Displacement of Black Liquor from Pulp Bed*

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Received 11 March 2004

Dedicated to the 80th birthday of Professor Elemír Kossaczký

Brownstock washing was simulated using a laboratory displacement washing cell. The displacement of black liquor from the kraft pulp bed was described by the dispersion flow model containing one dimensionless parameter, the Peclet number, for alkali lignin and sodium as the tracers. To characterize washing operation, the traditional wash yield, dispersion coefficient, mean residence time of both solutes, as well as the holding time of wash liquid were evaluated. With respect to various size of lignin fragmented in black liquor and sodium ions, the rate of leaching from within the fibres is different for both solutes. Therefore, the displacement washing efficiency should be expressed not only by the traditional wash yield, but also by the amount of both solutes washed out at the wash liquor ratio equal to unity, and the total amounts removed during washing operation must be taken into account as well.

The goal of pulp washing operation is to remove maximal amount of solutes, expensive cooking chemicals and organics for their heating value, using minimal amounts of wash water. In displacement washing, the wash liquid passes through pulp pad, displacing mother liquor from it. Nonuniformity of fibre pad in pore structure is one of the important effects influencing the efficiency of washing. Pulp pad consists of randomly oriented compressible porous particles, where geometrical similarity does not exist. Displacement washing is not purely mechanical process, but displacement and leaching operate simultaneously. The amount of a solute that is leached out of the fibre walls is negligible compared to the amount in the concentrated liquor being displaced during the initial stages of an industrial pulp washing operation. However, in the final stages of washing, where solute concentrations in the liquor surrounding the pulp fibres have been reduced substantially, the contribution of the leached solute becomes very significant.

For displacement washing of sulfate pulp at low solute concentration of the mother liquor, approximately $\rho(\text{lignin}) = 1.3\ \text{g dm}^{-3}$ and $\rho(\text{Na}) = 0.6\ \text{g dm}^{-3}$, *Grähs* [1] measured the lignin and sodium content in the outlet stream. The great differences between the washing of both solutes are attributed to the differences in their adsorption onto the pulp and their different mass transport times. The authors [2, 3] reported different washing efficiencies measured for lignin and sodium at low initial concentration ($\rho(\text{lignin}) = 1.455$—$8.1\ \text{g dm}^{-3}$ and $\rho(\text{Na}) = 0.548$—$4\ \text{g dm}^{-3}$) and at high liquor concentration ($\rho(\text{lignin}) = 22.4$—$33.0\ \text{g dm}^{-3}$ and $\rho(\text{Na}) = 8.4$—$12.8\ \text{g dm}^{-3}$). They concluded that the sodium desorption became relatively more important as initial liquor concentration decreased. For dilution washing, *Trinh* and *Crotogino* [4] investigated the relationship between lignin and sodium concentrations in the wash liquid surrounding kraft pulp fibres.

The present study was carried out as an extension of former published works [1—4] for the region where lignin and sodium concentrations in the black liquor are relatively high, about $\rho(\text{lignin}) = 48\ \text{g dm}^{-3}$ and $\rho(\text{Na}) = 35\ \text{g dm}^{-3}$.

EXPERIMENTAL

Displacement washing was simulated under laboratory conditions. The stimulus-response experiments, using a step input, were performed in the displacement washing cell consisting of a vertical glass cylinder 110 mm high, having 35 mm inner diameter. The fibre bed occupied the volume between the permeable septum

*Presented at the 31st International Conference of the Slovak Society of Chemical Engineering, Tatranské Matliare, 24—28 May 2004.

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and piston, covered with 45 "mesh" screens to prevent fibre loss from the bed.

For each experiment, the slurry of unbeaten unbleached kraft pulp in black liquor was used. After compressing it to desired thickness of 30 mm, the consistency of oven-dried pulp in the bed was maintained within the limits from 11.8 to 13.9 %, the mean value being 12.5 %. Length of softwood fibres in the wet state was characterized by the weighted average of 3.34 mm, as well as the numerical average of 1.46 mm. Estimated coarseness of fibres was about 0.151 mg m^{-1}. The degree of pulp delignification, expressed in terms of the kappa number, was found to be 32. The Schopper—Riegler freeness of unbeaten fibres of 13 SR was obtained.

