Scientific Paper

Study of the Influence of Dissolved and Colloidal Components on Paper Sizing by Simulation of Process Water Loop Closure

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Abstract

Simulation of process water loop closure in a papermaking system was performed on laboratory scale by means of the Rapid-Köthen sheet former. The concentrations of sulphate and dissolved inorganic ions, expressed as conductivity, as well as the concentration of dispersed rosin size Sacoccel 309 were systematically measured during the process. The influence of increasing concentrations on paper sizing efficiency was the main objective of our research. Therefore, we determined the highest degree of water closure at which the examined dissolved and dispersed components do not negatively interfere with the paper sizing process yet.

Key words: paper sizing, water loop closure, simulation

Introduction

In paper industry, water is used for the preparation of fiber suspensions and chemicals, their transportation to the sieves of paper machine, as well as for cleaning purposes and energy transfer.[1,2] In addition, it has a major role in forming bonds between pulp fibers.[3] During the past years, fresh water consumption has strongly decreased owing to economical and ecological reasons such as higher costs of fresh water, loss of process substances and strict environmental legislation.

Water systems can be closed to various extents. In completely open systems, only fresh water is used, whereas in closed loops all water is recycled. Thus, there are practically no effluents, and minimal fresh water consumption serves only as compensation for the loss in drying section of the paper machine.[4]

Process water reuse has economical and ecological benefits, yet on the other hand, it can cause technical problems. The most serious disadvantages are increased concentrations of dissolved and colloidal compounds, the rise of water temperature, intensified microbiological activity and corrosion. All the mentioned phenomena affect the system, and they have to be evaluated for each case separately.[5]

Paper properties may significantly change due to the water closure process. Any quality reduction should be predicted, which is partly possible by simulating real systems with experiments on a laboratory level. The results obtained help paper mills cut down fresh water consumption without significantly changing the paper properties.

The simulation of paper machine wet end process can be efficiently performed by appropriate tests on a laboratory sheet former. Although it works discontinuously in contrast to the industrial paper machine, the acquired results are often a good prediction of the real situation.

Paper sheets are formed on the laboratory sheet former by applying different pulp suspensions and process chemicals. Either fresh water or process water can be applied for paper sheet formation. In both cases, the whole amount of water may be reused during the experiment, meaning that the system approaches or reaches zero effluent conditions. Paper properties and process water quality can be monitored throughout this test in order to evaluate the influence of decreasing fresh water consumption on paper properties. In reality, it is very important to maintain constant paper quality despite the changes in technological conditions.

One of the most important characteristics of printing paper is the degree of sizing. The main purpose of paper sizing is to protect the surface of paper fibers against the penetration of water and printing inks. This can be achieved by internal sizing during which size is added to paper suspension, as well as by surface sizing, during which size is applied directly to paper surface. The negative charges of paper fibers and rosin size make sizing impossible if no positively charged ions are added. Fibers and rosin size are bound by means of aluminium ions from aluminium sulphate.[6]

Laboratory simulation was conducted to determine the influence of water closure on paper sizing. The main objectives of our research were to determine the

Table 1. Plan of the experiments.

Experiment number	1	2	3
Conc. of suspension (g/L)	15	10	15
Water used for dilution	PW* from paper mill	PW from paper mill	PW from paper mill
Water in the tank at the beginning of the experiment (V=10L)	PW from paper mill	⅞ PW from experiment 1, ⅛ PW from paper mill	¾ PW from experiment 2, ¼ PW from paper mill
Number of cycles	45	90	90

PW...process water.

dependence of paper sizing on increasing concentrations of chosen parameters in process water, and to evaluate the degree of process water loop closure at which dissolved components do not interfere with paper sizing yet.

Experimental

STOCK PREPARATION

Paper sheets were formed on a laboratory level according to the ISO 5269-1 standard procedure. The following raw materials were applied: fresh chemical pulp fibers of 3.5% consistency, kaolin, Sacoccel 309 rosin size, aluminium sulphate, cationic starch and retention aid. Process water and all chemicals were obtained from a paper mill producing high quality printing paper.

Fibers were diluted with industrial process water in a mixing vessel to a desired consistency of 1 or 1.5%. Chemicals were added to fiber suspension in the same sequence as in the paper mill, first kaolin and then Sacoccel 309 rosin size. Retention aid, aluminium sulphate and cationic starch were added during paper formation directly into the sheet former.

