Displacement of Black Liquor from Pulp Fibre Bed*

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Using distilled water and/or aqueous polyacrylamide solutions, the mechanism of the displacement washing of unbleached kraft pulp was investigated. The step change technique has been employed in the investigation of displacement of black liquor. To characterize the displacement of black liquor, the washing curves as well as wash yield at the wash liquor ratio equal to unity were determined. The results obtained for pure wash water were compared with those for polyacrylamide solutions.

Pulp washing is one of the key unit operations in chemical pulping of wood and chemical bleaching of pulp. The goal of the pulp washing operation is to remove maximal amounts of solute using minimal amounts of water. Dissolved solids remaining with the pulp after washing increase the cost of bleaching, pulping, chemical make-up, and effluent treatment. On the other hand, if the wash water is used in excess, the dilution of the recovered liquor adds to increased costs for its evaporation and for heating the excess wash water. Two basic pulp washing operations, namely dilution-thickening and displacement washing, are used industrially. In displacement washing, wash liquor is forced to flow through a pulp pad, displacing the mother liquor from it.

In order to enhance the efficiency of displacement washing, *Lee* [1] used solutions of 2, 5, and 10 ppm of high-molecular-mass polyacrylamide in water as wash liquids. His results showed that the wash yield increases with increasing polyacrylamide concentration.

Displacement washing can be simulated simply using the laboratory displacement washer described in this work. The purpose of our investigation was to clarify the displacement washing of the bed of wood pulp fibres. The axial dispersion model [2] was used for describing the displacement washing of black liquor from packed beds using pure wash water and aqueous solutions of two types of nonionic polyacrylamides.

EXPERIMENTAL

Distilled water and aqueous solutions of two types of polyacrylamide Praestol 2300 and Praestol 2500 (pure, Stockhausen) were used as wash liquids. The concentration of polyacrylamide Praestols in aqueous solutions varied in the range from 1 to 50 g m^{-3}.

The experiments were carried out in the displacement washing cell consisting of a vertical glass cylinder 110 mm high, 36.4 mm inside diameter, and closed at the lower end by a permeable septum. The fibre bed occupied the volume between the septum and a piston which could be slid into the top of the cylinder. Both the piston and the septum were made permeable by 64 holes of 1 mm diameter.

To start the washing experiment, wash liquid maintained at a temperature of 20 °C was distributed uniformly through the piston to the top of bed, approximating a step change in concentration. Samples of the washing effluent taken at different time intervals until the effluent was colourless were analyzed for lignin using an ultraviolet spectrophotometer operating at a wavelength of 295 nm. The initial bed liquor lignin concentration was 57 g dm^{-3}. Experiments are described in detail in [3].

Pulp beds were formed from a dilute suspension of unbeaten unbleached kraft pulp in black liquor. In all runs, the beds were compressed to a final desired thickness of 30 mm. The consistency of oven-dried pulp in bed varied in the range from 8.0 to 13.8 %. In order to characterize the pulp fibres used in experiments, physical properties of kraft pulp were determined as well. The Schopper—Riegler freeness had a value of 13 deg SR. The degree of delignification of pulp was expressed in terms of the kappa number equal to 17. The fibre length was determined from measurements in the wet state using the Kajaani FS-100 instrument. The weighted average length was 2.13 mm, while the numerical average length was only 1.15 mm. The effective specific volume of fibres had a value of 2.57 cm^3 g^{-1} and the specific surface of fibres was 1.07 × 10^4 cm^2 g^{-1}.

The rheological measurements to determine the de-

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pendence of the apparent viscosity on the shear rate were made using a capillary viscometer. The average molar masses determined by viscosimetric method were 8.75 × 10^6 g mol^{-1} and 1.21 × 10^7 g mol^{-1} for Praestol 2300 and Praestol 2500, respectively. In order to investigate viscoelastic behaviour of both types of polyacrylamide, dynamic tests with oscillating stresses were made using rheometer RS 150 working in the control-stress mode at a constant stress input of 0.1 Pa.

