DISPLACEMENT WASHING OF KRAFT PULP WITH AQUEOUS SOLUTIONS OF SURFACTANTS

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The aim of this work was to investigate the effect of the addition of surfactants to the wash liquid on the washing efficiency during displacement of black liquor from the fibre bed of unbleached kraft pulp. Aqueous solutions of two non-ionic surfactants and an anionic one were used. For comparison, distilled water was also used as wash liquid. Laboratory displacement washing experiments were performed in a cylindrical glass cell. A step change response method was chosen to describe the displacement of black liquor. The breakthrough curves were measured for alkali lignin using ultraviolet spectrophotometry. The flow of the wash liquid through a pulp bed was described by the dispersion model involving one dimensionless parameter known as the Péclet number. In order to characterize the displacement washing efficiency with aqueous solutions of surfactants, not only was the wash yield correlated with the Péclet number, but also a new dimensionless criterion involving intrinsic properties of aqueous solutions was derived.

Keywords: kraft pulp, displacement washing, surfactants

INTRODUCTION

Surfactants (the abbreviation of surface action agents) have been used in the various processes involved in the pulp and paper industry, *e.g.*, at first as a part of the sizing agents in the paper manufacture.

Over the past three decades, new surfactant-based digester additives have been developed to help mills realize such improvements to their pulping, bleaching and recovery operations. Adding surfactant-based digester additives reduces the surface tension between the liquor and the wood, allowing a more thorough wetting of the chip surface and thereby facilitating penetration of the cooking liquor into the inner matrices of the wood. The use of surfactant-based digester additives can provide a number of benefits, resulting in increased yield, reduced rejects, reduced kappa number, improved brownstock washing, etc.[1]

Thus, surfactants can influence wood impregnation by modifying the surface properties of wood and liquor, by removing resins, or by a combination of both. Chen *et al*.[2] focused on the influence of surfactants upon the rate of kraft liquor penetration into chips. It was found out that the amount and chemical composition of extractives play an important role in the efficiency of surfactants, which were more effective with highly resinous wood.

Mixtures of surfactants have been also examined as additives to hardwood kraft pulping. The kappa number of kraft pulp, the charge of active alkali, the amount of rejects and pitch in pulp significantly decreased. Under laboratory conditions, the pulp washing efficiency was also increased.[3]

The colloidal pitch substances are another very important problem that is solved with the use of surfactant solutions. Pitch is extracted from wood *via* the action of pulp production chemicals, heat and mechanical stress. However, it seems that mill water closure together with the growth of production and qualitative requirements has lately increased the need for pitch prevention in mechanical pulp and softwood sulfate pulp processes.[4]

Applying surfactants, an improved deresination during oxygen delignification stage in kraft pulping of aspen, birch and some tropical hardwoods was found by Allen *et al*.[5] The first laboratory experiments showed that the addition of a linear alcohol ethoxylate led to the decrease of the extractives by an additional 11% during oxygen delignification and subsequent washing. However, selected linear alcohols ethoxylate blends tested later provided an additional 30% reduction in extractives over oxygen delignification alone, for a total of 69% extractives reduction relative to the initial pulp before oxygen delignification and washing.

Surfactants also play a key role in paper de-inking, promoting ink detachment from cellulose fibres and separation of dispersed ink particles from pulped waste paper. Alcohol ethoxylates and alkylphenol ethoxylates are commonly used in wash de-inking whereas alcohol alkoxylates and fatty acid alkoxylates are commonly used in flotation de-inking and combined flotation/wash de-inking processes.[6]

In the paper of Zhao *et al*.,[7] positive and negative effects of surfactants on the flotation deinking process are mentioned. Although surfactants play important roles in de-inking, they can also have some adverse effects on ink removal, fibre quality, and water reuse. For example, the adsorption of dispersant and frother on fibre surfaces may reduce interfibre bonding and create foaming problems in paper machines.

Moreover, surfactants from a commercial chemical supplier are often blends of many different functional surface and non-surface active agents, therefore, their effect on pulp and paper properties is not unambiguous. For example, the addition of commercial washing liquid *Lenor*, containing surfactants, decreased the retention of fines, which was reflected in the lower tensile strength of the paper.[8]

The main aim of our paper was to investigate the effect of the addition of non-ionic and anionic surfactants to the wash water on the washing efficiency during the displacement of black liquor from the fibre bed of unbleached kraft pulp.

