency (right), current 20A and flow rate 8l/h.

As mentioned, the electrochemical generation is performed only seconds before dosing to avoid the reduction in conversion. This is not possible with conventional methods. Electrochemistry allows also possibility to switch the raw material for the electrolysis in case different biocide is needed. This requires only change of salt. There are several different options for electrochemical biocides, some of those having also other positive features besides biocidal performance, as described in the next chapters.

11.2 Efficiency in papermaking

Electrochemically produced halogen-containing biocides were found to be effective even at low concentrations in clear filtrate samples, which contained practically no bacterial spores (Figure 35, left). A 99.99% reduction in cell number was observed when 5ppm of hypochlorite and 10ppm of hypobromite were added. The biocidal efficiency was similar for biocides generated from NaCl and NaBr salts when the dosages were compared at equimolar concentrations at a process pH of 8.5. Sodium percarbonate (SPC) was a less powerful biocide than those containing halogens. Higher dosages were needed for effective microbe reduction with SPC (Figure 35, right).

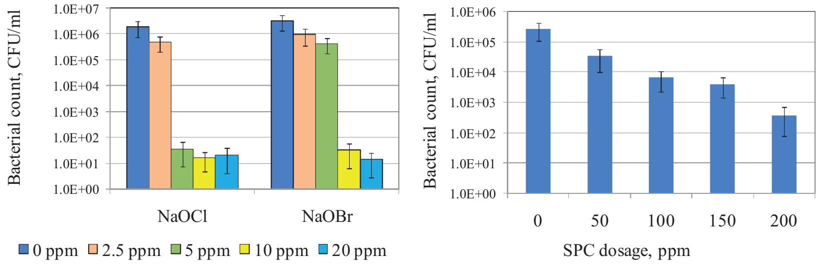

Figure 35 Efficiency of electrochemically formed biocides in fine papermaking clear filtrate. The dosage is presented as active substance (free active chlorine, free active bromine, or hydrogen peroxide). Error bars represent standard deviation between three independent experiments. *Paper II.*

Based on the literature and prior art teaching, NaOBr should more biocidal than NaOCl at pH 8.5. At this pH a large part of the hypochlorite is in the charged form that cannot penetrate cell membranes, whereas hypobromite is still membrane-permeable (Elsmore 1995). Despite several repetitions, we did not observe significant difference between biocidal actions of the chemicals. The reason might be associated with the electrochemical generation. In the production, it is likely that also other active substances are formed. These can affect biocide performance. Also, one cannot exclude the possibile presence of free radicals resulting from the electrochemical generation of biocides.

In this study the combinations of hypochlorite and hypobromite were found to be no more effective than the individual biocides. Halogen-containing biocides have a similar action against bacteria cells, and therefore the addition of different biocide did not offer additional benefit in a particular situation. The order in which biocides were added to the sample did not affect their effectiveness either.

In several studies it has been shown that the disinfecting capabilities of electrolyzed water were higher than those of chlorine alone (Rychen et al. 2003; Abadias et al. 2008). This is believed to be caused by synergism of several oxidants produced during electrochemical reaction. In some of the laboratory trials we were able to show the improved biocidal performance of electrochemically generated biocides but the results were not consistent. In order to fully utilize the potential of the electrolysis an extremely short delay between electrolysis and dosing should be maintained. Mill scale trials would be needed to verify the effects. However, in the laboratory trials the redox potential of electrochemically generated hypochlorite was higher

(Figure 36). This could indicate formation of other oxidative compounds in addition to hypochlorite.

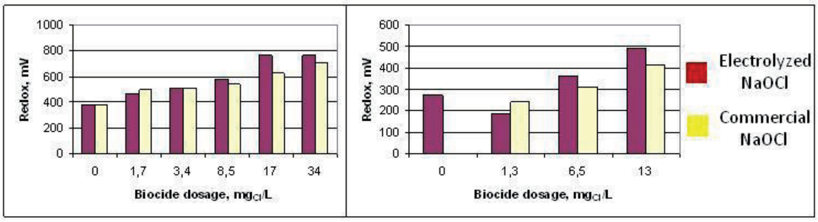

Figure 36 Comparison of the effect of commercial and electrolyzed NaOCl on the redox potential of clear filtrate from two fine paper mills (left and right graphs present the results from different mills).