SIMULATION OF PROCESS WATER LOOP CLOSURE

Process water loop closure simulation was accomplished on the Rapid-Köthen laboratory sheet former (Figure 1).

Figure 1. Rapid-Köthen sheet former.

The Rapid-Köthen sheet former is designed to allow production of laboratory made hand-sheets. The sheet-forming cycle can be operated completely automatically using one of the pre-set programmes. Either fresh or process water can be selected for the experiments. In our case, process water from the paper mill was chosen because it enables better simulation of water closure. Since the sheet former works in cycles, one cycle is needed to form one sheet.

The sheet-forming cycle starts by process water being poured from the water tank into the former, during which fibers and chemicals are added. Compressed air is used for the agitation of diluted stock. The next stage of the sheet-forming cycle is dewatering. The vacuum pump is designed to suck process water through the wire. Process water is returned to the water tank and reused for paper formation in the next cycle. The formed hand-sheet is removed from the sieve by means of a carrier board and is subsequently being put into the dryer.

Water loop closures result in a decrease of specific fresh water consumption which is defined as fresh water consumption in m^3/t of formed paper. The consumption of fresh water for the preparation of chemicals needs to be taken into consideration as well. The volume of fresh water in the tank at the beginning of the experiment is based on an estimation from the paper mill and includes all fresh water consumed in the process with the exception of fresh water used for the preparation of chemicals.[7]

The equation for specific fresh water consumption on the former can be described as:

$$spec.\ comsumption\ of\ \ FW(\tfrac{m^3}{t}) = \frac{V + n \cdot V_s}{n \cdot m_a}$$

In the equation, V is the volume of fresh water in the former at the beginning of the experiment, n is the number of cycles, V_s is the volume of fresh water in fibers and m_a is the average weight of paper sheets.

According to the equation, the specific consumption of fresh water depends only on fresh water in the tank at the beginning of the experiment, and on the number of cycles.

Three experiments were conducted (Table 1). Process water from the paper mill was used for fiber

dilution. Chemicals were prepared with fresh water. Paper basis weights, which are defined as mass of paper on square meter of paper, and concentrations of chemicals were the same in all tests.

In the first experiment, 10 L of process water from the paper mill was poured into the water tank. In the following two experiments, the water from the previous experiment was reused for paper formation. Thus, the consumption of fresh water decreased while the level of water loop closure increased.

45-90 cycles were conducted in each experiment. Hand sheets and process water were sampled for analyses after 5 or 10 cycles. All hand sheets were preconditioned at 23 °C and 50% relative humidity.

WATER AND PAPER ANALYSES

Conductivity was measured with the Tetracom 325 conductivity cell (WTW pH 537pH-meter).

The concentrations of sulphate ions were determined on the METROHM 761 compact ion chromatograph, using the Metrosep Anion Dual 2 column. The mobile phase was composed of a mixture of 2.0 mmol $NaHCO_3$, 1.8 mmol $Na_2CO_3 \times 10\ H_2O$ and 15% acetone. The suppressor solution was 50 mmol H_2SO_4. The flow of the mobile phase was 0.8 mL/min and the volume of the injected sample was 20 μL. A conductivity detector was applied. Concentrations were calculated from the calibration curve of standard sulphate solutions.

The concentration of rosin size in process water was measured on the HP 5890 gas chromatograph. Rosin size was isolated from water by solid phase extraction on the BAKER SPE 12GV extraction apparatus. The BOND ELUT-AL-N (Varian) 3 mL extraction cartridges were used. The aqueous sample was acidified and 50 mL eluted through the column. For extraction, 2 mL of CH_2Cl_2 was used. The methylenchloride extract containing rosin size was subsequently methylated by gaseous diazomethane which was synthesized in a reaction between N-methyl-N-nitroso-4-toluenesulfonamide and 50% potassium hydroxide. 2 g of N-methyl-N-nitroso-4-toluenesulfonamide (diazald) was dissolved in a mixture of diethyl ether (6 mL) and diethylenglycolmonoethylether (4 mL). 1 mL of 50% KOH solution in water was poured into a 4 mL reaction vial equipped with a small magnet and capped with septum through which a capillary was inserted. 1 mL of diazald solution was added to the same reaction vial. Diazomethane produced during stirring on a phase border between the two solutions was introduced through the capillary into another reaction vessel containing a sample solution. The end of methylation was expressed by yellow colour indicating excessive diazomethane. The methylated sample was concentrated to exactly 0.2 mL and analysed by gas chromatography at the following experimental conditions: capillary column SPB 1 (15 m), injector temp. 250 °C, split ratio 1:15, init. oven temp. 200 °C (2 min), heating rate 3 °/min, final oven temp. 300 °C (10 min), det. FID temp.300 °C, N_2 flow 1.5 mL/min.