Concentrations of alkali lignin and sodium in the black liquor taken from SuperBatch cooking plant were 48 g dm^{-3} and 35 g dm^{-3}, respectively. Further properties of sulfate liquor were as follows: solids content of 16.3 %, of which the ash made up 64 % and organics 36 %, chemical oxygen demand $\rho(O_2) =$ 165 g dm^{-3}, density of 1089 kg m^{-3} at 20 ℃, and pH value of 11.6.

Distilled water at a temperature maintained within the limits of 20 to 22 ℃ was employed as wash liquid. The superficial wash liquid velocity, based on empty cross-sectional area, varied in the range from 0.07 to 0.5 mm s^{-1}. Samples of the washing effluent leaving the pulp bed were analyzed for alkali lignin and sodium using ultraviolet spectrophotometry and atomic absorption spectroscopy, respectively. More detailed description of experiments can be found elsewhere [5].

RESULTS AND DISCUSSION

A response to step change in concentration provided two time dependences called washing or breakthrough curves, one for lignin and the other for sodium. To normalize the breakthrough curve ordinate, each concentration at the outlet stream, ρ_e, was divided by the initial solute concentration in the bed, ρ_0. The abscissa was normalized in terms of the wash liquor ratio, RW, defined as the mass of wash liquid passed through the bed to the given time divided by the mass of liquor originally present in the bed.

Typical breakthrough curves measured for lignin and sodium during one washing experiment are shown in Fig. 1. According to the solute concentration profile in the stream leaving the pulp bed, the breakthrough curves may be divided into four parts. For RW less or equal to about 0.3, the concentrated mother liquor is leaving the bed. As soon as the first portion of the wash liquid appears in the outlet stream, the concentration of both solutes falls very rapidly. However, for the values of RW ranging from about 0.3 to 1.5, the normalized sodium concentration is somewhat higher than that of lignin in accordance with Refs. [2, 3]. For

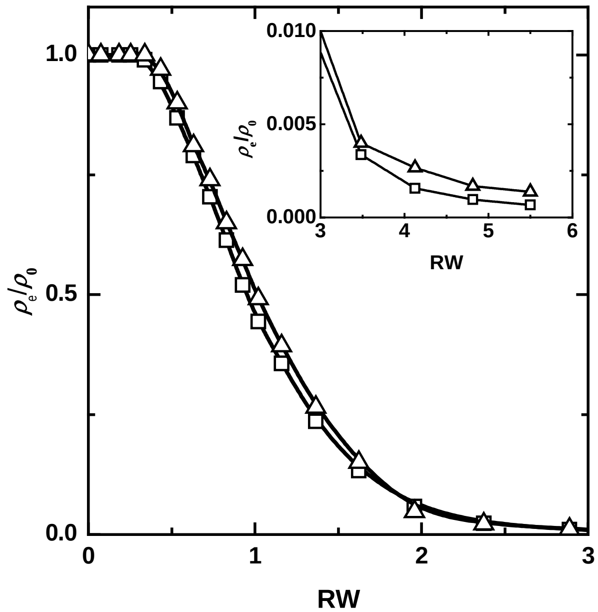

Fig. 1. Breakthrough curves measured for lignin (□) and sodium (△).

the wash liquor ratio in the range approximately from 1.5 to 3.5, the difference in outlet concentrations of both solutes is negligible. At higher RW values, above approximately 3.5, the discharge-normalized concentration of sodium is again higher in comparison with that of lignin. It is worth mentioning that the differences in the concentrations of both solutes in the outlet stream were considerably lower than those measured by *Grähs* [1] for low concentrations of lignin and sodium in the mother liquor.

The shape of the washing curve can be characterized in terms of the dimensionless Peclet number, Pe, derived from the mass balance of the tracer for the given system in unsteady state, in the following form

$$Pe = \frac{hu}{D\varepsilon} \qquad (1)$$

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

Displacement washing efficiency can be characterized by the traditional wash yield, $\mathrm{WY}_{\mathrm{RW}=1}$

$$\mathrm{WY}_{\mathrm{RW}=1} = \frac{\int_{\mathrm{RW}=0}^{\mathrm{RW}=1} \frac{\rho_e}{\rho_0}\mathrm{d(RW)}}{\int_{\mathrm{RW}=0}^{\mathrm{RW}\to\infty} \frac{\rho_e}{\rho_0}\mathrm{d(RW)}} \qquad (2)$$

defined as the amount of a solute washed out at RW = 1 divided by the total amount of a solute removed from the pulp bed during the washing run. In eqn (*2*),

