

ELECTROCHEMICALLY GENERATED BIOCIDES FOR CONTROLLING CONTAMINATION IN PAPERMAKING

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Feasibility of electrochemically generated biocides in papermaking was evaluated in pilot scale trials. The trials indicated that electrochemically generated biocides prevent microbial growth and proliferation in broke systems, as well as in water circulations. The spoilage of broke can be delayed, and already spoiled broke can be recovered using these biocides. The improved broke quality increases the stability of the paper machine and, consequently, less broke is produced. The biocides can be added to water or pulp, and they have hardly any negative effect on the process or the end product. The presence of reducing compounds may cause limitations in the use of these oxidative biocides. It was observed that electrochemically generated biocide was also efficient against heat-resistant spores. However, the biocide was less efficient against spores as compared to vegetative cells, both aerobic and anaerobic, especially when the spore numbers were higher than 10^4 cfu/ml. Onsite oxidant production eliminates the transportation and storage of biocides. Moreover, due to the short time between the production and use, the degradation of the active compounds can be minimized.

Keywords: Oxidizing biocide; Bacteria; Papermaking; White water; Broke; Microbial control; Electrochemical treatment; Wet end chemistry

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INTRODUCTION

Paper manufacturing is a water-based process, employing a range of raw materials that introduce a vast range of microorganisms (Väisänen et al. 1991; Suihko et al. 2004; Suihko et al. 2005; Maukonen 2006; Tirola et al. 2009, Lahtinen et al. 2006). Raw materials, together with the current operational process conditions, such as closed water loops, high temperatures (up to 50°C), and neutral pH, provide favorable environmental conditions for the microbial growth. The nature of the microorganisms present in a paper mill system depends both on the source of microbial contamination and the subsequent growth conditions (Suihko et al. 2004, 2005; Öqvist et al. 2008; Väisänen et al. 1991).

There are various problems associated with microbial growth at paper and board mills, such as raw material spoilage and the formation of slime deposits, which affect the paper making process and the quality of final products, resulting in productivity losses due to wet end breaks and cleaning downtime. Bacterial contamination may increase the odor both at the mills and in the end products (Rice et al. 2003; Stojacic and Lustenberger 1995). Health risk associated with exposure of workers to aerosols containing bacteria has been also reported (Haug et al. 2002; Sikkeland et al. 2007).

Although methods of bacterial contamination control vary between mills, most of the mills use biocides as bacterial control agents. In light of the Directive 96/61/EC the paper industry should aim to reduce the use of biocides that accumulate in the process and may remain in effluents (European Commission 2001). Moreover, in many cases, the presence of biocidal residues in a final product is unwanted. Therefore, the biocide used in paper manufacturing should be not only of high antimicrobial efficiency, but also environmentally friendly. In general, oxidative biocides may meet such demands. Conventionally (until the late 90's) biocides used in paper mills have been mostly non-oxidative. Since that time, oxidative biocides have gained more attention due to better biocidal performance and low cost.

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 MgCl₂ can also be used (Buck et al. 2002).

Electrochemically generated biocides have been studied intensively during last decade in terms of using them in food industry, drinking water, and waste water sanitation and hospitals (Huang et al. 2008; Park et al. 2002; Al-Haq et al. 2005).

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 water treatment, in hospitals for washing medical devices, and in vegetable and fruit processing (Huang et al. 2008). An electrolyzed water generator has also been approved for applications in the food industry by the US Environmental Protection Agency (EPA) (Park et al. 2002).

A search of the literature came up with only one set of articles related to the use of electrochemically generated biocides in the pulp and paper industry. Issues on electrochemical production of oxidative biocides and their use in paper industry were addressed is by Särkkä et al. (2007, 2008). The authors investigated the direct electrolytic treatment of synthetic paper machine water as a means to inactivate the primary biofilm-forming bacteria *Deinococcus geothermalis*, *Pseudoxanthomonas taiwanensis*, and *Meiothermus silvanus*. Inactivation was believed to be due to hypochlorite/chlorine generated electrochemically at the anode.

This paper describes the potential use of electrochemically formed biocides in papermaking. The paper presents a case study in pilot scale, where the potential of the electrochemically formed biocides was evaluated in the broke system. The pilot results were supported by laboratory trials on biocide interactions with the process. This study puts focus on the microbiological effects of the electrochemically formed biocides and their interactions with process chemistry.

EXPERIMENTAL

Electrochemical Cell

Biocides for the pilot trials (case study) were produced from NaCl (8 g/L) using an electrochemical round cell Envirolite[®] R-40 (Envirolite Group, Estonia) according to the manufacturer's instructions. The electrochemical cell was equipped with a membrane

separator between the anode and cathode compartments. Anode product used as biocide is called electrochemically formed hypochlorite. The production was performed in two compartments, followed by mixing to adjust the pH. Part of the catholyte was mixed with anolyte to adjust the pH of the biocide to the process pH of 7.6.

Microbial Cultivation

Enumeration of bacteria was done 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 72 h at 40 °C (relevant for paper machine).