EXPERIMENTAL

Displacement washing experiments simulated under laboratory conditions were performed in a cylindrical glass cell with an inner diameter of 35 mm, under constant bed height of 30 mm. The fibre pulp bed occupied the volume between the permeable septum and a piston, covered with 45 mesh screens to prevent fibre loss from the bed.

Pulp beds were formed from a dilute suspension of unbeaten unbleached kraft pulp in black liquor. The pulp was obtained from a blend of softwoods containing approximately ¾ of spruce and ¼ of pine. After compressing to the desired thickness of 30 mm, the consistency, *i.e.* mass concentration of moisture-free pulp fibres in the bed varied within the limits from 11 to 14%. In order to characterise the pulp fibres used in the experiments, the physical properties of kraft pulp were determined. The Schopper-Riegler freeness had a value of 13 ^{o}SR. The degree of delignification of the pulp was expressed by a kappa number of about 27. Using the Kajaani FS-100 instrument, the mean length of the fibres was also measured. The weighted average length was of 2.56 mm, while the numerical average length was of 1.48 mm. The specific surface of fibres having a coarseness of 0.176 mg m^{-1} was of $2.67{\cdot}10^5$ m^{-1}.

Distilled water and aqueous solutions of three non-ionic and anionic surfactants were used as wash liquids. Two non-ionic surfactants DEZ 10 and MIX 7 were prepared by the condensation of aliphatic alcohol C12–C18, from 3 to 25 moles of ethylene oxide.[9] The anionic surfactant SPOLAPON AES 242/70 (thereinafter SPOLAPON 242) produced by ENASPOL is a technical grade of sodium linear alkyl ether sulphate 12÷14/2 EO (CTFA/INCI: Sodium Laureth-2 Sulphate) $R\text{-}(\text{-}O\text{-}CH_2\text{-}CH_2\text{-})_2\text{-}O\text{-}SO_3Na$.[10] The concentration of surfactants in water solutions varied in the range from 0.05 to 2 kg m^{-3}. The density, dynamic viscosity and surface tension of all tested solutions were measured. Only the values of surface tension of the tested surfactant solutions were significantly different from those for distilled water. The dependences of surface tension on the concentration of surfactant solutions illustrated in Figure 1 show that the surface tension of the surfactant solutions decreases with increasing concentration. For comparison, the surface tension of black liquor measured at 21 °C was 39.7 mN m^{-1}.

Distilled water or wash liquids were distributed uniformly through the piston to the top of bed at the start of the washing experiment. At the same time, the displaced liquor was collected at atmospheric pressure from the bottom of the bed *via* the septum. The washing effluent was sampled at different time intervals until the effluent was colourless. Samples of the washing effluent leaving the pulp bed were analysed for alkali lignin, using an ultraviolet spectrophotometer operating at a wavelength of 295 nm. The displacement washing experiments on pulp fibres, as well as the washing equipment, were described in detail in a previous paper.[11]

RESULTS AND DISCUSSION

The quality of the displacement washing can be characterized by the wash yield. The displacement wash yield is defined as the amount of solute washed out at some wash liquor ratio divided by the total amount of solute removed during the washing period. The traditional wash yield evaluated at the wash liquor ratio equal to unity may be expressed as:

$$WY_{\mathrm{RW=1}} = \frac{\int_{\mathrm{RW=0}}^{\mathrm{RW=1}} \frac{\rho_e}{\rho_0} d(RW)}{\int_{\mathrm{RW=0}}^{\mathrm{RW\to\infty}} \frac{\rho_e}{\rho_0} d(RW)} \tag{1}$$

where ρ_e and ρ_0 are the exit and initial alkali lignin concentrations, respectively, and RW is the wash liquor ratio.

The dimensionless Péclet number is defined as

$$Pe = \frac{h\,u}{D\,\varepsilon} \tag{2}$$

where h is the thickness of the pulp bed, u is the wash liquid superficial velocity, D is the axial dispersion coefficient, and ε is the average porosity of the packed bed.