Typically, the GC chromatogram was composed of two peaks representing methyl esters of dehydroabietic (DA) and abietic acids (A) being the active compounds of the sizing agent and as such responsible for sizing reaction. The two peaks were integrated and their concentration calculated from the calibration curve. Calibration was performed by applying the following concentrations of a standard acid mixture (DA : A – 75 : 25) in CH_2Cl_2: 0.05; 0.1; 0.25; 0.5; 0.75 and 1.0 mg/mL. The weight ratio of dehydroabietic and abietic acids was 75 : 25 in the sizing agent as well as in all water samples. The calibration graph was prepared by plotting the sum of the two standard peak areas against concentration. It is presented by the equation and correlation coefficient ($y = 7E+06x + 123920$; $R^2 = 0.9985$). All chromatographic determinations were performed in 3 parallels.

The $Cobb_{60}$ test was used for paper sizing evaluation. The result of the test is $Cobb_{60}$ value defined as the amount of water absorbed into 1 m^2 of paper surface in 60 seconds. Obviously, higher $Cobb_{60}$ values indicate worse paper sizing. The $Cobb_{60}$ test is particularly suitable for measuring medium sized paper ($Cobb_{60}$ values 28-65 g/m^2).[8]

Results and discussion

The specific consumption of fresh water decreased with increasing cycle numbers (Figure 2). Depending on the experiment, curves have approached the limiting values which are defined by fresh water in the tank at the beginning of a particular experiment. The amount of fresh water in process water at the beginning of the tests was estimated in the paper mill.

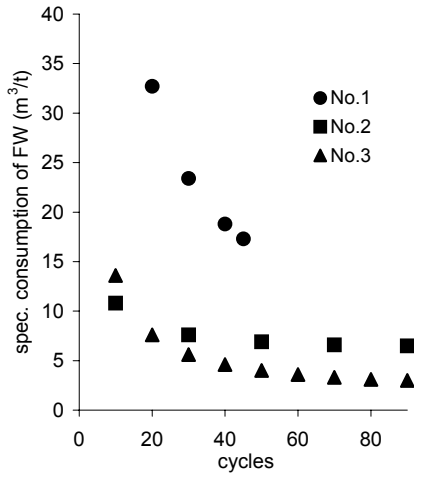

Figure 2. Specific fresh water consumption in dependency on cycle numbers in the three experiments.

Table 2. Results of water and paper analyses.

Experiment number	Spec.cons.of FW (m^3/t)	Sulphate (mg/L)	Conductivity (μS/cm)	Rosin size (mg/L)	$Cobb_{60}$ (g/m^2)
1	60.4	26.9	778	–	28.3
	32.7	28.3	787	–	30.2
	23.4	29.4	790	–	29.7
	18.8	31.1	806	–	32.8
2	10.8	30.8	848	0.75	31.2
	7.6	32.4	918	0.79	33.2
	6.9	33.2	972	–	36.8
	6.6	36.1	1011	1.68	37.8
	6.5	37.1	1043	2.34	38.5
3	13.7	35.6	969	–	27.3
	7.6	36.3	976	–	33.9
	5.6	36.9	980	1.49	32.3
	4.6	37.7	989	–	42.8
	4.0	37.9	997	1.78	37.7
	3.6	38.3	1008	–	44.0
	3.3	38.7	1020	2.48	45.9
	3.1	39.2	1035	–	44.2
	2.9	39.3	1044	3.07	49.6

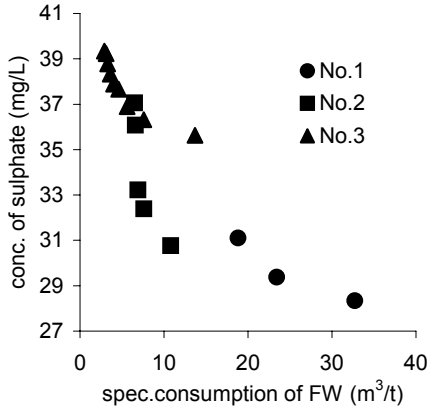

Figure 3. Dependence of sulphate conc. to specific fresh water consumption.