Effect of Reductive Chemicals

To determine the effect of dithionite (a reductive bleaching agent for mechanical fibers) on the efficiency of electrochemically formed biocides, clear board machine filtrate was treated with dithionite (dose 6-120mg/L). After dithionite addition the samples were treated with electrochemically formed hypochlorite (dose 44 ppm measured as free active chlorine content). Biocide dosage was selected based on preliminary trials (results are not shown). The amount was selected so that the differences between trial points would be as large as possible (i.e. the dosage would be optimal in the presence of small dithionite concentrations). The experiment was repeated three times.

Effect of Sample Consistency

To determine the effect of sample consistency on biocide performance, machine stock from a board mill was treated with biocide, and the stock was further diluted with clear filtrate from the same board machine. The biocide dosage was 44 ppm (measured as free active chlorine content). The experiment was repeated three times.

Analytical Methods

Free active chlorine was measured using a photometer Dulcotest[®] DT1 (ProMinent, Germany) according to the manufacturer's instruction.

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 measured using a Müttek 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.

Handsheets Properties

Laboratory handsheets were made from the broke samples according to EN ISO 5269-1 standard. Target grammage of the sheets was 60 g/m².

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.

Pilot Trials

The simulator

A Wet End Simulator was used in this study. The detailed information on the simulator has been presented by 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 when sampled at the mill. Upon its receipt, the filtrate was kept in containers stored for a few days to promote spoilage.

A biocide solution prepared for the trial for treating the spoiled broke and clear filtrate had following characteristics: free active chlorine 1400 ppm, pH 7.6, and redox potential 880 mV. The biocide was added to the process at different amounts to achieve the needed concentration.

Preparations

Dry broke and clear filtrate were disintegrated in several 150 L batches for 10 minutes. The target consistency in the pulper was 3%. Prior to disintegration the filtrate was preheated to 40°C. After the disintegration the pulp was pumped to one of the broke towers. The temperature in both broke towers was maintained at 40°C throughout the trial.

After the disintegration, the pulp was stored in two pilot broke towers, the Tank with biocide and the Reference tank. The only difference in preparation step between these tanks was the treatment of the clear filtrate: the broke in the reference tank was disintegrated using untreated clear filtrate. The broke in the biocide tank was disintegrated using clear filtrate which had been treated with 28ppm (free active chlorine) electrochemically generated hypochlorite solution just before mixing it with the dry broke.

Progress of the trial

After the preparation, the actual trial included four different steps (see Fig. 1):

- **Step 1: Spoilage.** After the preparations, both towers were kept under poor mixing at a constant temperature for approximately two days.
- **Step 2: Treatment of the broke exit flow with the biocide.** After the broke in both towers had been spoiled, the ability of the biocide to recover the broke was evaluated. In mill scale, this would mean treating the contaminated broke with biocides. The biocide was pumped into the exit flow of the broke tower. The duration of this step was only a few minutes. The biocide dose was 28ppm of the broke flow. Treated broke was not circulated back to the tanks in this step.