For all washing runs, the values of the Péclet number were evaluated from the displacement washing curves, which were measured as a response to the input step signal, expressed as the time dependence of the lignin concentration in the outgoing stream of liquor. Details of the experimental data analysis were reported elsewhere.[11] The Péclet number indicating a level of dispersion in the pulp bed is equal to zero when a perfect mixing exists, and approaches to infinity for perfect plug flow.

Comparing the washing curves measured for water and aqueous solutions of surfactants, it is evident that in the first falling part of the washing curve up to $t \approx 2.5$ min, when the first portions of wash liquid appear in the outlet liquor stream, the lignin concentration is lower when surfactants are present in the wash liquid (Figure 2). However, in the second falling part of the washing curve ($t >$ 2.5 min), when a leaching mechanism prevails over displacement, the lignin concentration in the outlet liquor stream is higher in the case of surfactants than in that of water. With respect to the shape of the washing curves measured for the surfactant solutions, one can suppose that the presence of surfactants may have a positive effect on wash yield in the cases when leaching will play a significant role in the washing process. The different shape of the washing curves measured for water and aqueous solutions of surfactants resulted in the various values of the Péclet number, which varied for water between 4.5 and 20.5, while in the case of surfactant solutions reached 5-8.4, 4.4-6, and 5.2-5.8 for MIX 7, DEZ 10, and SPOLAPON 242, respectively.

In Figure 3, the wash yield is plotted against the Péclet number. The experimental points measured for water are located below or along the curve derived for the bed of non-porous particles by Brenner.[12] The correlation between the wash yield and the Péclet number can be described by the equation in the form:

$$WY_{RW=1} = 0.716\, Pe^{0.0539} \tag{3}$$

with a mean relative quadratic deviation of 2.1% for the Péclet number ranging from 4.5 do 20.5.

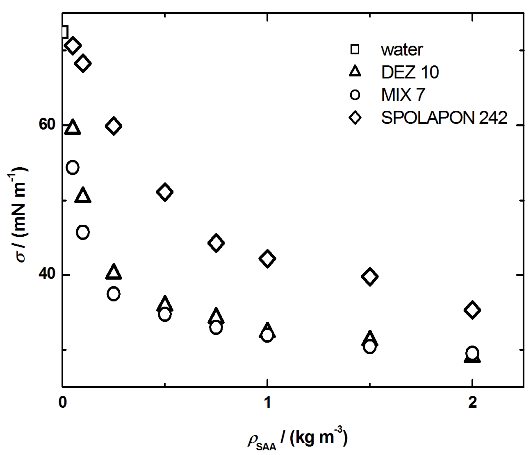

Figure 1: Surface tension at 21 °C as a function of the concentration of aqueous solutions of surfactants

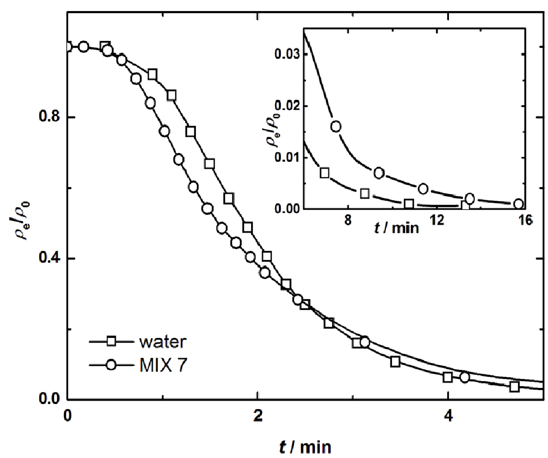

Figure 2: Displacement washing curves for water and 0.25 kg m^{-3} MIX 7 solution

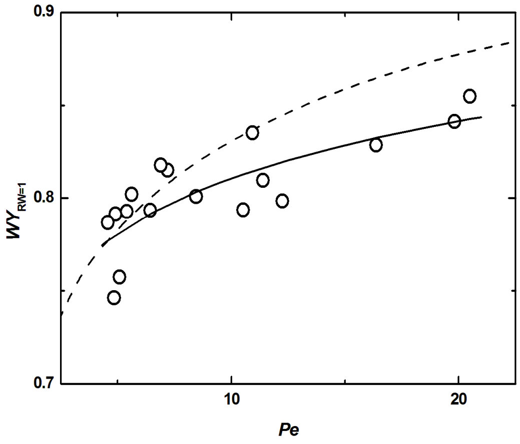

Figure 3: Wash yield for water as a function of the Péclet number. Solid line – equation (3), dashed line – calculated for non-porous particles[12]