RESULTS AND DISCUSSION

Breakthrough Curves

The displacement of the black liquor from the pulp fibre bed was described by the time dependence of the outlet wash liquor concentration. In dimensionless form, this can be expressed in terms of the concentration ratio between outlet wash liquor and the original solute, ρ_e/ρ_0, as a function of the wash liquor ratio, RW, defined as the ratio of the mass of wash liquid passed through the bed and the initial mass of mother liquor present in the bed, *i.e.* in the interparticle voids as well as in fibre walls and lumens. Typical displacement washing curves are illustrated in Fig. 1. The shape of the curves indicates that the washing model of flow was nonideal, *i.e.* it is between the limits of plug flow and perfectly mixed flow. From displacement washing curves obtained it is obvious that the washing process can be divided into three periods. At first, for water as wash liquid up to RW equal to approximately 0.4, the wash liquid pushes the mother black liquor ahead of itself so that the first portions discharged from the bed are as concentrated as was the mother liquor. As soon as the first portion of wash liquid appears in the outlet stream of liquor, the concentration of solute falls off very rapidly. In this second washing period occurring for RW of 0.4 to 1.5, it can be supposed that the major part of mother liquor in interparticle voids is removed and replaced by wash liquid. At the end of the washing curve for RW above approximately 1.5, a small tailing can be watched. In this third period, the leaching operation prevails. The solute adsorbed on the surface of the fibres as well as the solute inside the fibre walls is transferred by diffusion to the wash liquid as long as the driving force exists.

The fibre bed consisted of randomly oriented porous particles which are not necessarily geometrically similar, since the length-to-diameter ratio may vary. An unpredictable labyrinth of the pores of various tortuosity forms a void volume of the bed. The spent liquor in the pulp bed includes two parts (Fig. 2). The first part of total fills in the spaces between fibres, its quantity depends mainly upon the consistency of the pulp. This part of spent liquor can be removed by a simple displacement by the wash liquid. The second part is contained in the walls and lumens of cells. The transport of the solute from inside the fibres to the bulk liquid consists of several steps. The solute must diffuse out of the internal structure of the fibre to the external surface of the liquid immobilized on the external surface of the fibre before it can become available for displacement. Washing of pulp fibres can be thought of as two separate operations: a displacement operation and a leaching operation, both of which occur simultaneously to some extent. Displacement refers to the removal from the pulp slurry of the solute in the liquor surrounding the fibres. Displacement occurs by replacing solute-laden

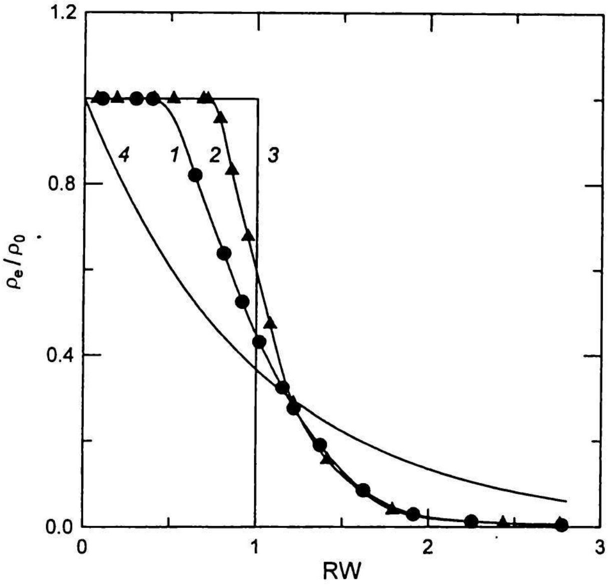

Fig. 1. Washing curves. Wash liquid: *1.* water, *2.* aqueous solution of Praestol 2500 (conc. of 12.5 g m^{-3}), *3.* plug flow, *4.* perfectly mixed flow.

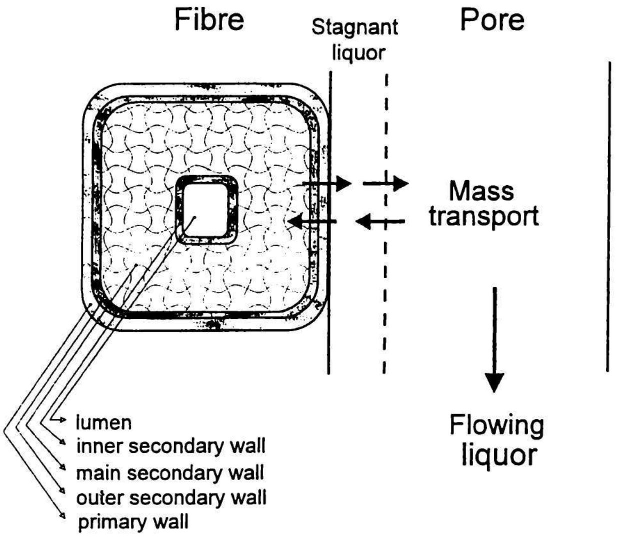

Fig. 2. Model of pulp fibre bed.

liquor with cleaner wash liquor. The leaching operation refers to the desorption and diffusion of solute from within the fibres.