Effect of sample consistency

Efficiency of generated biocides was tested at different process stages on samples having consistencies between 0.01 and 4.0%. The process stage at which the biocide was added had a clear effect on the biocidal efficiency (Figure 37). The efficiency of the treatment decreased with increased sample consistency. In a clear filtrate a dosage of 3.0ppm hypochlorite was found to be a sufficient, whereas in the case of a mixing tank sample, only a slight decrease in the bacteria amount could be seen when the same dosage of biocide was added. Proper mixing of the samples with different consistencies was taken into account.

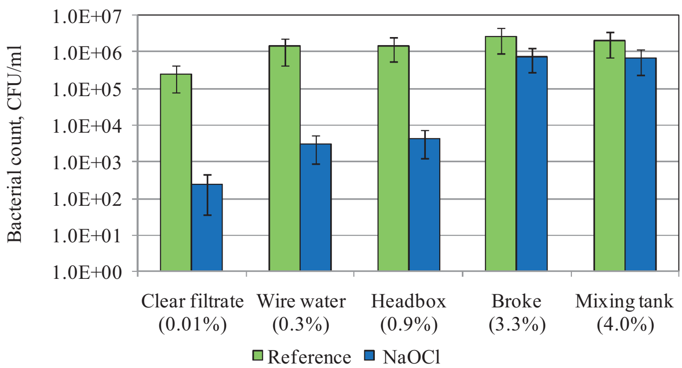

Figure 37 Biocidal efficiency of electrochemically formed hypochlorite against bacteria in samples from different process stages of fine papermaking. The consistency of the sample is presented below the name of the sample. Hypochlorite addition was 3ppm. Error bars represent standard deviation between three independent experiments. References indicate the samples without biocide addition. *Paper II*.

Addition of filler (calcium carbonate) to a wire water (filtrate) sample did not result in loss of biocidal effect. This suggests that the loss of biocidal efficiency with increasing sample consistency is due to the increase of the fiber consistency.

In the past it was common to run fine paper machines using sodium hypochlorite or hypobromous acid as the main biocide (up to 2-3kg/ton). These fast-acting, strong oxidizers were effective in killing, but the reason for their replacement with stabilized halogens was related to the damages caused to other additives such as dyes, fluorescent whiteners (OBA), sizing agents, retention aids, etc. (Simons and da Silva Santos 2005). The impact seen in Figure 37 is a typical result when using strong oxidizers. When fibers are present, the usage of hypochlorite and hypobromite is limited. In such cases, solutions such as SPC (as will be described later in this chapter) or stabilized halogens should be used. On the other hand, the results show that strong oxidizers are still a good solution for dilute samples.

Importance of mixing in biocide dosing

The effectiveness of biocide treatment can be enhanced when proper mixing of biocide is applied (Figure 38). In a clear filtrate sample, a correctly mixed 1ppm biocide dose reduced the amount of bacteria by as much as 2ppm when no mixing was applied. Proper mixing becomes important at high concentrations, especially when the biocide dose is optimized to a lowest possible level.

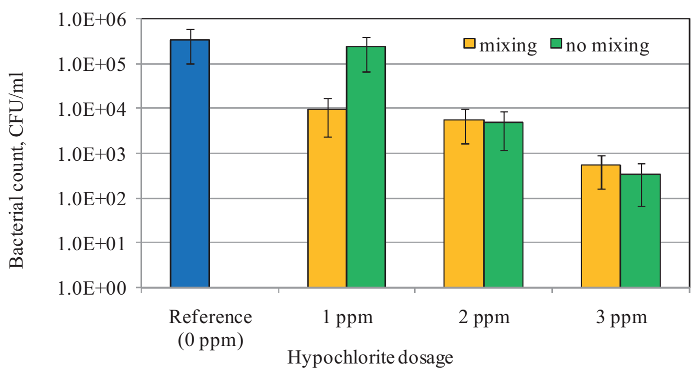

Figure 38 Effect of mixing on the clear filtrate biocide treatment efficiency with electrochemically formed hypochlorite. Error bars represent deviation between 3 parallel platings. Mixing was applied with a three-blade mixer with rotation speed 180rpm. *Paper II.*

In practical cases in mill processes, biocide additions are made to pipes and tanks. In a tank addition the following issues must be considered:

- Selection of which tank within the process will be used for the addition (size, consistency of the sample, hydraulic retention time)
- Mixing (mixer type, mixing efficiency, "natural mixing")
- Dosing point (to surface or to bottom of the tank)

Proper mixing for addition into the flow can be achieved by utilizing pumps or by installing static mixers (Matula and Ejima 2005). According to Paananen at al. (2009) optimization of chemical mixing is just at the beginning. Higher paper machine speeds have resulted in higher flows and an increased significance of the mixing. With mixing optimization, benefits such as reduced chemical usage, reduced water usage, and cleaner process and product can be achieved (Paananen et al. 2009).The effect of mixing is even more significant in the case of samples having higher consistency in which no "natural mixing" occurs. By applying correct mixing, the costs of the biocide treatment can be reduced.

Effect of dosing sequence

There are two possibilities for biocide dosing in a papermaking process

- Continuous dosing: The biocide solution can be pumped with constant flow into a process.
- Batch dosing: The biocide can be dosed in sequences. A constant flow is then followed by a period with no biocide feed to a process.

Both modes are commonly used in papermaking (Schrijver and Wirth 2007). Based on pilot trials with electrochemical biocides, the dosing mode had no significant influence on bactericidal effect of the biocide treatment. When biocide was added continuously, the bacteria level remained constant during the trial, which was not the case when biocides were added in batches (Figure 39).

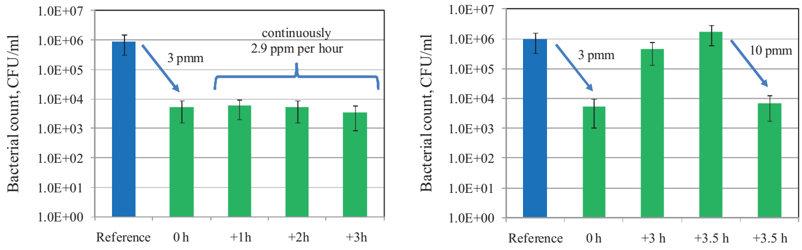

Figure 39 Comparison of continuous (left) and batchwise (right) addition of biocide to the clear filtrate. Electrochemically formed hypobromite was used as the biocide. Error bars represent deviation between 3 parallel platings. Reference indicates the sample without biocide addition. *Paper II*.

A benefit of continuous mode addition is that it causes less chemical variations in the process compared to batch dosing. Rice et al. (2009) have showed that stable chemical conditions together with functioning microbial control enable stable production and acceptable product quality. On the other hand, when biocide is added in batches, it allows a temporarily high concentration of biocides, which kills more microbes (Schrijver and Wirth 2007). Continuous treatment with low biocide dosage may increase the growth of biocide-tolerant bacteria (Hubschmid 2006). This can lead to higher need of the biocide or inefficient operation of the treatment.

Interactions with reductive chemicals

Electrochemically formed biocides using halogen salts as raw material are oxidizing agents, and therefore their efficiency may be reduced in the presence of reducing compounds such as dithionite. Even small dithionite concentrations (30mg/L) reduced the efficiency of the biocide, while at higher dithionite concentrations there was no antimicrobial effect (Figure 40). Thus, usage of the electrochemically generated biocides in mills where dithionite is used for bleaching may be limited.

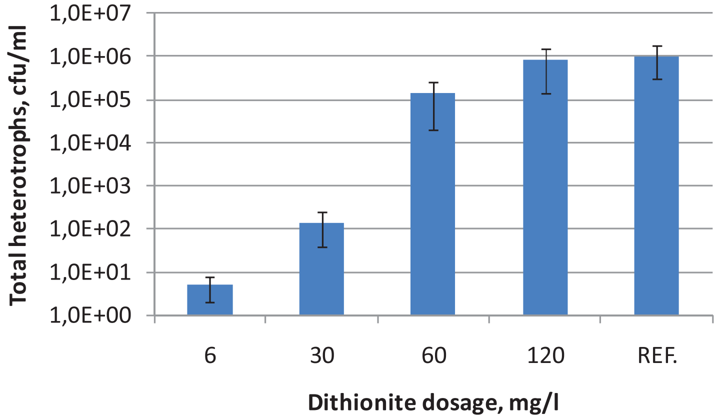

Figure 40 Effect of dithionite on the biocidal efficiency against aerobic bacteria of electrochemically generated hypochlorite in a clear filtrate from a board machine. Biocide dose was 44ppm as free active chlorine. REF = Clear filtrate without biocide treatment. Error bars represent standard deviation between three independent experiments. *Paper I.*