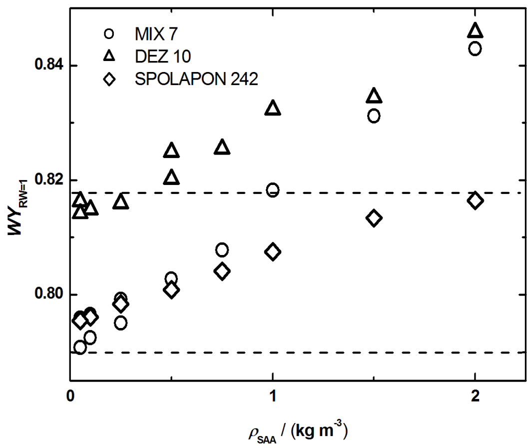

Figure 4: Wash yield as a function of the concentration of aqueous solutions of surfactants. Dashed lines – 95% confidence limits for water

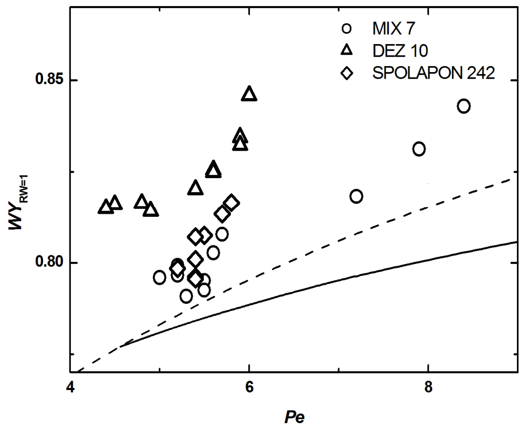

Figure 5: Wash yield as a function of the Péclet number. Solid line – Eq. (3), dashed line – calculated for non-porous particles[12]

The dependence of wash yield on the concentration of the tested wash liquids with surfactants is shown in Figure 4. The dashed lines represent 95% confidence limits for water with the lower limit equal to 0.790 and with the upper limit equal to 0.818. From Figure 4, it follows that the higher wash yield can be achieved only for aqueous surfactant solutions containing MIX 7 with a concentration above 1 g dm^{-3} and DEZ 10 with a concentration above 0.5 g dm^{-3}. However, the packed bed of the pulp fibres is a very tangled system with randomly oriented porous, compressible particles with different size, having a central cavity, known as lumen. Even if the experimental conditions were strictly identical, the bed of fibres was always different, at least, with various local porosities. Thus, the properties of pulp fibres along with their spatial configuration affect substantially the flow of wash liquid through the pulp bed and have a noticeable impact on the shape of the displacement washing curve describing lignin removal from the pulp bed.

Hence, wash yield data measured for aqueous solutions of surfactants are also illustrated as a function of the Péclet number, characterizing the shape of the washing curves (Figure 5). The correlation equation (3) derived for distilled water is located below the curve calculated for the packed bed of non-porous particles according to Brenner.[12] However, the points indicating the wash yield for aqueous solutions of all types of surfactants are located above the theoretical curve derived for non-porous particles.

If distilled water at constant temperature is used in displacement washing of pulp fibres, the wash yield may be correlated with the Péclet number only. The dimensionless Péclet number (Equation (2)) involves the bed height, the interstitial velocity of wash liquid and the axial dispersion coefficient. However, when aqueous solutions of surfactants are applied to pulp washing, then their different intrinsic properties may also influence washing efficiency. By dimensional analysis, the intrinsic properties of aqueous solutions of surfactants may be grouped into a dimensionless criterion:

$$\pi = \frac{a_V \mu^2}{\rho \sigma} \qquad (4)$$

which involves the dynamic viscosity, μ, density, ρ, and surface tension, σ, of wash solutions along with the specific surface, a_V, of pulp fibres. Mathematical treatment of the experimental data showed that two independent dimensionless groups, the Péclet number, *Pe*, and criterion π, derived on the basis of dimensional analysis, are sufficient to describe our results.