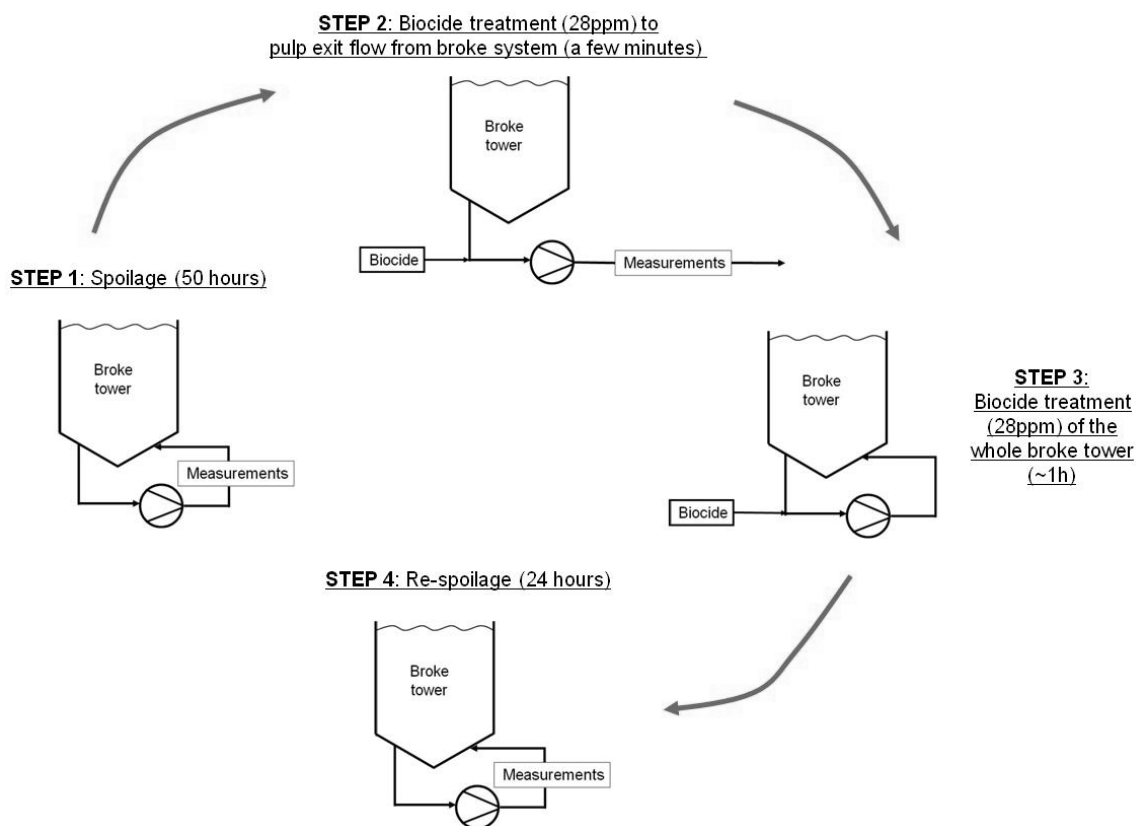


Fig. 1. Progress (steps) of the trial. The biocide additions are measured as free active chlorine.

- **Step 3: Biocide treatment of the broke tower.** The treatment was done in the same way as in step 2, except that the broke was pumped back to the tower. The duration of step 3 was approximately 1 hour per tower. The biocide dose was 28 ppm.
- **Step 4: Re-spoilage.** After the biocide treatment the spoilage of the towers was monitored for an additional 1 day.

Sampling

Sampling was done after each step. Hereafter the samples are marked as follows: **Clear filtrate** - samples taken from the dilution water before disintegration (mixing with dry broke); **disintegrated broke** - samples taken just after disintegration; **spoiled broke** - samples taken after 50 hours monitoring; **Biocide treated broke exit flow** - samples after step 2 (treatment of broke exit flow); **Biocide treated broke in broke tower** - samples after step 3 (treatment of broke tower)

RESULTS AND DISCUSSION

It is generally accepted that chlorine is the primary oxidant in the electrolyzed brine solution (Patermarakis and Fountoukidis 1990; Son et al. 2004; Len et al. 2000; Kiura et al. 2002; Casson and Bess 2003; Park et al. 2004). The oxidation-reduction potential (ORP) was shown to be an important factor that defines the biocidal activity of electrolyzed anode water (Kim et al. 2000). Nevertheless, the mechanisms of biocidal activity of electrolyzed brine are not yet fully understood. This could be partially due to the fact that commercial systems differ from each other in many parameters: electrolytic cell structure, electrode material, voltage, NaCl concentration, and many others. Moreover, there are many different laboratory prototypes of electrolytic cell used in the research. Due to these major differences between the cells, it is very difficult to compare the efficiency of the produced biocides.

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.

Growth of Bacteria in Broke System

The amount of heterotrophic bacteria in dry broke was only 60 cfu/g. After the spoilage period the total amount of microbes in the clear filtrate was over 10^6 cfu/mL. The amounts of heterotrophic bacteria in Fig. 2 indicate that adding electrochemically generated hypochlorite to the water eliminated nearly all the microbes (< 10 cfu/ml).

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 of 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.

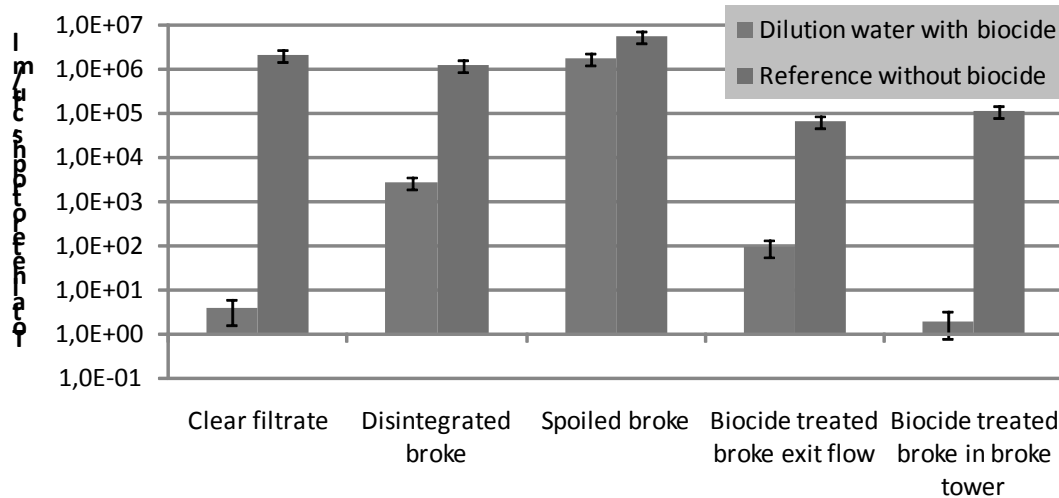


Fig. 2. Total heterotrophic microbial count (plate counting) in pilot trials. Error bars represent deviation between 5 parallel platings.

Anaerobic bacteria are more sensitive to oxidizing compounds than aerobic, and hence, electrochemically generated biocides are powerful against anaerobes (Fig. 3). When such biocide was used for disinfection, it was initially able to eliminate all the anaerobes (case when dilution water was treated with biocide).