11.3 Dual biocide concept

Combinations of different biocides are often used in fine papermaking. For instance, oxidizers are commonly used to prevent slime formation, and organic compounds are used as preservatives. In papermaking, especially in retention systems, there are several dual-concepts available (Baker and Moore 2001). The aim is to have a more effective system than with the use of a single chemical. Philosophy behind the dual concepts applies also to biocide treatments. A biocide treatment program containing only one biocidal component make it easier for bacteria to form adapted or resistant strains (Hubschmid 2006).

This study presents an actual dual biocide concept with two different electrochemically formed biocides. The ability of electrochemically formed SPC to boost the efficiency of electro-chemically formed halogen treatment was observed in WES trials. Figure 41 presents the results from a "worst case", involving broke of high consistency. Similar results were also achieved in the laboratory study with the clear filtrate. The biocidal efficiency of the dual system (even in broke samples containing high organic load) was clearly better than that of hypobromite alone (Figure 41). By introducing SPC, the need of halogen-containing biocides could be clearly reduced. Figure 41 shows that 5 or 7ppm of hypobromite alone could not significantly reduce the microbial count. By introducing an additional 20ppm SPC to a hypobromite-treated sample, the reduction in bacterial count was achieved. 5ppm hyporomite and 20ppm SPC together reduced bacterial count by 99.8%. This was significantly better than the effect of 12ppm hypobromite alone.

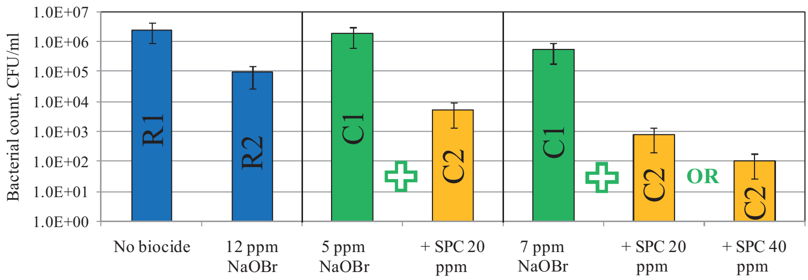

Figure 41 Combined effect of electrochemically formed hypobromite (C1) and SPC (C2) in broke. C2 bars (orange color) present the combined effect of hypobromite and SPC. R1 and R2 present the reference trials; C1 is component 1, and C2 is component 2. Error bars represent deviation between 3 parallel platings. *Paper II.*

The dosing order was important when a combination of halogen-containing biocide and SPC was used. In laboratory trials with the clear filtrate, highest efficiency was obtained when the clear filtrate was first treated with hypobromite and then with SPC (Figure 42). This can also be applied to hypochlorite / SPC combinations. It is possible that when the time delay between biocide additions is short, the biocides react with each other, resulting in poor efficiency of the treatment or excessive use of biocides.

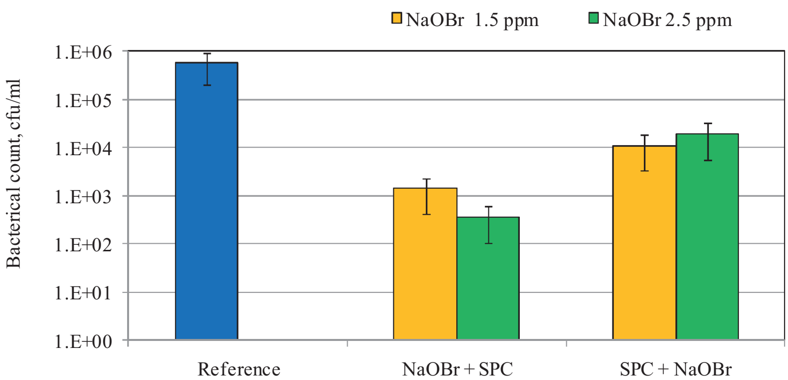

Figure 42 Effect of dosing order of electrochemically formed SPC and hypobromite. Sample treated was the clear filtrate from a fine papermaking. Hypobromite addition was 1.5 and 2.5ppm. SPC addition was 50ppm. Error bars represent deviation between 3 parallel platings. Reference indicates the sample without biocide addition. *Paper II.*