For DEZ 10 solutions used as wash liquid, the correlation in the form:

$$WY_{RW=1} = 0.810\, Pe^{0.0622}\, \pi^{0.0168} \qquad (5)$$

was derived with a mean relative quadratic deviation δ = 0.55%. Equation (5) is valid in the range of the Péclet number of 4.4 to 6 and of criterion π of 3.9×10^{-3} to 8×10^{-3}.

When MIX 7 solution was used in displacement washing, the Péclet number varied in the limits from 5 to 8.4 and criterion π from 4.2×10^{-3} to 8.7×10^{-3}. Then, the following correlation equation was derived as:

$$WY_{RW=1} = 0.731\, Pe^{0.0956}\, \pi^{0.0142} \qquad (6)$$

with δ = 0.53%.

When displacement washing was performed with aqueous solutions of anionic surfactant SPOLAPON 242, the Péclet number ranged within a narrow interval from 5.2 to 5.8 and dimensionless criterion π varied from 3.3×10^{-3} to 6.9×10^{-3}. On the basis of our data, the correlation for the wash yield was expressed as:

$$WY_{RW=1} = 0.750\, Pe^{0.116}\, \pi^{0.0237} \qquad (7)$$

with δ = 0.23%.

Finally, the presence of non-ionic and anionic surfactants in the wash liquid had an effect on the concentration profile of alkali lignin in the liquor stream removed from the pulp bed. For surfactants, a slower drop in exit alkali lignin concentration was usually reached. However, in the last segment of the washing period, when leaching is a dominant mechanism, the surfactants led to an increase of the exit lignin concentration in the outgoing liquor stream. From the above results, one can deduce that the addition of surfactants, which leads to a decrease in the surface tension of the wash liquid, may have a positive effect upon the displacement washing efficiency in washers with relatively long contact time between wash liquid and pulp fibres, such as in the Kamyr diffusion washer or in the pressure diffuser.

CONCLUSION

The displacement wash yield evaluated at the wash liquor ratio equal to unity is influenced by the shape of the breakthrough curve characterized by the Péclet number. Generally, with increasing the Péclet number, which signifies a ratio of the convective to the diffusive transport mechanisms, the wash yield increases. However, displacement washing is affected by a number of factors either directly or indirectly, such as attributes of the pulp bed and fibres, sorption, electrokinetic phenomena, and intrinsic properties of miscible liquids. The presence of surfactants in the wash liquid affected the shape of the breakthrough curve, mainly its tail portion, when leaching dominates over displacement. Hence, in this case, a new dimensionless criterion, π, involving intrinsic properties of aqueous solutions of surfactants, was derived to describe a correlation between it and the Péclet number, on the one hand, and the wash yield, on the other hand.

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SYMBOLS

a_v specific surface area of fibres, m^{-1}
D axial dispersion coefficient, $m^2\,s^{-1}$
h thickness of bed, m
n number of measurements
Pe Péclet number defined by Equation (2)
RW wash liquor ratio
t time, s, min
u superficial wash liquid velocity, m s^{-1}
$WY_{RW=1}$ wash yield at RW = 1 defined by Equation (1)
δ mean relative quadratic deviation of wash yield, WY, defined as

$$\delta_{rel} = \sqrt{\frac{1}{n}\sum_{i=1}^{i=n}\left(\frac{WY_{exp} - WY_{calc}}{WY_{exp}}\right)_i^2} \cdot 100\,,\ \%$$

ε average porosity of pulp bed
σ surface tension of wash liquid, N m^{-1}
μ viscosity of wash liquid, Pa·s
π criterion defined by Equation (4)
ρ density of wash liquid, kg m^{-3}
ρ_e exit solute (in our case lignin) concentration from bed, kg m^{-3}
ρ_{SAA} concentration of aqueous solution of surfactants, kg m^{-3}
ρ_0 initial solute (in our case lignin) concentration in bed at t = 0, kg m^{-3}

Subscripts
calc referring to calculated value
exp referring to experimental value

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