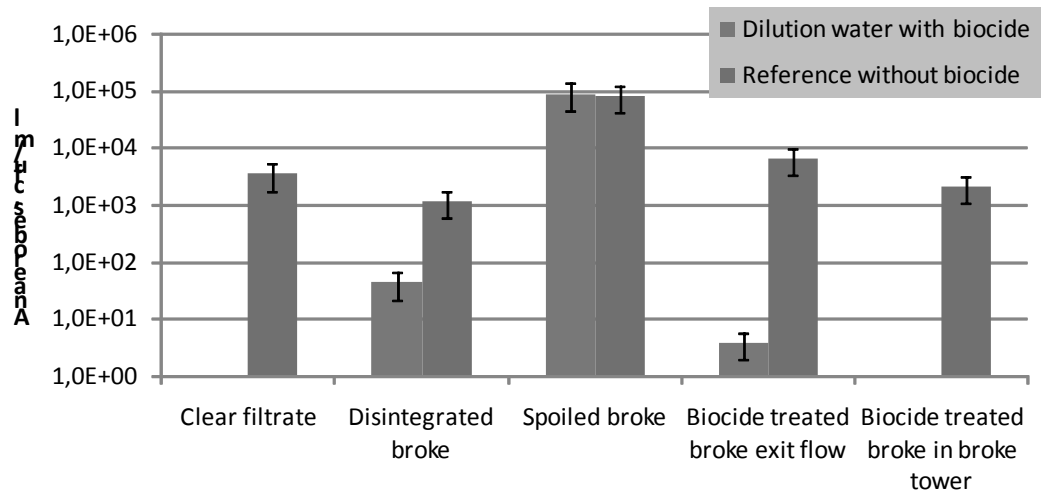


Fig. 3. Total amount of anaerobes (plate counting) in broke samples. Error bars represent deviation between 5 parallel platings.

Bacterial spores are highly resistant to many traditional organic biocides (McDonnell 2007a,b; Russell 2003). Oxidizing biocides such as hypochlorite are proven to be more effective against spores (Setlow 2005; McDonnell 2007a,b; Russell 2003). We observed that electrochemically generated biocide was efficient against spores (Fig. 4). The biocide was less efficient against spores as compared to vegetative cells, both aerobic and anaerobic, especially when the spore numbers were higher than 10^4 cfu/ml. The results indicate that once spores are developed it is difficult to eliminate them.

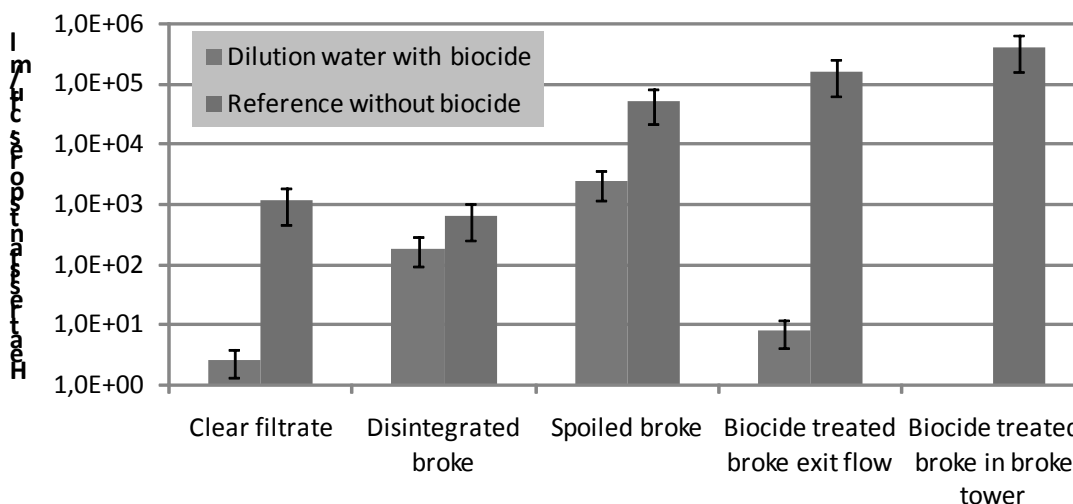


Fig. 4. Number of heat resistant bacterial spores (plate counting). Error bars represent deviation between 3 parallel platings.

Our results show that electrochemically generated biocides can be used for preventing broke spoilage. Biocide treatment effectively eliminated the majority of the bacteria in the clear filtrate used for pulping broke, and the initial broke quality was good. This gives a “buffer time” before the growth starts again.

Factors Disturbing Biocide Performance

Interactions with reductive chemicals

Electrochemically formed biocides using NaCl 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 (30 mg/L) reduced the efficiency of the biocide, while at higher dithionite concentrations there was no antimicrobial effect (Fig. 5). Thus, usage of the electrochemically generated biocides in mills where dithionite is used for bleaching may be limited.

