A NEW DUAL BIOCIDE CONCEPT FOR FINE PAPERMAKING

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Electrochemical generation of oxidants was studied to find new solutions to control microbial contamination at paper mills. Laboratory and semi-pilot trials using a Wet End Simulator indicated that the combination of an electrochemically produced halogen-containing oxidant together with sodium percarbonate was an efficient new biocide concept, especially in fine papermaking. Addition of sodium percarbonate considerably reduced the need for halogen-containing biocides, thus lessening risk of corrosion. The trials with samples from fine paper machines indicated that the new concept required halogenated biocides to be dosed first, and the time delay between additions of biocide needed to be sufficient to ensure that no residual halogen was left when sodium percarbonate was added. Electrochemical generation enables on-site biocide production, which decreases transportation cost, risk associated with storage of hazardous chemicals, and biocide lost due to degradation. Thus, on-site generation of biocides together with potential reduction in amount of halogen containing oxidants make this dual concept economically attractive and environmentally positive.

Keywords: Biocide; Oxidant; Papermaking; White water; Broke; Electrochemical treatment; Microorganism control

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INTRODUCTION

Microbial growth is an important issue both for papermaking and for the end product. System closure makes conditions more favorable for microbial growth. At the same time, product safety and the use of biocides are getting more attention. The end product must be hygienic (no harmful microbes) but also chemically benign (no toxic compounds). In the future more efforts should be directed towards customized solutions and more environmentally friendly biocides.

Oxidizing biocides have been used in the paper and pulp industry for decades. The benefits of oxidizing biocides over traditional ones include reduced costs and high effectiveness. Oxidizing biocides are relatively fast-reacting, and the degradation products are non-toxic (at the ppm levels used) (Casini 2003; Elsmore 1995). Chemical suppliers have their own oxidative biocide programs. The most common ones are: 1) bromide-activated chloramine based on the combination of ammonium bromide and hypochlorite (Casini 2003), 2) the combination of hypochlorite and hydantoin (Schenker et al. 2006), and 3) a technology based on onsite generation of chlorine dioxide (Koepenick 2006).

Especially over the past 10 years the trend in oxidizing biocides has drifted from strong oxidizers such as sodium hypochlorite towards stabilized halogens. The usage of strong oxidizers has decreased due to concerns about corrosion, interference with wet end additives, and paper machine clothing damage. 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 Santos 2005). Potential problems with corrosion have also led to a search for alternative non-halogen containing oxidative biocides. One potential candidate could be sodium percarbonate (SPC), which has widely been used as a household bleaching agent for textiles. Peroxygen compounds have also been used as a bleaching agent in paper industry. Earlier studies have indicated that these chemicals could have biocidal effects against bacteria (Baldry 1984; Cochran and Ordal 1973).

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). There are a number of different technologies for electrolytic cells available on the market (Casson and Bess 2003).

Electrochemical generation of biocides enables on-site production. This can decrease biocide costs by decreasing degradation of the product and by decreasing transportation cost. On-site generated biocides are used for instance for water treatment, and in hospitals for washing medical devices. To our knowledge applications of electrochemically formed biocides in pulp and paper industry has not been reported. On the other hand, electrolysis has been utilized in several applications such as in pollutant reduction at pulp mill (Ghatak 2009) and in waste water treatment (Wang et al. 2007).

This paper describes a new dual biocide concept suitable especially for fine papermaking. The first part of the paper describes the efficiency of single biocide components and their interactions with the process. The latter part presents the efficiency of the dual biocide concept and evaluates the economical potential of it.

EXPERIMENTAL

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 0.02 m^2.

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 were 9.9 and 10.7, respectively. The pH of the SPC solution was adjusted to 8.5 (pH of papermaking process) with 1 M HCl. The parameters for the production of electrochemically formed biocides are presented in Table 1. The term halogen-containing biocide refers to hypobromite and hypochlorite in this study.

Table 1. Parameters for the Electrochemical Generation of Biocides

Biocide	Raw material	Concentration of salt, M	Current density, A/cm^2	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 (15 mmol/L) and magnesium sulphate (0.3 mmol/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 2. The potential of the oxygen evolution reaction is pH-dependent. With an oxygen evolution reaction, the reduction potential is 1.3 V, 0.8 V, and 0.4 V 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 2. 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. The WES has been presented earlier by Kiuru et al. (2003), Seppälä (2003), Kiuru et al. (2008), and Rice et al. (2009). Samples for the trials were obtained from a Finnish paper mill producing fine paper. The samples used in the laboratory trials are presented in Table 3. 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 3. 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 3 ppm. 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 3.5 ppm 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 Fig. 1 and Table 4.