Wash Yield

Quality of the displacement washing can be characterized by the wash yield. The displacement wash yield, $\mathrm{WY}_{\mathrm{RW}=1}$, evaluated at the wash liquid ratio equal to unity may be expressed as

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

An axial dispersion model containing only one dimensionless parameter, the Peclet number, was chosen to describe [2] the experimental breakthrough curves mentioned above. The Peclet number which indicates the level of dispersion in the bed was defined as

$$Pe = \frac{hu}{D\varepsilon} \qquad (2)$$

where h is the thickness of the bed, ε its average porosity, u is the superficial wash liquid velocity, and D is the dispersion coefficient which may be evaluated from eqn (*2*) for known value of the Peclet number.

In Fig. 3 the wash yield, $\mathrm{WY}_{\mathrm{RW}=1}$, evaluated from eqn (*1*) is plotted against the Peclet number. The experimental points measured for water are located below the curve which was derived for the bed of nonporous particles by *Brenner* [4]. On the basis of our own data measured for pulp bed, the correlation between the wash yield and the Peclet number in the form

$$\mathrm{WY}_{\mathrm{RW}=1} = 0.488 Pe^{0.194} \qquad (3)$$

was derived. The mean relative quadratic deviation of the wash yield, δ (defined in Symbols), was 0.8 %.

Both types of polyacrylamide used exhibit pseudoplastic behaviour, as follows from Fig. 4. In a porous medium, however, elastic effects may occur [5, 6]. Preliminary dynamic tests with oscillating stresses provided data on viscosity and elasticity related to their time response. For both nonionic polyacrylamides it was found that the elastic character dominated over viscous properties. Of course, it is likely that the conditions under which the rheological characters of polyacrylamide solutions were measured are seldom fulfilled in the case of the wash liquid flowing through the pores in the pulp fibre bed.

The influence of polyacrylamide addition on the wash yield is ambiguous. The experimental results show that the wash yield at first increases and then decreases with increasing polyacrylamide concentration (Fig. 5). By comparing washing curves measured for pure water and aqueous solution of Praestol 2500 (Fig. 1), the achievement of higher values of the wash yield for polyacrylamide solution is evident. Also, the Peclet number in the limits of 12.6 to 33.3 around an average value of 22.1 obtained for Praestol 2500 indicates that the wash yield could be greater than that for Praestol 2300. The Peclet number for Praestol 2300 varied in the range of 11.2 to 16.8 around an average value of 13.4, similarly as for pure water. Maximum

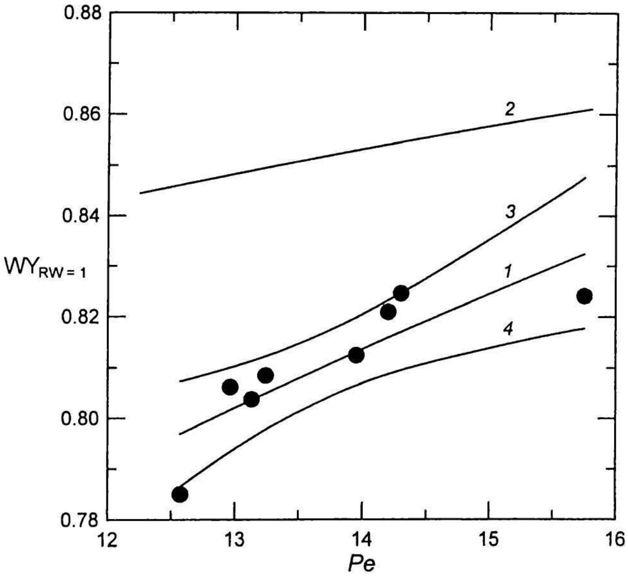

Fig. 3. Displacement wash yield as a function of the Peclet number for water. *1.* Eqn (*3*), *2.* theoretical dependence of $\mathrm{WY}_{T=1}$ on *Pe* according to *Brenner* [4], *3.* upper 95 % confidence limit for eqn (*3*), *4.* lower 95 % confidence limit for eqn (*3*).