Effect of sample consistency

Biocide treatment of machine stock from a board mill at 2.6% consistency reduced the number of bacteria only slightly, whereas the same biocide dose at a low fiber consistency of 0.1 to 0.01% resulted in microbiologically clean ($< 10^3$ cfu/mL) process water (Fig. 6). The bacterial load was roughly the same in both machine stock and clear filtrate (10^6 cfu/mL). Therefore, the sample dilution did not affect the number of aerobic bacteria prior to biocide treatment.

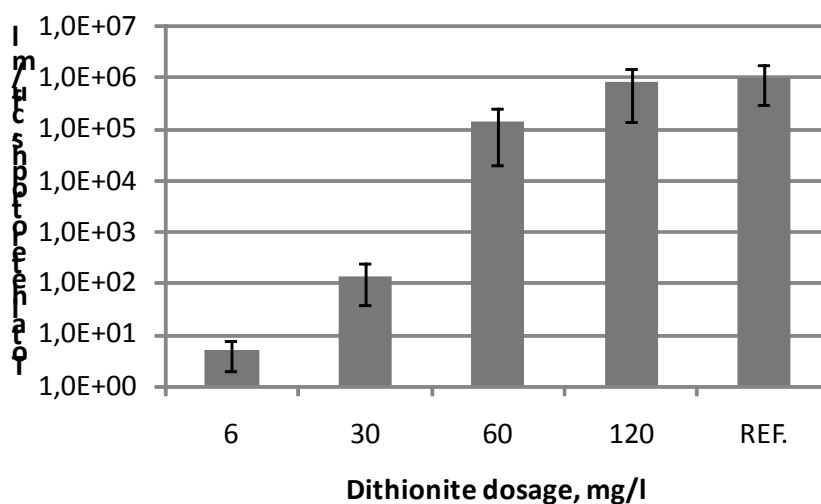


Fig. 5. Effect of dithionite on the biocidal efficiency against aerobic bacteria of electrochemically generated hypochlorite in a clear filtrate from a board machine. Biocide dose was 44 ppm as free active chlorine. REF = Clear filtrate without biocide treatment. Error bars represent standard deviation between three independent experiments.

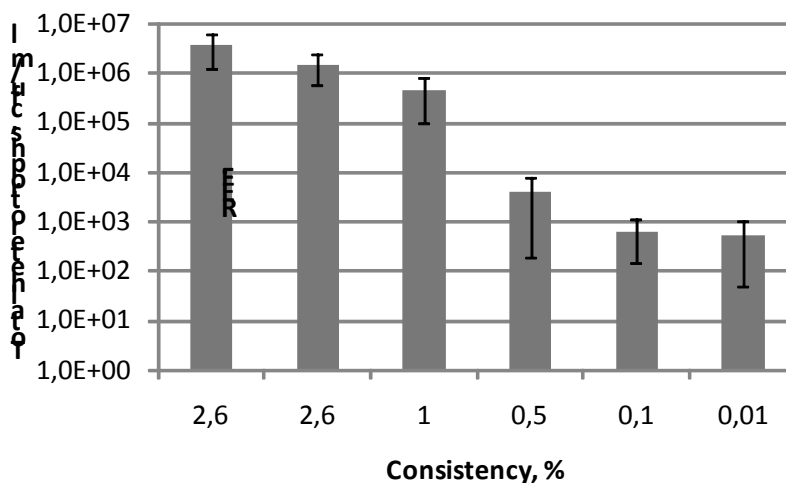


Fig. 6. Effect of fiber consistency on biocide performance. All samples were treated with 44 ppm (free active chlorine) biocide. Consistency was adjusted by diluting machine stock with clear filtrate. REF. = Machine stock without biocide treatment. Error bars represent standard deviation between three independent experiments.

Online Monitoring of Broke Spoilage

Figure 7 illustrates the changes in the values of the chemical parameters redox potential, pH, and conductivity during the trial. The monitoring started immediately after the disintegration of the brokes and lasted approximately 70 hours. The duration of the spoilage step was approximately 50 hours, starting from the disintegration.