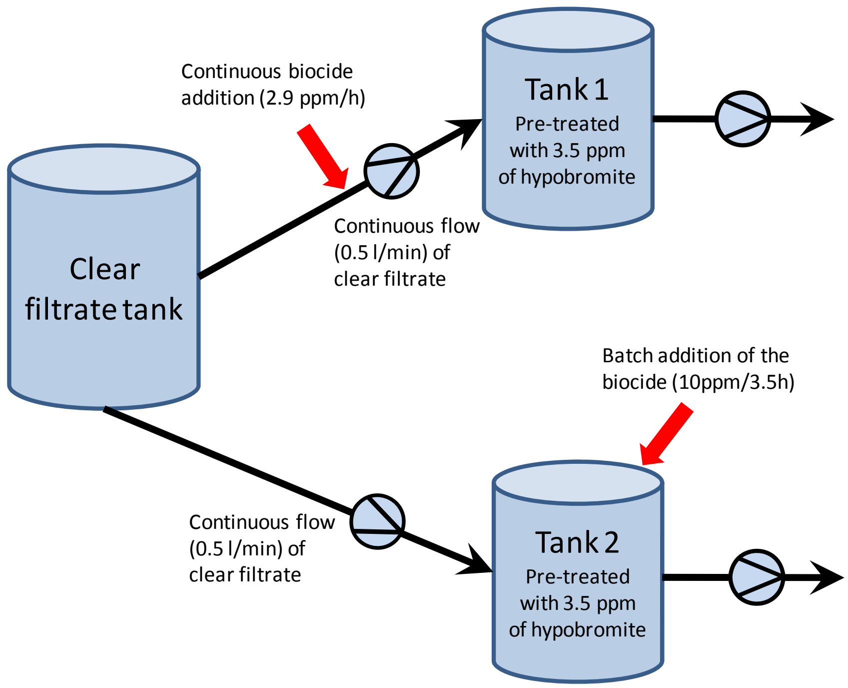

Fig. 1. Trial setup for the determination of the effect of dosing mode. Flow rates of the pumps were synchronized so that the clear filtrate levels in the tanks 1 and 2 were constant.

Table 4. Setup for the Dosing Mode Trials

	Tank 1	Tank 2
Retention time in tanks	3 h	3 h
Dosing sequence	Continuous, 2.9 ppm/h	Batch, 10 ppm 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.

Analysis

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) according to ISO-8784-1 standard. In case of a dry sample, the sample was prepared into homogenized suspension and plated out according to the same method. Plates were incubated at 37 °C for 48 h, after which the colony-forming units (CFU) were counted. To determine the amount of bacterial spores, the water samples were heated at 80 °C for 20 min before the plating. To ensure statistical validity of the cultivation results, all laboratory experiments were repeated three times. Large scale pilot trials were performed once. Therefore, bacterial count standard deviation for each sampling point was calculated from 3 parallel platings (pilot trials) or from three independent experiments (laboratory trials).

RESULTS AND DISCUSSION

Efficiency of Electrochemically Formed Biocides 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 (Fig. 2). A 99.99% reduction in cell number was observed when 5 ppm of hypochlorite and 10 ppm 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 (Fig. 2).