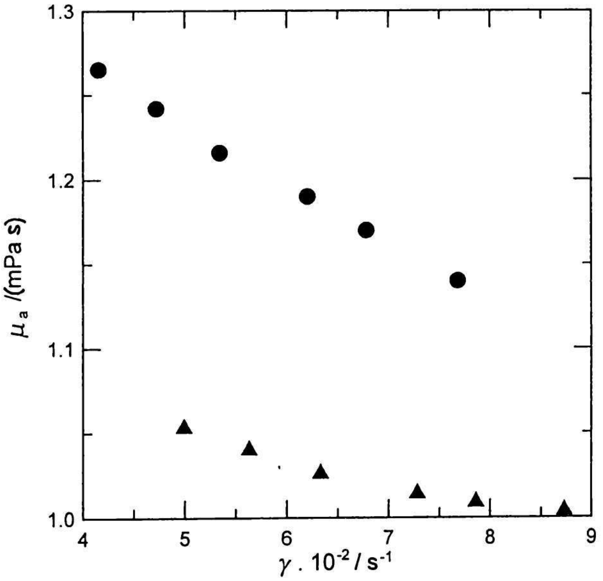

Fig. 4. Shear rate dependence of apparent viscosity for Praestol 2300 (▲) and Praestol 2500 (●) at a temperature of 20 °C (conc. of 25 g m^{-3} for both Praestols).

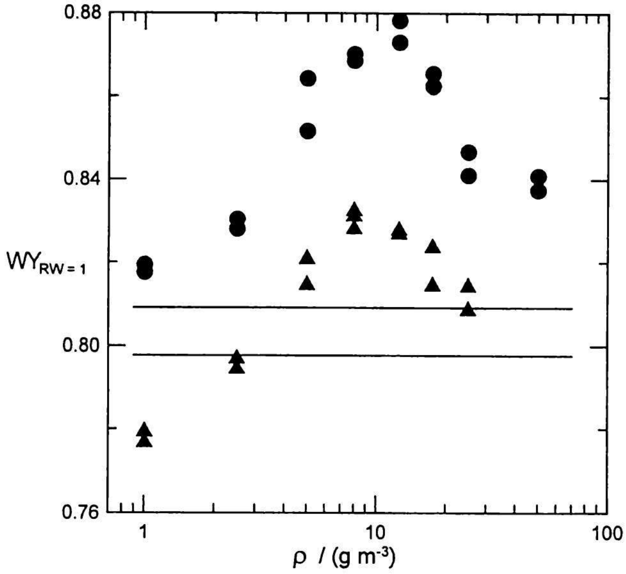

Fig. 5. Influence of the concentration of Praestol 2300 (▲) and Praestol 2500 (●) on the wash yield. Solid lines: 95 % confidence limits for water.

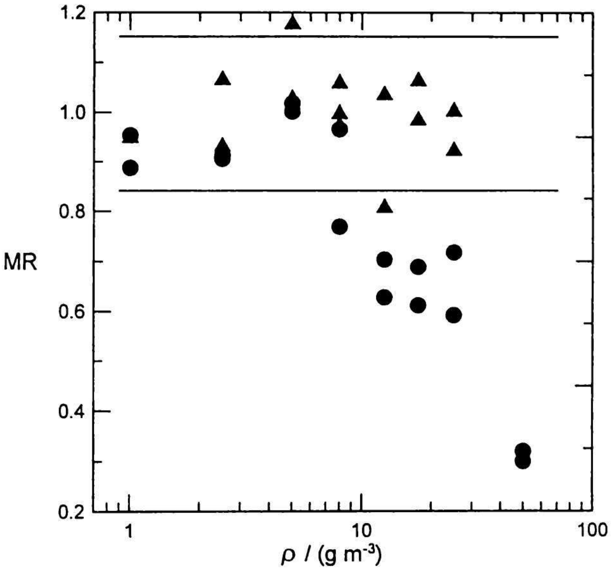

Fig. 6. Dependence of the mobility ratio on the polyacrylamide concentration for Praestol 2300 (▲) and Praestol 2500 (●). Solid lines: 95 % confidence limits for water.

values of the wash yield are reached in the range of polyacrylamide concentration of 8 to 12.5 g m^{-3}. The question why this maximum exists, however, remains uncleared. As seen in Fig. 5, the addition of Praestol 2500 brings higher values of the wash yield in comparison with Praestol 2300.