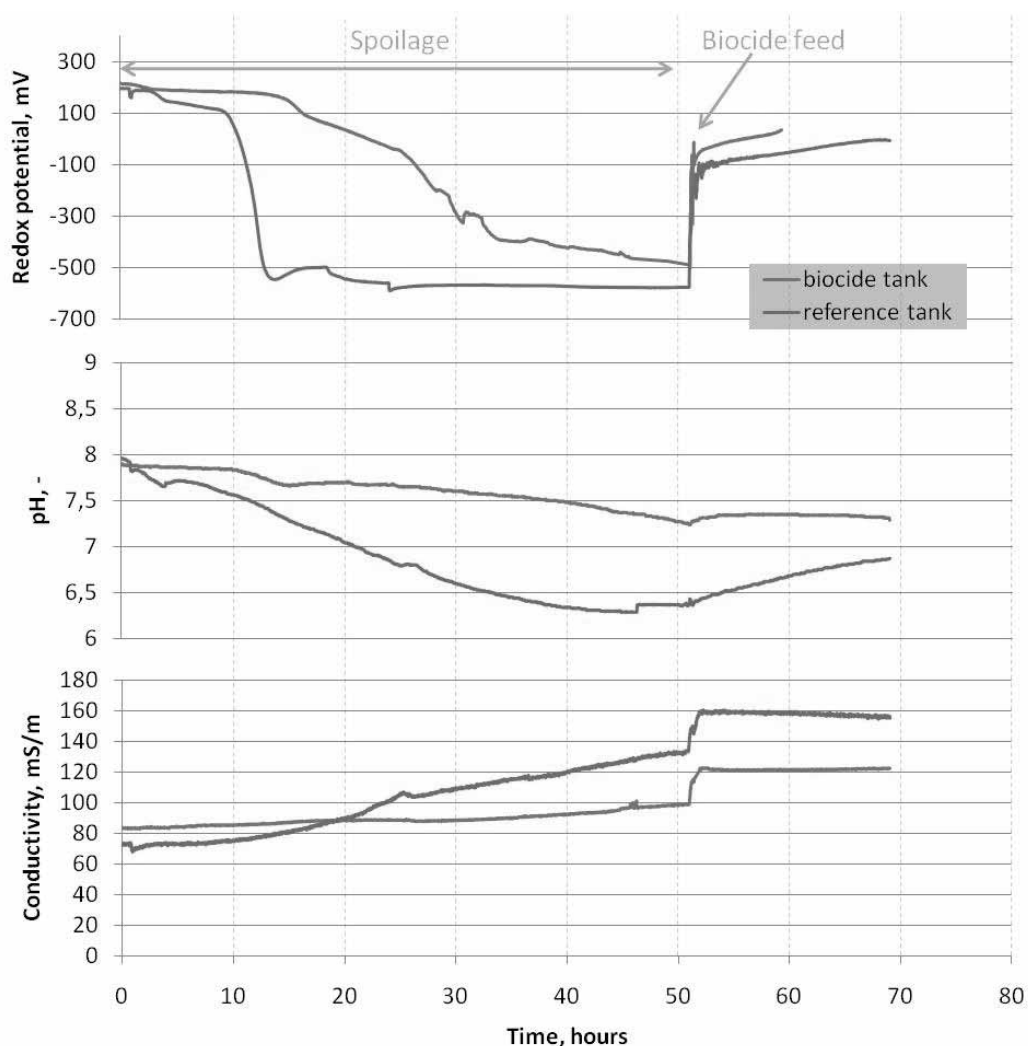


Fig. 7. Online trends from the trial in both tanks. Biocide treatment to the biocide tank was performed just before the monitoring started. Biocide treatments to both tanks were performed after the spoilage period (approximately 50 hours after disintegration of the brokes).

Just after the disintegration both brokes had identical pH and redox potential values. The biocide did not have an effect on those parameters when it is added, but it effectively inhibited growth of microbes. The difference in initial conductivities can be explained by NaCl addition with the biocide. The pH increased slightly when the biocide was added after the spoilage. The pH of the biocide was adjusted to 7.8, which was the original pH of the broke before the spoilage. An increase in conductivity due to NaCl in biocide can also be seen in the figure.

The redox potential started to decrease heavily after five-hour spoilage, reaching the lowest reading in ten hours. This change was accompanied with a reduction in the pH level due to acid formation. 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. Based on these chemical measurements, we

can conclude that treatment with electrochemically generated biocide significantly inhibited microbial activity.

Implication of Pulp Deterioration and Biocides on Wet End Chemistry

Stable conditions in the wet end of paper machines are necessary for good runnability and product quality. It is especially important to prevent chemical variations, which easily lead to uncontrollable agglomeration and which may further cause deposits, breaks, poor formation, etc. The role of biocides in this matrix is twofold: They are added to the system to prevent microbial growth. Besides well known problems such as an odor and end product contamination caused by microbial growth, chemical variations at wet end are of high importance. 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.

In our trial acid formation due to microbial growth in the reference tank resulted in notable pH reduction. This led to dissolution of CaCO_3 , which increased conductivity. Biocide addition at earlier stage prevented massive bacterial growth and, thus, acid accumulation was also prevented at least for 50 h. A few chemical measurements that were done in the laboratory also clearly highlighted this phenomenon (Table 1).

Table 1. Laboratory Analysis Performed on the Broke Samples

	Disintegrated broke	Spoiled broke	Biocide treated broke exit flow	Biocide treated broke in broke tower
Dilution water with biocide				
Dissoved calcium, mg/L	30	47	53	62
Adsorbable organic halogen, mg/L	1,3	0,9	2.1	2.2
Colloidal charge, $\mu\text{eqv/L}$	-215	-196	-176	-175
Total organic carbon, mg/L	68	82	88	100
pH	8,0	7.3	7.3	7.1
Conductivity, mS/m	72	84	106	118
Zeta potential, mV	-22	-19	-16	-18
Reference without biocide				
Dissoved calcium, mg/L	23	150	160	180
Adsorbable organic halogen, mg/L	0.5	0.6	1.7	1.8
Colloidal charge, $\mu\text{eqv/L}$	-244	-138	-142	-137
Total organic carbon, mg/L	71	220	220	240
pH	8.0	6.6	6.5	6.3
Conductivity, mS/m	49	112	126	140
Zeta potential, mV	-29	-27	-23	-22

Electrochemically generated biocide did not have an instant effect on the amount of total organic carbon (TOC). The TOC levels in both broke tanks at the beginning of the trial were almost the same. In this study the sample was filtered before the TOC measurement, and therefore the reading describes the amount of dissolved organic carbon. The level of TOC in the reference tank increased notably during broke spoilage period and remained twice higher than in the biocide tank throughout of whole trial. Since there was no difference between tanks except for biocide treatment, this was attributed to volatile acid accumulation due to microbial growth. Thus, the level of TOC may be a good indicator, even though indirect, of microbial metabolite accumulation.