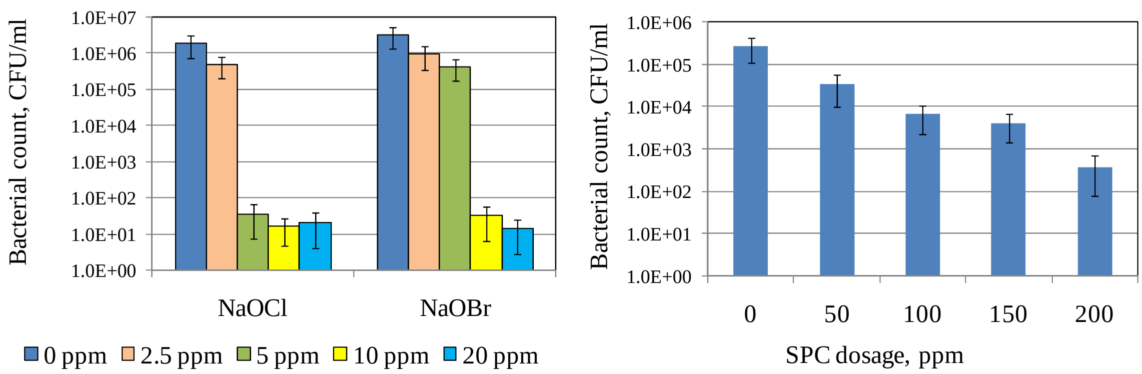

Fig. 2. Efficiency of electrochemically formed biocides in fine papermaking clear filtrate. The dosage is presented as active substance (free active chlorine, free active bromine, or hydrogen peroxide). Error bars represent standard deviation between three independent experiments.

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 to biocide performance. Also, one cannot exclude the possibile presence of free radicals resulting from the electrochemical generation of biocides.

It is well known that bacterial spores are more resistant to biocides than vegetative cells. Oxidative biocides are able to damage spores, preventing their germination

(Young and Setlow 2003). However, a much higher concentration of the biocide is needed for removal spores than for removal of vegetative cells (Rose et al. 2005). Therefore, special attention should be paid to sporicidal performance of the biocides. Electrochemically formed SPC and hypochlorite did not prove to be sporidical when applied at low concentrations. The required hypochlorite dosage to destroy the spores from a clear filtrate was 80 ppm.

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.

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 (Fig. 3). The efficiency of the treatment decreased with increased sample consistency. In a clear filtrate a dosage of 3.0 ppm 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.

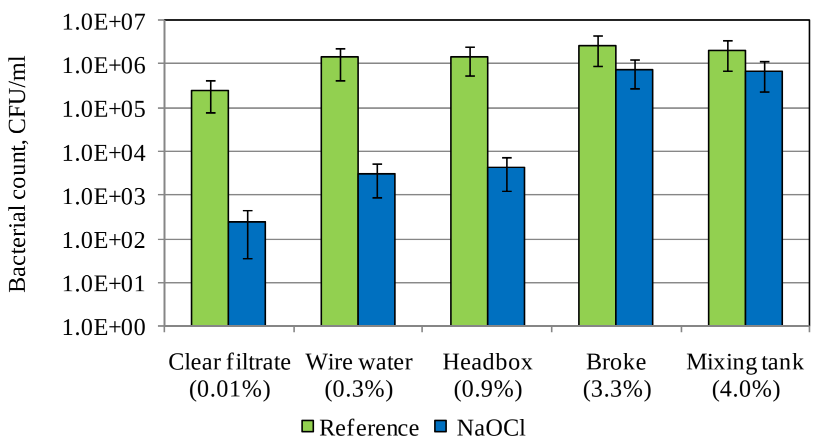

Fig. 3. Biocidal efficiency of electrochemically formed hypochlorite against bacteria in samples from different process stages of fine papermaking. The consistency of the sample is presented below the name of the sample. Hypochlorite addition was 3 ppm. Error bars represent standard deviation between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

Addition of filler (calcium carbonate) to a wire water (filtrate) sample did not result in loss of biocidal effect (results are not shown). This suggests that the loss of biocidal efficiency with increasing sample consistency is due to the increase of the fiber consistency. However, we cannot exclude the effects of other chemicals or other reasons.

In the past it was common to run fine paper machines using sodium hypochlorite or hypobromous acid as the main biocide (up to 2-3 kg/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 Santos 2005). The impact seen in Fig. 3 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 paper) 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 (Fig. 4). In a clear filtrate sample, a correctly mixed 1 ppm biocide dose reduced the amount of bacteria by as much as 2 ppm when no mixing was applied. Proper mixing becomes important at high concentrations, especially when the biocide dose is optimized to a lowest possible level.