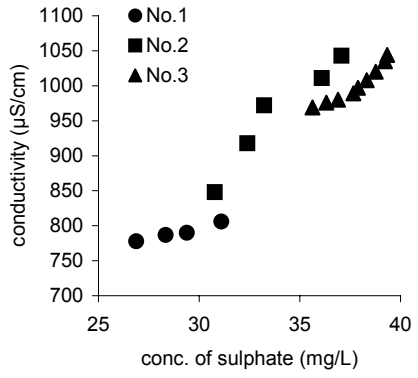

Figure 4. Dependence of conductivity to the concentration of sulphate.

As a result of water loop closure, the concentrations of sulphate ions and rosin size (Sacoccel 309), which entered the process as papermaking chemicals increased. Due to the accumulation of inorganic ions in process water (Table 2), conductivity increased as well.

The concentrations of measured components strongly increased when the limiting values of specific fresh water consumption were reached. The limiting values were specific for each component, which is most likely connected to the equilibrium between the concentrations of individual components in process water and in paper. A strong gradual increase in sulphate concentrations was noticed when the level of fresh water consumption was lower than 15 m^3/t. Presumably the constant bonding of components in paper structure which resulted in accumulation of sulphate ions in process water (Figure 3) occurred at the attained equilibrium when the above-mentioned values were reached. The accumulation of sulphate ions as the main inorganic species, caused an increase of conductivity (Figure 4).

$Cobb_{60}$ values that characterize paper sizing were relatively constant at above 15 m^3/t of specific fresh water consumption (Figure 5). Below this value, paper sizing was less efficient. A substantial increase of $Cobb_{60}$ values was noticed under 7 m^3/t of specific fresh water consumption.

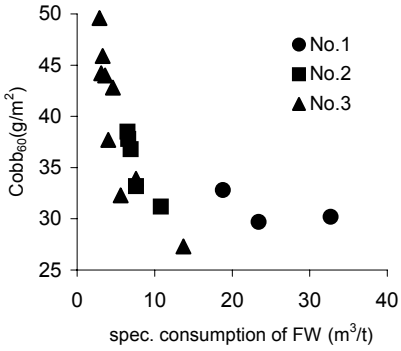

Figure 5. Dependence of $Cobb_{60}$ values to specific fresh water consumption.

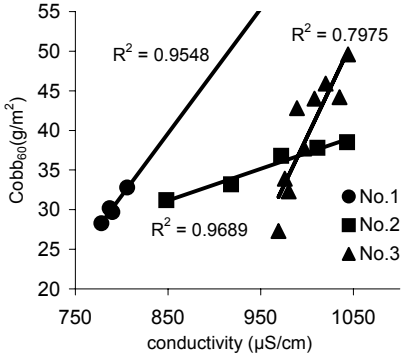

Figure 6. $Cobb_{60}$ values in dependence to the conductivity of water.

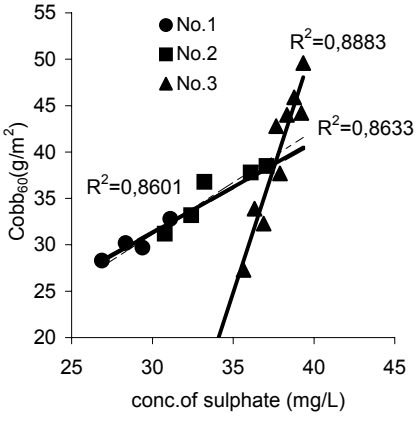

Figure 7. $Cobb_{60}$ values in dependence to the sulphate ions concentration in water.