The common biocidal mechanism of oxidative compounds is based on reactive oxygen species (ROS) formation in vivo, resulting in oxidative stress and cell death. For hypochlorite, further biocidal mechanisms have been demonstrated. Hypochlorite represses genes essential for energy generation, such as those coding enzymes of electron transport chain (ATP production) and glucose transport (Small et al. 2007). These findings could explain why in our trials, dual systems, where hypobromite was used as a primary biocide worked better: starving cells with damaged membranes were not able to cope with additional oxidative stress caused by SPC. On the other hand, when SPC was added first at a sublethal concentration, it activated all enzymes needed for neutralizing ROS in the bacterial cell. So, bacterial cells were "prepared" and made more susceptible to oxidative attack.

The decomposition of electrochemically formed halogen-containing biocides was tested in a bacteria-free clear filtrate from a fine paper machine. When the initial dosage of the biocides was low (20ppm), the biocides decomposed rapidly: after a 30 minute reaction time the biocides were present in trace amounts. Only a few minutes contact time was enough to decrease the halogen content with approx. 90%. With higher initial biocide dosage, significant amounts of halogens were still present after 60 minutes (Figure 43).

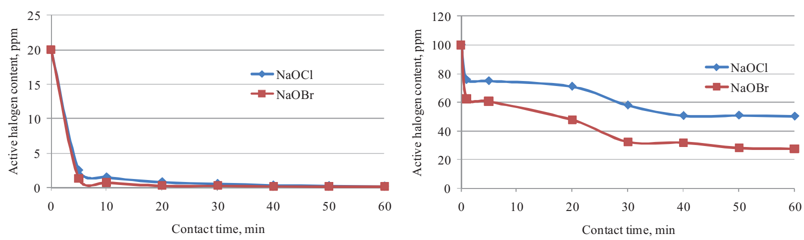

Figure 43 The decomposition of electrochemically formed hypochlorite and hypobromite in a bacteria free clear filtrate when the initial biocide concentration was 20ppm (left) and 100ppm (right). *Paper II.*

SPC acts more slowly than the halogen-containing biocides used in this study. The effectiveness of the treatment was greater when the reaction time was longer. For halogen-containing biocides, a 15min treatment time was sufficient (the results are not shown), whereas for SPC, 60 minutes were needed for effective reduction of bacterial count. After 60 minutes there was no additional reduction in the amount of bacteria.

Modern paper machines usually have pH control loops to maintain a stable pH, although alkaline systems using calcium carbonate are sometimes operated without any pH control. Control loops use chemicals such as CO_2,

SO_2, $NaHCO_3$, or alum to adjust the pH (Almegård 2004; Rauch 2005). When properly produced and dosed, electrochemically formed biocide systems had very little influence on pH. A raw material for electrochemically formed SPC was sodium bicarbonate. Only part of sodium bicarbonate is converted into SPC in the cell. As a result of this, the biocide is a mixture of SPC and sodium bicarbonate. Sodium bicarbonate is known to have a strong buffering capacity. Therefore, electrochemically formed SPC solutions could potentially replace pH control chemicals as well as biocides on the paper machine. By operating the pH control loop with SPC, one could have added value from the pH control program.

In most cases, the biocidal effect of SPC is not enough to handle the entire process. But it could be used as an additional chemical to replace some of the conventional or halogen-containing biocides. In practice there are two limitations to this process: 1) SPC's biocidal effects are weakened under highly oxidative conditions (it cannot be used directly after halogen addition); and 2) SPC decomposes into hydrogen peroxide (there are limitations for usage with a mechanical pulp due to possibility of brightness reversion or yellowing). On the other hand, another synergistic effect could be an increase in brightness especially with chemical pulps, due to peroxide.

In practice, our dual system could be utilized in fine papermaking as follows:

- Water (fresh and purified filtrates) - with electrochemically formed hypochlorite
- Broke - with electrochemically formed hypochlorite (before the tower) and SPC or hydrogen peroxide (after the tower)
- Short circulation - with electrochemically formed SPC.

This concept would allow hypochlorite enough time to decompose before the SPC phase. It would increase buffering capacity of the short loop and, when correctly dosed, also stabilize the pH. There might also be a minor increase in brightness. Hypochlorite is used for treatment of waters, where it does not interact with fibers or other chemicals. In the broke, hypochlorite is used only at low dosages just to generate an oxidative stress leading to starving of the microbes. SPC is responsible for the actual killing. In short, circulation hypochlorite should not be used, and therefore SPC is added. Based on a preliminary cost evaluation the new concept is also economically attractive alternative.