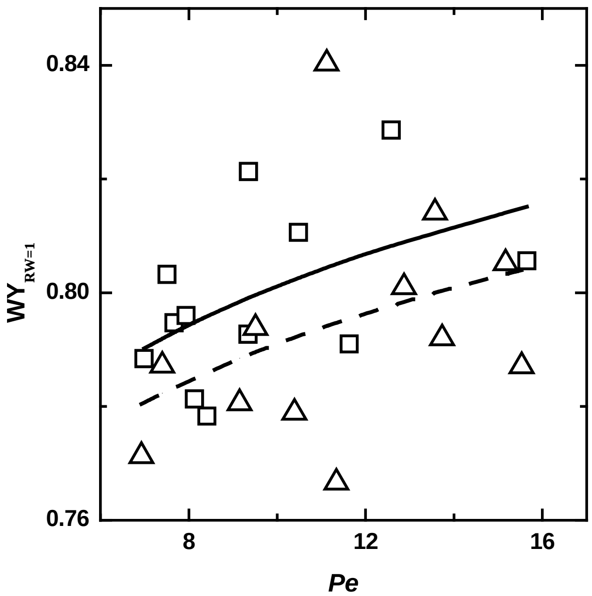

Fig. 2. The wash yield as a function of the Peclet number for lignin (□) and sodium (△). Experimental data fit for lignin, eqn (*3*) – solid line; and for sodium, eqn (*4*) – dashed line.

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

In Fig. 2, the wash yield measured for both lignin and sodium is plotted against the Peclet number. In spite of the scatter in the data, it is evident that the wash yield slightly increases with increasing Peclet number. For the qualitative evaluation of the effect of the Peclet number on the wash yield, the following correlation equations were derived

$$\mathrm{WY}_{\mathrm{RW}=1} = 0.73\, Pe^{0.039} \qquad (3)$$

for lignin, and

$$\mathrm{WY}_{\mathrm{RW}=1} = 0.73\, Pe^{0.037} \qquad (4)$$

for sodium. Both correlations (*3*) and (*4*) fit the experimental data with the mean relative quadratic deviation of the wash yield, δ, equal to 1.6 % and 2.5 %, respectively. Since the values of regression coefficients, which were evaluated by the least-squares method, represent an estimate of the real values, the 95 % confidence limits were calculated as well. They are (0.66; 0.82) and (0.61; 0.86) for coefficient in eqn (*3*) and eqn (*4*), respectively, and (0.025; 0.053) and (0.016; 0.058) for the power in eqn (*3*) and eqn (*4*), respectively. In accordance with earlier papers [5—8], the results obtained for both lignin and sodium washout confirmed that the wash yield depends on the Peclet number in a small degree.

Comparing the wash yields evaluated from eqn (*2*), they are on average 0.5 % higher for lignin than for sodium although the average Peclet numbers for lignin and sodium were 9.6 and 11.4, respectively. Then the greater values of the wash yield for sodium should be expected. A possible explanation of this discrepancy can be attributed to the different leaching rates of both solutes from within the fibres.

The area under the breakthrough curve is directly proportional to the amount of a solute removed from the bed of particles. Hence, the denominator on the right-hand side of eqn (*2*) is proportional to the total amount of a solute washed out during washing run, TA. The denominator of eqn (*2*) should be equal to unity for solutes which do not leach out of particles but are found only in the interparticle voids. Since both lignin and sodium leach out of the pulp fibres during washing operation, as long as the driving force exists, the area under their breakthrough curves was found to be greater than unity, as shown in Fig. 3. The total amount of sodium removed from the pulp bed was essentially greater than that of lignin, except for one experiment when the wash liquid velocity reached the highest value.

In Fig. 3, the values of area under breakthrough curve up to RW = 1, which is proportional to the amount of a solute washed out from the pulp bed, $A_{\mathrm{RW}=1}$, are also shown. Except for one experiment, when the highest wash liquid velocity was used, the amount of sodium removed for RW $\leq$ 1 is substantially larger than that for lignin. It should be noted that alkali lignin is one of the macromolecular substances with different distribution of molecular masses depending on wood species and the degree of delignification reached in cooking process. It can be supposed