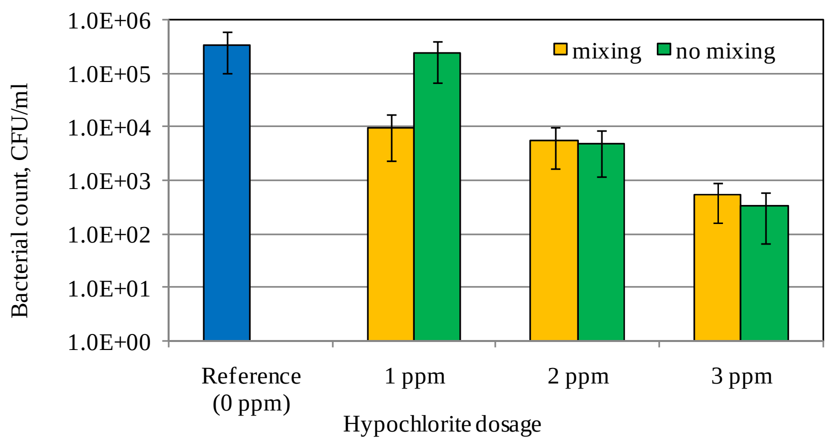

Fig. 4. Effect of mixing on the clear filtrate biocide treatment efficiency with electrochemically formed hypochlorite. Error bars represent deviation between 3 parallel platings. Mixing was applied with a three-blade mixer with rotation speed 180 rpm.

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). 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. Some effects of dosing sequence on the level of microbial growth and chemical variations at paper machines have been earlier documented in publically available literature (Kiuru et al. 2010). Based on pilot trials in this study, 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 (Fig. 5, left), which was not the case when biocides were added in batches (Fig. 5, right).

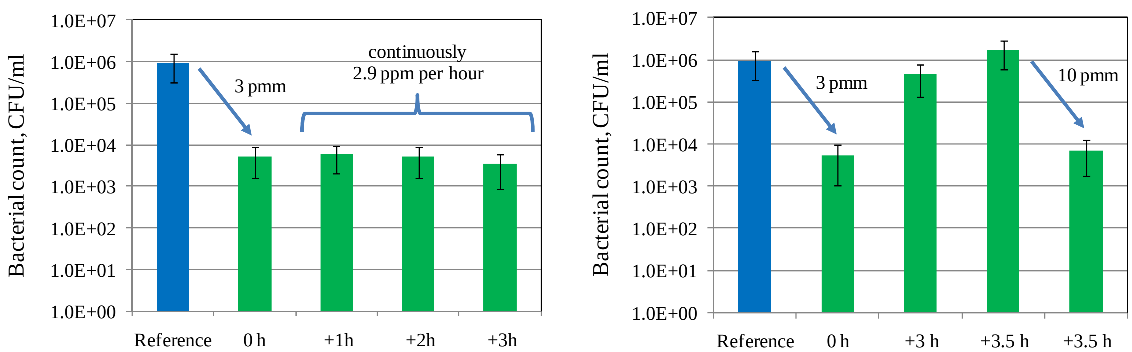

Fig. 5. Comparison of continuous (left) and batchwise (right) addition of biocide to the clear filtrate. Electrochemically formed hypobromite was used as the biocide. Error bars represent deviation between 3 parallel platings. Reference indicates the sample without biocide addition.

A benefit of continuous mode addition is that it causes less chemical variations in the process compared to batch dosing. On the other hand, when biocide is added in batches, it allows a temporarily high concentration of biocides, which kills more microbes. Continuous treatment with low biocide dosage may increase the growth of biocide-tolerant bacteria. This can lead to higher need of the biocide or inefficient operation of the treatment.

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. 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. This paper 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 (results not shown).The biocidal efficiency of the dual system (even in broke samples containing high organic load) was clearly better than that of hypobromite alone (Fig. 6). By introducing SPC, the need of halogen-containing biocides could be clearly reduced. Figure 6 shows that 5 or 7 ppm of hypobromite alone could not significantly reduce the microbial count. By introducing an additional 20 ppm SPC to a hypobromite-treated sample, the reduction in bacterial count was decreased. 5 ppm hyporomite and 20 ppm SPC together reduced bacterial count by 99.8%. This was significantly better than the effect of 12 ppm hypobromite alone.