Adsorbable organic halogen compounds (AOX) are a sensitive indicator of the dosage of halogen containing electrochemically generated biocides. AOX compounds are also stable and do not disappear as a function of time. Electrochemically generated hypochlorite treatment increased AOX level of the broke. AOX level of the biocide broke was constantly higher compared to the reference broke (without initial biocide addition). Further biocide treatments of broke increased the AOX equally in both tanks.

Biocide in this study was generated from brine solutions. Because all the salt did not react in the electrolysis cell, the final product contains salt. Brine solution used for electrolysis contained 8 g/L NaCl. When 2% of biocide was added to the process, it equals 160 mg/L of NaCl addition. Based on equivalent conductivities and ion concentrations this amount of salt added, contributed to approximately 28mS/m conductivity increase. Conductivity increase was caused equally by sodium and chlorine ions (Vanysek 2008). In papermaking these free anions and cations have a significant role. The functioning of most of the wet end chemicals is based, at least partly, on charge (eg. retention aids, fixatives, starch). Charge and conductivity are coupled, and thus any changes in conductivity may cause problems. The addition of salt to the process might lead to increased agglomeration or to problems with retention. Changes in conductivity must be taken into account when selecting the chemicals for optimal process operations.

Biocides eliminate acid-forming microbes that reduce the pH, and they therefore prevent calcium carbonate from dissolving. Sodium from the electrochemically generated hypochlorite is far less harmful than calcium, which dominates when no biocide is present. After the disintegration stage, sodium from the biocide treatment increased the conductivity of the treated broke. But the large increase in calcium content caused by the pH drop turned the situation upside down during the spoilage. After 50 hours spoilage conductivity of the reference broke was significantly higher (Fig. 8). Considering calcium to be more harmful than sodium, it is clear that electrochemically generated biocides have significant advantages, not only for the microbiology, but also for the chemistry. The biocide addition contributed to an increase of 23 mS/m in conductivity, and all of this was caused by NaCl (a 2% biocide addition introduced 160 mg/l salt to the broke tower). But the effect of not adding biocide resulted to 63 mS/m higher conductivity indirectly, most of which was caused by the dissolution of CaCO₃. Experimental results are perfectly in line with theoretical calculations (Vanysek 2008). Another factor is the amount of Cl⁻ ions entering the process. These ions might be harmful and cause corrosion. This is always a matter specific to the process and must be considered case by case.