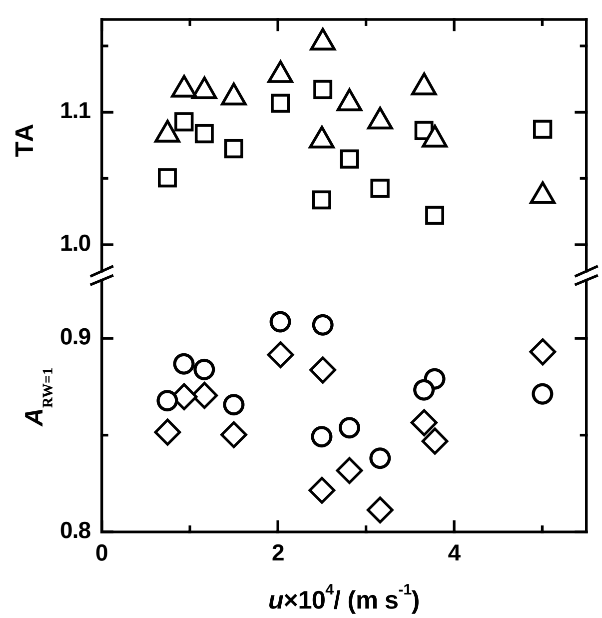

Fig. 3. Influence of the wash liquid velocity on the total amount of lignin (□) and sodium (△), and the amount of lignin (◇) and sodium (○) washed out at RW = 1.

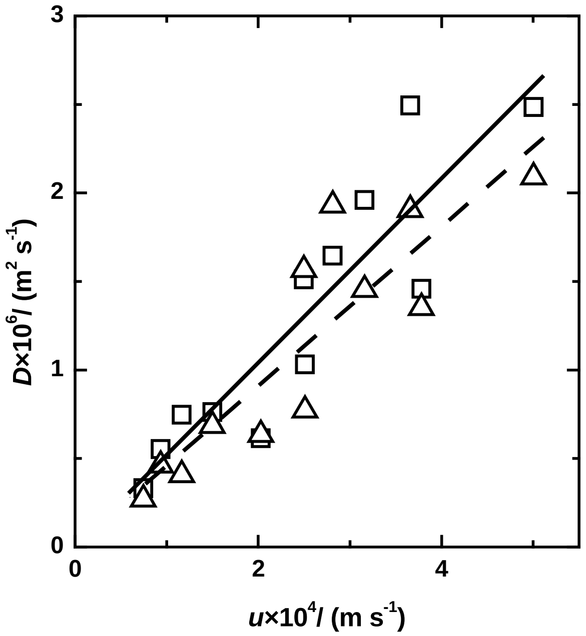

Fig. 4. Lignin (□) and sodium (△) dispersion coefficient as a function of the wash liquid velocity. Experimental data fit for lignin, eqn (*5*) – solid line; and for sodium, eqn (*6*) – dashed line.

that, in comparison with sodium ions, large macromolecules of lignin fragmented in alkaline solution are pushed out preferentially from large pores with lower hydraulic resistance. The lower values of the Peclet number obtained for lignin confirm this statement, although small amount of sodium may begin to desorb from the pulp fibres even for RW < 1. The authors [4] noticed that the removal of both solutes out of pulp fibres is influenced by the pH change, especially when pH value of the liquid surrounding the fibres drops below 7.

Furthermore, the differences in dispersion of both solutes influence the axial dispersion coefficient, which is plotted against the wash liquid velocity in Fig. 4. In agreement with the previous papers [5, 7, 9], linear increase of the dispersion coefficient with the wash liquid velocity was observed independently of the pulp bed structure. The effect of the wash liquid velocity, $u/(\mathrm{m\ s^{-1}})$, on the axial dispersion coefficient, $D/(\mathrm{m^2\ s^{-1}})$, was fitted using a linear function

$$D = 5.2 \times 10^{-3}\, u + 3.2 \times 10^{-9} \qquad (5)$$

for lignin, and

$$D = 4.5 \times 10^{-3}\, u + 1.0 \times 10^{-8} \qquad (6)$$

for sodium with correlation coefficients 0.91 and 0.88, respectively. It should be noted that the differences in the axial dispersion coefficient found for both solutes are in accordance with the Peclet numbers.