Channelling is an extremely complex phenomenon, having unfavourable effect on washing effectiveness. It can be assumed that a labyrinth of the pores together with leaching of solute from within the fibres are the main factors causing deviations from the ideal plug flow in the displacement washing. The permeability is dependent on the fibre distribution in the pulp bed. It can be supposed that channelling between dissimilar miscible liquids during displacement in a bed of wood pulp fibres occurs primarily as a result of preferential penetration of the wash liquid in regions of the porous structure having a higher permeability. Liquid viscosity and the interaction of the liquid with the permeability of the porous medium are characteristics that function as resistance factors to flow. The ratio of permeability to viscosity, B/μ, called the mobility of a liquid with respect to a particular medium may be evaluated from Darcy's law as follows

$$\frac{B}{\mu} = \frac{Vh}{A\Delta P} \tag{4}$$

In Fig. 6 the dependence of the ratio of the mobility of the displacing liquid (in our case wash water or polyacrylamide solutions) to the mobility of displaced liquid (in our case mother black liquor), MR, defined as

$$\mathrm{MR} = \frac{(B\mu^{-1})_{\mathrm{WL}}}{(B\mu^{-1})_{\mathrm{ML}}} \tag{5}$$

on the polyacrylamide concentration is shown. Nearly all data obtained for Praestol 2300 lie within the 95 % confidence limits calculated for wash water. On the contrary, the mobility ratio for Praestol 2500 is lower than that for Praestol 2300, particularly in the region of concentration above 8 g m^{-3}. The apparent viscosity of both polyacrylamides is of the same order of magnitude as the dynamic viscosity of water at given temperature (Fig. 4). Presumably, lower values of mobility ratio obtained for Praestol 2500 can be partly caused by higher values of apparent viscosity in comparison with Praestol 2300. *Lee* [1] reminds that a decrease in mobility of polymeric solutions can be due to their tendency to partially hydrate and form microgels in suitable ionic environments. It should be noted that, in our case, the mobility ratio results obtained for water show no trend with the wash yield.

Our results can be compared with those of *Lee* [1] who demonstrated the effect of mobility ratio on the effectiveness of displacement washing for pads of unbeaten, unbleached kraft pulp fibres. Spent liquor was displaced under gravity from pads the consistency of which was only 3.75 %. Mobility ratios relative to black liquor for pure water and water with 10 ppm polyacrylamide were to be found 2.4 and 0.23, respectively. The addition of 10 ppm of polyacrylamide to the wash liquid increased wash yield at zero dilution factor from 0.78 to 0.98 in comparison with pure water.

In conclusion, it was found that the addition of nonionic polyacrylamides to wash water has the influence on the wash yield. Although the elastic behaviour of both polyacrylamides may be supposed, the values of the wash yield obtained for solutions of Praestol

2500 were always greater than those for Praestol 2300 solution and pure water. The difference in mobility of both polyacrylamides offers a possible explanation for greater values of the wash yield attained for Praestol 2500. Since the addition of polyacrylamides into wash liquid brings many problems, it is necessary to verify the results of the present work on other polymers.

SYMBOLS

A	cross-sectional area	m^2
B	permeability	m^2
D	dispersion coefficient	$m^2\ s^{-1}$
h	thickness of bed	m
MR	mobility ratio defined by eqn (*5*)	
n	number of measurements	
ΔP	pressure drop	Pa
Pe	Peclet number defined by eqn (*2*)	
RW	wash liquor ratio	
T	dimensionless time ($= ut/(h\varepsilon)$)	
t	time from start of experiment	s
u	superficial wash liquid velocity	$m\ s^{-1}$
V	volumetric flow rate	$m^3\ s^{-1}$
$\mathrm{WY}_{\mathrm{RW}=1}$	wash yield at RW = 1 defined by eqn (*1*)	
$\mathrm{WY}_{T=1}$	wash yield at $T = 1$ according to *Brenner* [4] defined as	

$$\mathrm{WY}_{T=1} = \frac{\displaystyle\int_{T=0}^{T=1} \frac{\rho_\mathrm{e}}{\rho_0} \mathrm{d}T}{\displaystyle\int_{T=0}^{T\to\infty} \frac{\rho_\mathrm{e}}{\rho_0} \mathrm{d}T}$$

Greek Letters

γ	shear rate	s^{-1}
δ	mean relative quadratic deviation of wash yield defined as	

$$\delta = \left[\frac{1}{n}\sum_{i=1}^{i=n}\left(\frac{\mathrm{WY}_\mathrm{exp} - \mathrm{WY}_\mathrm{calc}}{\mathrm{WY}_\mathrm{exp}}\right)_i^2\right]^{1/2} \times 100\%$$

ε	average bed porosity	
μ	dynamic viscosity	mPa s
μ_a	apparent viscosity	mPa s
ρ	bulk polyacrylamide concentration	$g\ m^{-3}$
ρ_e	exit lignin concentration from bed	$kg\ m^{-3}$
ρ_0	initial lignin concentration in bed at $t = 0$	$kg\ m^{-3}$

Subscripts

calc	referring to calculated value
exp	referring to experimental value
ML	referring to mother liquor
WL	referring to wash liquid

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