An approximate cost evaluation of electrochemical biocide production needs to consider both the operational (raw materials, electricity and maintenance) and investment costs. The calculations were based on the technical data provided by the cell manufacturer (ElectroCell's Chlor-O-Safe hypochlorite generator) (Electrocell 2011), on the market price of electricity in Finland (January 2011, 0.06 €/kWh) (Nordpool 2011), and on the prices of the salts from Finnish suppliers (0.15€/kg for sodium chloride and 0.33€/kg for sodium bicarbonate and carbonate). The price of hydrogen peroxide is estimated to be 1€ per kg (estimated as theoretical pure 100% hydrogen peroxide).

The calculation was made for the case of a mill producing 300,000 tons of fine paper/year. The fresh water consumption in the mill is ca. 16 tons/ton of the product. The amount of clear filtrate to be treated is approximately 10 tons/ton of paper if 10% of the water removed from the wire section goes to the disc filter. It was assumed that the pulp mix contains 20% broke and the amount of broke to be treated is about 4 to 5 tons/ton of paper. In the selected biocide program the fresh water and clear filtrate are treated with hypochlorite, the broke with hypochlorite and SPC/hydrogen peroxide, and the short circulation with SPC (Table X).

The generator can be automated and does not require a full-time operator. However it needs to be serviced regularly to ensure proper operation. For the calculation it was estimated that the supplier needs to visit the mill once a week. The cost of this is estimated to be 48,000 €/year. Estimated investment costs of the electrochemical cell are 150,000 € (including the cell with required accessories). Two electrochemical cells are needed when the dual system based on the use of SPC and hypochlorite. The estimated operating life of the cells is ten years.

Table 5 summarizes the cost structure of the biocide program. The total cost will be less than 0.5€/ton of paper produced. In these calculations, hydrogen peroxide is used for the broke treatment to decrease the costs. SPC could replace all the peroxide, but in the current application the cost for the broke treatment with SPC would be too high (current efficiency in SPC trials was only 20%). It is possible to decrease the costs by optimizing the cell performance.

Table X Cost structure of the biocide treatment with electrochemically produced hypochlorite, SPC, and hydrogen peroxide

	Mass of treated sample/ mass of produced paper	Biocide dosage (ppm)	Cost (€/ton of paper)
Fresh water treatment	16	2 (NaOCl)	0.024
Treatment of clear filtrate	10	3 (NaOCl)	0.023
Broke treatment	4	5 (NaOCl) + 20(SPC/hydrogen peroxide)	0.095 *
Short circulation	95	0.2 ** (SPC)	0.13 ***
Maintenance	---	---	0.16
Investment cost	---	---	0.05
Total cost	---	---	0.48

*) Calculated with hydrogen peroxide. **) Maximum amount of SPC that can be used for pH control. Excess can be added to the broke to replace the peroxide. ***) Replaces pH control chemical and reduces the amount of hydrogen peroxide to the broke.

12. CONCLUSIONS

The consequence of a poor biocide program or wrong strategy is twofold. Wrong strategy increases production costs due to increased need of chemicals. Biocides must be added excessively to control the microbes and at the same time the biocide decrease the efficiency of other chemicals. On the other hand the costs are increased via decreased runnability of the machine or as decreased product quality which might cause performance losses in converting.

A batch dosing of the biocide generated chemical variations, which were detrimental to the process. Most of the runnability problems at the diagnosed paper machine were recognized immediately after the biocide addition and its increasing effect on the pH and conductivity. It is important to design the biocide dosing strategy (dosing points, dosing mode, and type of chemicals) so that it causes as little chemical variations as possible and does not interact with the other chemicals.

Base paper defects caused by chemical variations in the paper machine wet-end were observed to cause runnability problems at the coating machine. This was due to well-known phenomena that holes and spots on the web were the weakest parts, causing the web breaks in the coating. At the same time with the increasing web defects the adhesion of the web to the rollers increased. This further increased the runnability problems.