In addition, the solute leaching occurring in the pulp bed influences the relation between the mean residence time of a solute, t_m, defined by the following equation

$$t_\mathrm{m} = \int_{t=0}^{t\to\infty} \frac{\rho_\mathrm{e}}{\rho_0}\mathrm{d}t \qquad (7)$$

and the space-time, τ, which is defined as the void volume of the bed divided by the volumetric flow rate of the wash liquid. After rearranging it can be expressed as

$$\tau = \frac{\varepsilon\, h}{u} \qquad (8)$$

The space-time characterizes a holding time of wash liquid and is usually equal to the mean residence time of the tracer without sorbing it on the surface of particles in the bed. For pulp fibres, however, when the solute leaching occurs, the mean residence time is always higher than the space-time, as shown in Fig. 5. Owing to the fact that sodium is easily leachable solute in comparison with alkali lignin, the mean residence time of sodium is somewhat longer than that of lignin in agreement with the results reported by *Grähs* [1].

To conclude, the evaluation of displacement washing efficiency based on the traditional wash yield defined by eqn (*2*), which is determined for various solutes differing in their leachabilities, can lead to misleading findings. For RW $= 1$, the displacement washing efficiency of sodium is higher in comparison with that of lignin, probably due to the different size of

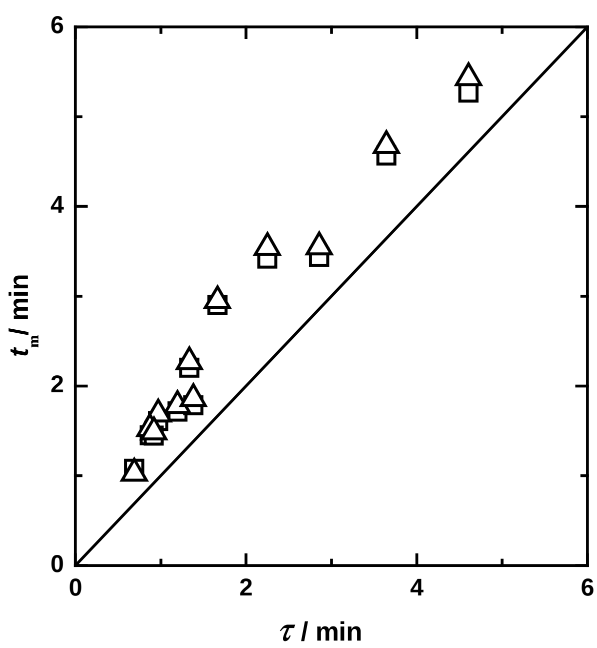

Fig. 5. Lignin (□) and sodium (△) mean residence time as a function of the space-time.

sodium ions and macromolecules of alkali lignin. However, for a more detailed comparison, the amount of both solutes removed at RW = 1 and the total amount washed out during washing run seem to be suitable parameters describing the displacement washing process. Various ability of both solutes to their displacement from the labyrinth of pores in the pulp bed by a miscible liquid results in the axial dispersion coefficient having greater values for lignin than for sodium. Leaching of both solutes accompanying the displacement process is confirmed unambiguously by the relation of the mean residence time of solutes and the holding time of the wash liquid.

SYMBOLS

$A_{\mathrm{RW}=1}$	area under breakthrough curve (proportional to the amount of a solute washed out) within the limits from RW = 0 to RW = 1 expressed by the numerator on the right-hand side of eqn (*2*)	
D	axial dispersion coefficient	$\mathrm{m^2\ s^{-1}}$
h	thickness of bed	m
n	number of measurements	
Pe	Peclet number defined by eqn (*1*)	
RW	wash liquor ratio	
t	time from start of experiment	s
t_{m}	mean residence time defined by eqn (*7*)	s, min
TA	total area under breakthrough curve proportional to the amount of a solute washed out from the bed expressed by the denominator on the right-hand side of eqn (*2*)	
u	superficial wash liquid velocity	$\mathrm{m\ s^{-1}}$
$\mathrm{WY}_{\mathrm{RW}=1}$	wash yield at RW = 1 defined by eqn (*2*)	

Greek Letters

δ	mean relative quadratic deviation of the wash yield, WY, defined as $\delta = \sqrt{\frac{1}{n}\sum_{i=1}^{i=n}\left(\frac{\mathrm{WY_{exp}} - \mathrm{WY_{calc}}}{\mathrm{WY_{exp}}}\right)_i^2} \times 100$	%
ε	average porosity of packed bed	
ρ_{e}	exit solute concentration from bed	$\mathrm{kg\ m^{-3}}$
ρ_0	initial solute concentration in bed at $t = 0$ s	$\mathrm{kg\ m^{-3}}$
τ	space-time defined by eqn (*8*)	s, min

Subscripts

calc	referring to calculated value
exp	referring to experimental value

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