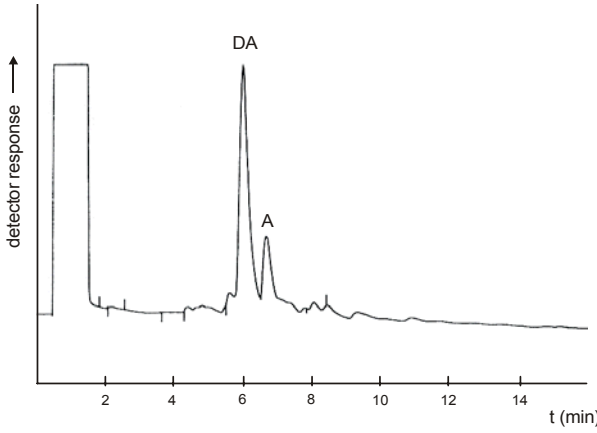

Figure 8. Gas chromatogram of extracted water sample (DA – dehydroabietic acid, A – abietic acid).

Paper sizing is not influenced only by temperature, pulp quality and refining procedures but also by the presence of dissolved ions. Above all, higher concentrations of inorganic ions deteriorate paper sizing. Both fibers and rosin size are negatively charged, while aluminium ions from aluminium sulphate are positively charged and serve as a connection between both negative components. Anions such as sulphate easily react with aluminium to form aluminium salts and thus decrease its positive charge. Cations can precipitate with negatively charged rosin size, which results in a reduced efficiency of paper sizing[9]. During the tests, $Cobb_{60}$ values of paper increased with the corresponding concentrations of sulphate ions and conductivity of water samples. Figures 6 and 7 clearly indicate a trend of linear dependency between conductivity, sulphate ions accumulation in water and paper sizing efficiency.

A characteristic chromatogram of rosin size from the extracted water sample is presented in Figure 8.

The concentration of rosin size in process water increased during the ongoing process of water closure. Typically, the higher the concentration of rosin size in process water, the greater were $Cobb_{60}$ values. The analysis of process water loop closure is mostly

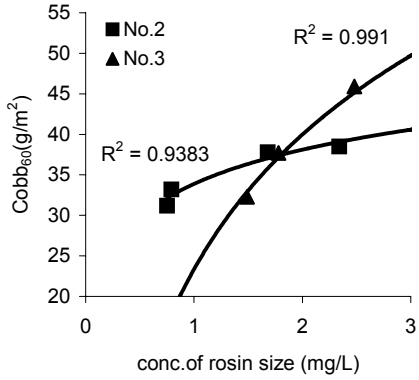

Figure 9. $Cobb_{60}$ values in dependence to rosin size concentrations in process water.

based on mass balances and equilibrium data, and may be used where equilibrium data is noted. In the case of rosin size, the equilibrium data is difficult to determine. For this reason, these phenomena may also be caused by the decrease of reactivity of rosin size adsorbed on paper after a higher number of cycles. Established logarithmic dependency between $Cobb_{60}$ values (Figure 9) and the concentration of rosin size in process water occurred repeatedly.

Conclusions

The laboratory experiment results indicate that the influence of water closure on paper sizing is negligible at values higher than 7 m^3/t of specific fresh water consumption. Paper sizing deteriorates below the specified limiting values.

$Cobb_{60}$ values increase almost linearly with the accumulation of sulphate ions and logarithmically with rosin size concentration in process water. One of the possible solutions to the problem is the surface sizing of paper, which increases the efficiency of paper sizing and prevents further pollution of process water. Excessive concentrations of anionic species are detrimental since they easily promote formation of insoluble, sticky deposits on paper machine equipment. In addition, they initiate corrosion. Long-term solutions can be found in removing components from process water or in changing the process chemicals.

Regarding the acquired and expected results, the Rapid-Köthen laboratory sheet former proves to be an appropriate tool for simulation and research of the influence of water loop closure on paper sizing and can therefore be used for similar purposes in the future.

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Povzetek

Na laboratorijskem oblikovalniku je bila izvedena simulacija zapiranja krogotokov procesne vode v papirni industriji. Zaradi zapiranja je pričela koncentracija sulfatnih in drugih ionov (izražena kot prevodnost) ter klejiva v procesni vodi naraščati. Glavni namen raziskave je bil ugotoviti, kako naraščajoče koncentracije komponent vplivajo na učinkovitost klejenja papirja in do katere meje je mogoče krogotok procesne vode v preiskovanem sistemu zapreti, da bo vpliv spremljanih komponent v procesni vodi na učinkovitost klejenja papirja še zanemarljiv.