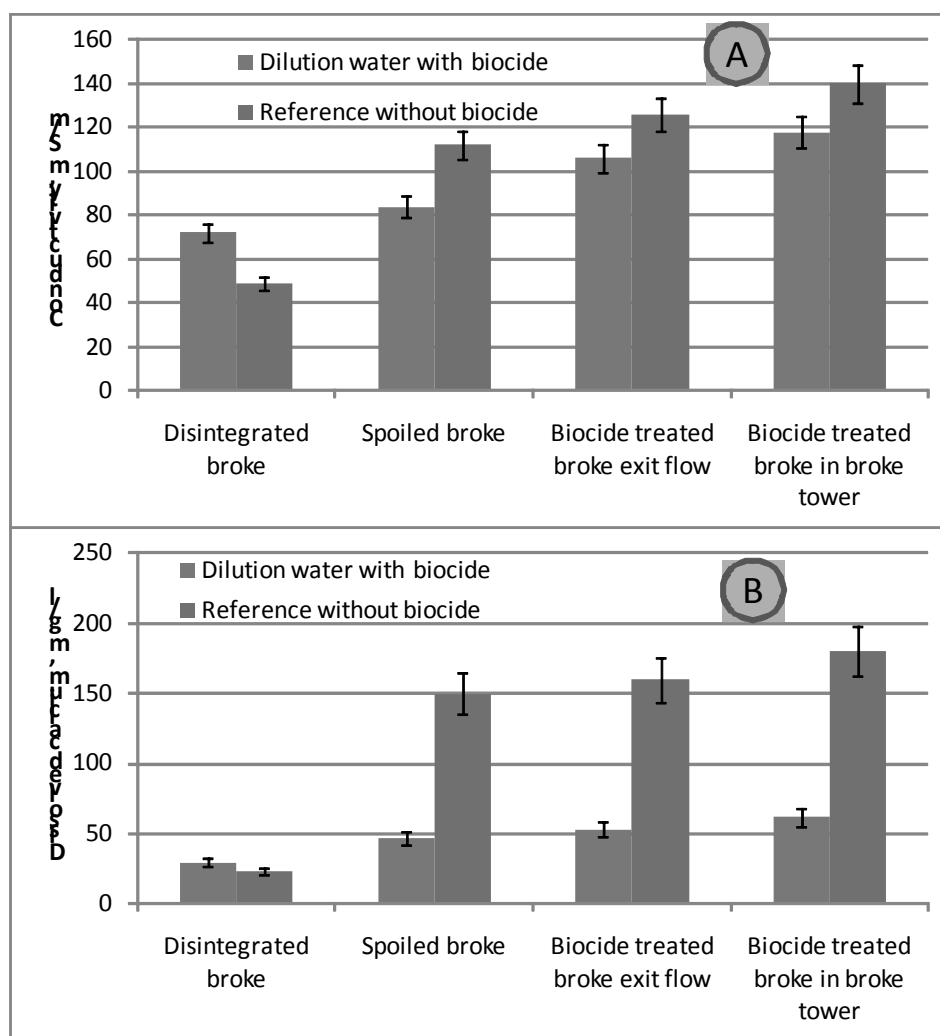


Fig. 8. Conductivity (A) and the amount of dissolved calcium (B) in broke samples

The stabilizing effect mentioned above was also seen in the colloidal charge values. The effect of the pH and the conductivity was seen as a more stable charge. The more stable charge can be explained by the increase in cationic demand (the charge becomes more negative) along with the pH, because the carboxylic groups (in this case mostly in carboxyl latex) easily deprotonate in an aqueous solution and give an anionic charge to the particles (Holmberg 1999). This was seen during a long spoilage from the disintegration to the spoilage step. The pH of the reference broke decreased and the latex particles became less anionic. The effect was not so obvious in the biocide-treated tank; because the pH drop was not as high as in the reference broke.

Effect of broke spoilage and biocides on sheet properties

Either the biocide dose itself or the effect of the biocide on the microbial growth had little impact on the sheet properties. Most of the properties were unchanged, within the confidence limits. There was basically no difference between most of the strength properties. Properties of the laboratory sheets are presented in Table 2.

Table 2. Properties of the Laboratory Sheets Prepared from the Broke Samples

	Broke stored with biocide		Broke stored without biocide	
	Disintegrated broke	Biocide treated broke in broke tower	Disintegrated broke	Biocide treated broke in broke tower
Grammage, g/m ²	65.7 ± 3.3	64.2 ± 3.2	65.8 ± 3.3	63.5 ± 3.2
ISO-brightness, %	89.4 ± 0.0	89.7 ± 0.0	88.3 ± 0.0	89.1 ± 0.1
Tensile index, Nm/g	40.2 ± 4.1	35.7 ± 3.7	42.8 ± 1.8	31.0 ± 3.5
Tear index, mNm ² /g	6.48 ± 0.24	6.85 ± 0.37	6.85 ± 0.24	7.10 ± 0.79
Zero-span tensile index, dry, Nm/g	111.5 ± 11.4	106.4 ± 10.0	111.0 ± 4.7	106.5 ± 12.0
Ash content, 525°C, %	25.39 ± 0.32	24.30 ± 0.10	24.56 ± 0.49	24.46 ± 0.30
Ash content, 900°C, %	16.55 ± 0.26	16.06 ± 0.11	15.99 ± 0.05	16.08 ± 0.05

Electrochemically generated hypochlorite had a bleaching effect, and that was apparent as an ISO brightness increase of approximately 1 unit. The increase was seen in disintegration when broke with biocide was compared with the broke without biocide in the disintegration phase. The same difference remained throughout the trial. Biocide addition to spoiled broke further increased ISO brightness.

A long spoilage of broke decreased its brightness, but the biocide treatments after spoilage were able to increase the brightness back to its original level or even slightly higher. The brightness of the biocide pulp was at the same level after 2 days of spoilage as the brightness of the reference broke just after the disintegration. In addition to the biocidal effect on microbes, it also resulted in a slightly higher brightness in the end product. We did not observe any differences in strength properties due to spoilage of broke or biocide usage.

CONCLUSIONS

1. Electrochemically generated biocides have been shown to be an effective way to control microbial problems at a paper mill. 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.
2. The presence of reducing compounds may cause limitations to the use of these oxidative biocides. In such cases, biocide programs should be based on their use in combination with non-oxidizing biocides. As an example, non-oxidative biocides could be used in reducing environments, while oxidative biocides could be added to fresh waters and water circulations.

3. Electrochemically generated biocides can be used for improving the broke usage. The application improves the quality of spoiled broke and/or prevents broke spoilage. The improved broke quality increases the stability of the paper/board machine and, consequently, results in less broke.
4. Electrochemically formed biocides are most efficient when they are used for treating relatively clear waters such as filtrates, shower water, or fresh water. The efficiency decreases when the solids content increases. This does not exclude usability, but the dose must be increased. It was shown that electrochemically generated biocides are also effective against bacterial spores.
5. For papermakers, this work 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.

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