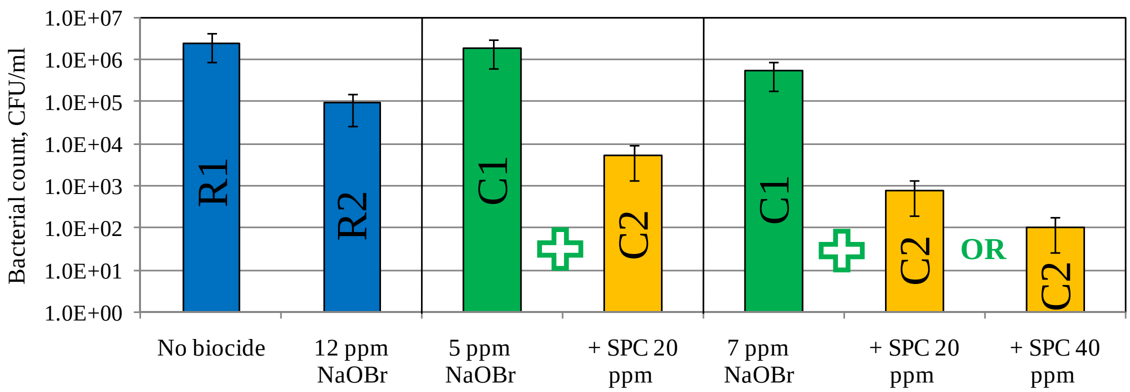

Fig. 6. Combined effect of electrochemically formed hypobromite (C1) and SPC (C2) in broke. C2 bars (orange color) present the combined effect of hypobromite and SPC. R1 and R2 present the reference trials; C1 is component 1, and C2 is component 2. Error bars represent deviation between 3 parallel platings.

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 (Fig. 7). 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.

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.

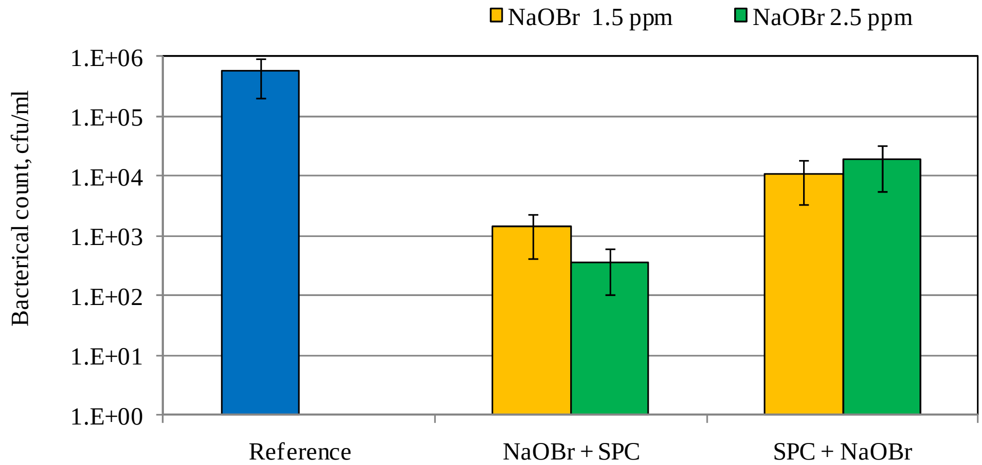

Fig. 7. Effect of dosing order of electrochemically formed SPC and hypobromite. Sample treated was the clear filtrate from a fine papermaking. Hypobromite addition was 1.5 and 2.5 ppm. SPC addition was 50 ppm. Error bars represent deviation between 3 parallel platings. Reference indicates the sample without biocide addition.

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 (20 ppm), 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 (Fig. 8).