In addition to biocide dosing itself, chemical variations were also due to the breaks at the paper machine and poor management of the broke. Poor broke management and poor biocide performance in the broke system caused the spoilage of broke. The spoiled broke decreased the system pH, increased the conductivity, and caused the defects to the web. These chemical variations were also observed as variation in cationic demand values. This probably caused unwanted particle flocculation generating the spots and holes to the web. The changes in charge also affected the adhesion of the web on the rollers, which further affected the runnability at the coating machine. Increased adhesion also required higher draws between the rollers which promote web breaks to occur from the weak positions of the web due to the defects in the paper or non-uniformity in the paper formation. The problems with the adhesion and the defects are coupled since both are due to the same origin. Improved broke management is needed in order to improve the machine runnability.

When revealing many such cause-effect relations and hidden phenomena, hand-held instrumentation gives additional references for existing basic measurements such as pH, conductivity, and redox potential. These parameters are now easy to install and measure. Measurements can be added to non-instrumented positions for additional data. This work also took in use measurements which have not been traditionally used in papermaking such as measurement of halogen, ammonium, dissolved calcium, and dissolved oxygen content. The reviewed instruments are not designed to be used in papermaking conditions for a long time. Therefore these instruments must be maintained daily and they cannot be used in continuous production monitoring for months. They are most valuable in trial runs and problem solving. ATP content measurement using a portable luminometer is a useful and easy-to-use method for evaluating microbial activity and optimizing biocide performance at paper mills.

Electrochemically generated biocides have been shown to be an effective way to control microbial problems and to reduce fluctuations and interactions causing production efficiency losses at paper mills. They can be added to water or pulp, and they have hardly any negative effect on the process or the end product. The positive effects are better microbial and chemical stability of the process (and less microbes), as well as increased product brightness. The presence of reducing compounds may cause limitations to the use of these oxidative biocides. It was shown that electrochemically generated biocides are also effective against bacterial spores.

A dual biocide concept based on the use of electrochemically formed hypochlorite or hypobromite and percarbonate is an effective alternative to conventional methods. Electrochemically generated percarbonate decreased the usage of halogen-containing biocides, leading to a reduction of AOX (adsorbable organic halogen compounds) load and corrosion risks. An additional benefit of the electrochemically formed percarbonate-based biocidal system might be the reduction in pH variation, if the biocides are dosed in the short recirculation loop.

This study provides a platform for development of new online measurement and control tools for paper machine diagnostics. A few new measurable parameters were demonstrated using ISE-technology. The potential around this technology is enormous. Almost anything can be measured using ISEs – online. And by utilizing the sample pretreatment, process analysis, and modeling even more information can be extracted from these analysis.

Also other technologies exist which could be developed into online/at-line applications. The most interesting ones could be lab-on-a-chip technologies and impedance tomography. Also the development of online methods for measuring microbial activity is needed. The most interesting is probably the online application for ATP analysis. It has been recently developed but, in author's knowledge, no publically available information from paper industry is available.

Altogether these tools combined with knowledge created in this study, it is possible to develop an industrial service concept to serve the paper industry. The concept would include measurement and analysis of chemical variation using new approach presented in chapter 9. The new tools would allow quick settlement and the findings, such as chemical interactions and other hidden phenomena, can be revealed as quickly as possible. Corrective actions are often rather straightforward to perform once recognized. The follow-up is as important as the recognition. In case new innovative solutions are needed, electrochemical concept can be applied. The development of electrochemical applications is just started in this work and the potential is far beyond what is presented here.

For papermakers, this work with electrochemical applications provides a basis for building a new control program. Onsite-generated biocides are low-cost solutions based on actual biocide need. Onsite oxidant production eliminates the transportation and storage of biocides, which reduce the cost substantially. Moreover, due to the short time between the production and use, the degradation of the active compounds can be minimized, reducing chemical variations.

Logical continuation of an electrochemical biocide development would be to further increase the conversion efficiency of salts into biocides and optimize the production. However, there are fundamental chemical and physical limits which will be reached possibly rather soon. Next step could be in utilizing the electrochemistry directly into process waters. These waters already contain significant amounts of ions such as chloride and bromine. By filtration and possibly by concentration, if needed, these impurities in the process could be turned into biocides. This would not only further reduce transportation costs but also contribute to reduction in fresh water usage at paper mills. Detrimental substances in the process water would be reused and therefore also water could be recycled more. This would have positive impact on waste water treatment and effluents as well.

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