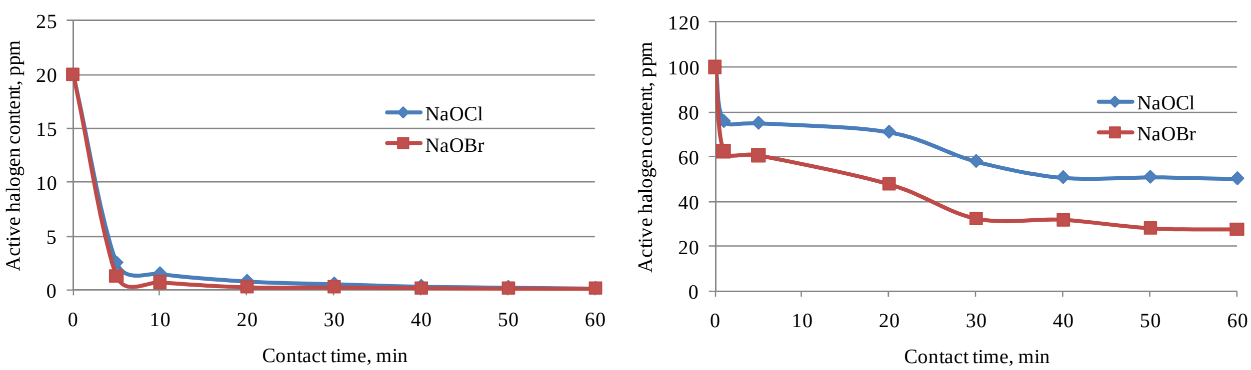

Fig. 8. The decomposition of electrochemically formed hypochlorite and hypobromite in a bacteria free clear filtrate when the initial biocide concentration was 20 ppm (left) and 100 ppm (right).

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 (Fig. 9). For halogen-containing biocides, a 15 min 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.

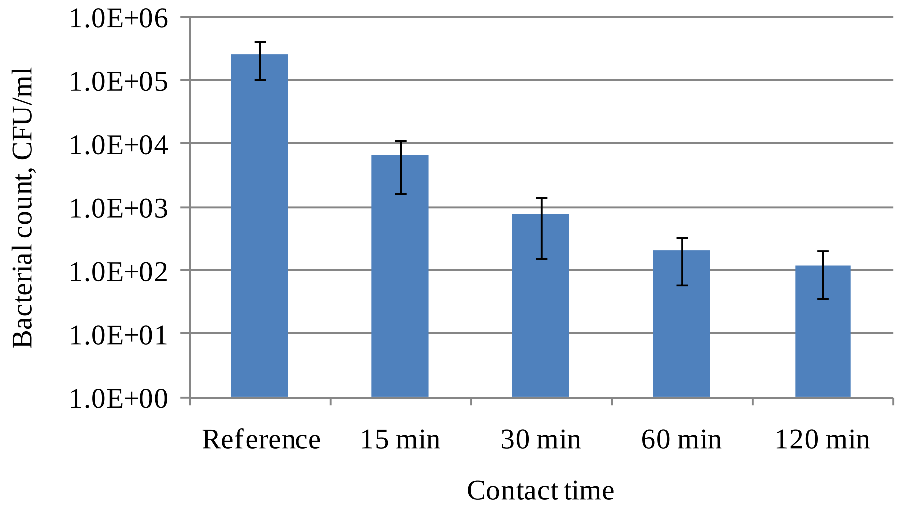

Fig. 9. Effect of contact time on a biocidal effect of electrochemically formed SPC solution. Clear filtrate was used as a test media, and an applied biocide dosage was 100 ppm. Error bars represent standard deviation between three independent experiments. Reference indicates the sample without biocide addition.

Modern paper machines usually have pH control loops to maintain a stable pH. 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 mechanical pulps, due to peroxide. For chemical pulps the brightness increase is expected to be rather insignificant.

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.

Cost Evaluation of the Concept

One of the most important benefits of oxidative biocides over traditional ones such as isothiazolone and DBNPA is their lower cost. The use of oxidative biocides has greatly reduced the cost of biocide treatment at the mills from 7-8 euros/ton of paper produced to between 4 and less than 1 euros/ton (Sievänen 2008).

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 5).

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 5. 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.

CONCLUSIONS

1. A dual biocide concept based on the use of electrochemically formed hypochlorite or hypobromite and SPC is an effective alternative to conventional methods. SPC 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 SPC-based biocidal system might be the reduction in pH variation, if the biocides are dosed in the short recirculation loop.
2. In this dual system, biocide dosing order plays an important role. In practical applications the dosing points need to be optimized to provide an adequate delay between additions of halogen-containing biocide and SPC. The halogen-containing biocide must be added first, and a check should be made to ensure there is no residual halogen left before the SPC is added.
3. The electrochemically generated halogen-containing biocides (NaOCl and NaOBr) had similar efficiency when they were compared in equimolar concentrations. The biocides proved to be efficient already at low concentrations (3 to 20ppm). Increase of consistency reduced biocidal efficiency. Combination of the halogen-containing biocides did not bring any benefit compared to single biocides. SPC was not an efficient biocide when it was used alone. However, it was able to improve the effectiveness of halogen-containing biocides.
4. 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.

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